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Abbes Laghrou University of Khenchela
Faculty of Science and Technology
Department of Science of Matter

Thesis

Presented to Obtain a Doctoral Degree in Chemistry

Specialty: materials chemistry

By:

Ghodbane Oumaima

Entitled:

Synthesis, characterization, and applications of polymorphs, Metal-Organic Frameworks (MOFs), and organic-inorganic hybrid compounds based on nitrogen bases: Towards new materials with physicochemical properties

Public defense scheduled for : May 24, 2026

Graduation Committee :

NEDJAR Zohir	Prof	Abbes Laghrou Khenchela University	President
BENALI-CHERIF Rim	Prof	Abbes Laghrou Khenchela University	Supervisor
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BENALI-CHERIF Nourredin	Prof	Jijel University	Invited



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Abbreviations and Symbols

MOFs: Metal Organic Frameworks

APIs: Active pharmaceutical ingredients

XRD: X-ray diffraction

DSC: Differential scanning calorimetry

IR: Infrared

CSD: Cambridge structural database

Cu(OAc)₂·H₂O : Copper (II) diacetate monohydrate

P1: Polymorph 1

P2: Polymorph 2

HS: Hirshfeld surface

FP: Fingerprint plots

2D: Two dimensions

DFT: Density functional theory

FMOs: Frontier molecular orbitals

MEP: Molecular electrostatic potential

HOMO: Highest occupied molecular orbital

LUMO: Lowest unoccupied molecular orbital

RDG: Reduced density gradient

EXP: Experimental

SC-XRD: Single-crystal X-ray diffraction

3D: Three dimensions

LCAO: Linear combination of atomic orbitals

NCIs: Noncovalent interactions

DNA: Deoxyribonucleic acid

RNA: Ribonucleic Acid

CYT⁺·GA⁻: Cytosinium gallate

DMAP: Dimethylamino pyridine

(Z)-DMAP-RDN: (Z)-5-{[4-(dimethylamino) phenyl] methyldene}-2-sulfanylidene-1,3-thiazolidin-4-one

0D: Zero dimension

1D: One dimension

(H⁺DMAP-RDN). Br⁻: N, N-dimethyl-4-[(Z)-(4-oxo-2-sulfanylidene-1,3-thiazolidin-5 ylidene) methyl] anilinium Bromide

Bzac: Benzoylacetate

M(bzac)₂: Bis benzoylacetate metal

BFDH: Bravais–Friedel–Donnay–Harker

Co(bzac)₂: Cobalt(II) benzoylacetate

PXRD: Powder X-ray diffraction

RMSD: Root-Mean-Square Deviation

SOMO: Singly occupied molecular orbital

TD-DFT: Time-dependent density functional theory

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GENERAL
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General Introduction

The relationship between molecular structure and material properties has long fascinated scientists across multiple disciplines. At the heart of this relationship lies a remarkable phenomenon: the ability of chemically identical compounds to adopt different crystalline arrangements, each exhibiting distinct physical and chemical properties. This phenomenon, known as polymorphism, represents one of the most intriguing and practically significant aspects of solid-state chemistry and crystal engineering. From the dramatic contrast between diamond-graphite both are forms of carbon yet vastly different in hardness, conductivity, and appearance to the subtle variations in pharmaceutical crystals that can determine drug efficacy and shelf-life, polymorphism continues to challenge our understanding and inspire innovation in materials design.

The significance of polymorphism extends far beyond academic curiosity. In the pharmaceutical industry, different polymorphic forms of the same active ingredient can exhibit dramatically different dissolution rates, bioavailability, and stability profiles, directly impacting therapeutic efficacy and patient safety. The notorious case of ritonavir, an HIV protease inhibitor that spontaneously transformed to a less soluble polymorph two years after market approval, underscores the critical importance of understanding and controlling polymorphic behavior. In materials science, the deliberate manipulation of crystal structure enables the design of functional materials with tailored properties for applications ranging from organic electronics and photovoltaics to catalysis and sensing technologies.

Complementing the study of polymorphism, the field of hybrid organic-inorganic materials has emerged as a frontier area offering unprecedented opportunities for functional material design. By combining the processability and structural diversity of organic molecules with the electronic, magnetic, and optical properties of inorganic components, hybrid materials transcend the limitations of their individual constituents. These materials, stabilized through various interactions ranging from weak van der Waals forces to strong coordination bonds, have found applications in diverse fields including energy conversion, drug delivery, catalysis, and optoelectronics.

Despite significant advances in crystallography, spectroscopy, and computational chemistry, the prediction and control of polymorphic behavior remain formidable challenges. The subtle interplay of thermodynamic and kinetic factors governing

GENERAL INTRODUCTION

crystallization, combined with the complex landscape of intermolecular interactions hydrogen bonding, π - π stacking, van der Waals forces, and electrostatic interactions makes polymorphism inherently difficult to predict from molecular structure alone. Similarly, while hybrid organic-inorganic materials offer tremendous potential, rational design principles for optimizing their structure-property relationships are still being developed.

This thesis is organized into three interconnected parts, each addressing a distinct yet complementary aspect of solid-state molecular chemistry:

Part One: Polymorphism explores the fundamental phenomenon of polymorphism through detailed investigations of three model systems: copper (II) diacetate monohydrate which consider as a metal-organic framework (MOF), cytosinium gallate, and a rhodanine derivative. Chapter I provides a comprehensive bibliographic overview of polymorphism, reviewing its historical development, theoretical foundations, characterization methods, and practical implications. Chapters II through IV present original research on the discovery and characterization of new polymorphic forms, establishing structure-property relationships through integrated experimental and computational analysis. These studies reveal how subtle differences in molecular packing and intermolecular interactions translate to measurable differences in electronic structure, stability, and potentially, functionality.

Part Two: Hybrid Organic-Inorganic Compounds investigates materials that bridge the organic-inorganic interface. Chapter I presents a bibliographic overview of hybrid materials, classifying them based on bonding characteristics and surveying their diverse applications. Chapter II reports the synthesis and comprehensive characterization of a novel proton-transfer hybrid compound, N,N-dimethyl-4-[(Z)-(4-oxo-2-sulfanylidene-1,3-thiazolidin-5-ylidene) methyl]anilinium bromide. This study demonstrates how proton transfer and ionic interactions can stabilize hybrid architectures with distinct donor-acceptor electronic characteristics, offering insights for designing materials with tailored electronic properties.

Part Three: Coordination Compounds examines metal-organic coordination complexes as a special class of hybrid materials. Chapter I provides an overview of coordination chemistry fundamentals, ligand classification, bonding theories, and applications in catalysis and materials science. Chapter II presents the synthesis and characterization of a new cobalt (II) benzoylacetate complex, $[\text{Co}(\text{bzac})_2]$, revealing how molecular planarity and strong intermolecular interactions drive anisotropic crystal growth and distinctive morphology. This work establishes structure-

GENERAL INTRODUCTION

morphology correlations relevant to the rational design of coordination complexes with controlled crystal habits.

Through this comprehensive investigation spanning polymorphism, hybrid materials, and coordination compounds, this thesis contributes to the fundamental understanding of structure-property relationships in molecular solids and provides practical insights for the rational design of functional materials. The integration of experimental and computational approaches demonstrated here represents a powerful methodology for tackling the complex challenges of crystal engineering and materials design in the 21st century.

PART ONE:

POLYMORPHISM

*“3 reactions a day, keeps
the promotor away”*



Chapter I.

Polymorphism in Molecular Solids: A Bibliographic Overview

I. Introduction

Polymorphism is a fundamental phenomenon in solid-state chemistry and materials science, defined as the ability of a compound to crystallize in two or more distinct structural forms. These forms, known as polymorphs, possess identical chemical compositions but differ in their molecular packing, intermolecular interactions, and crystal symmetry. Such structural variations often lead to pronounced differences in the physical and physicochemical properties of the material. As a result, they often exhibit markedly different physical and chemical properties such as melting point, solubility, density, stability, optical behavior, and mechanical strength.

A classical and widely cited example of polymorphism is provided by carbon, which exists mainly in two crystalline forms: diamond and graphite (Figure 1). Both are composed solely of carbon atoms, yet their structural organization leads to completely different properties. In diamond, each carbon atom is sp^3 -hybridized and tetrahedrally bonded to four other carbons, forming a rigid three-dimensional network responsible for its exceptional hardness and high thermal conductivity. In contrast, graphite consists of sp^2 -hybridized carbon atoms arranged in planar hexagonal layers held together by weak van der Waals forces, resulting in a soft, lubricating material with good electrical conductivity. This striking contrast between diamond and graphite vividly demonstrates how polymorphism can profoundly influence the macroscopic behavior of materials.

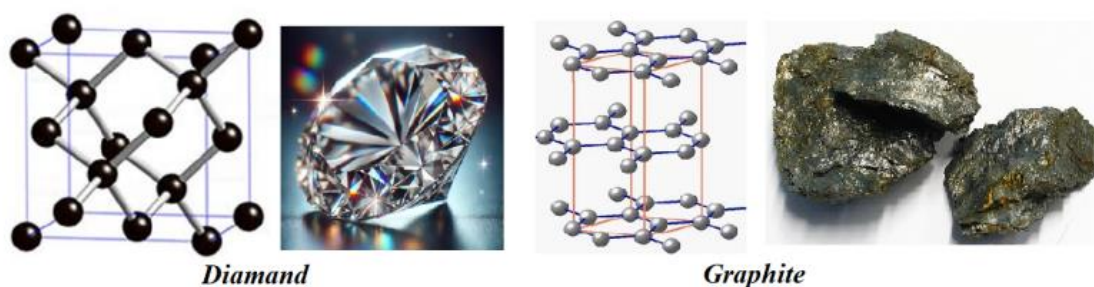


Figure 1. Crystalline polymorphs of carbon: diamond and graphite.

Exploiting new polymorphs of active pharmaceutical ingredients (APIs) has a significant role in the development of new processes for the pharmaceutical industry¹, coordination chemistry, and materials engineering, since the selection or control of a specific polymorph can critically affect a compound's performance and functionality. In pharmaceuticals, for instance, polymorphic forms may differ in solubility and bioavailability. In coordination and inorganic chemistry, polymorphism influences magnetic, catalytic, and adsorption properties, thereby playing a decisive

role in materials design and synthesis. Polymorphic transformations can occur due to variations in temperature, pressure, or solvent environment, and may involve reversible or irreversible structural rearrangements. Understanding these transformations provides key insights into the thermodynamic stability and kinetic behavior of crystalline materials.

Modern characterization techniques such as X-ray diffraction (XRD), differential scanning calorimetry (DSC), infrared (IR) and Raman spectroscopy, along with computational modeling are essential tools for identifying, differentiating, and studying polymorphic systems. The ability to control and predict polymorphism remains one of the central challenges in crystal engineering and solid-state chemistry, with far-reaching implications for the development of advanced functional materials.

From a thermodynamic point of view, polymorphism can be further classified into enantiotropic and monotropic systems. In an enantiotropic relationship, two or more polymorphs are thermodynamically stable over different temperature or pressure ranges, and reversible solid–solid phase transitions can occur between them. In contrast, monotropic polymorphs exhibit a unidirectional stability relationship, where one form remains thermodynamically more stable than the others over all conditions below the melting point, making the transformation irreversible. This distinction is crucial for understanding phase stability, transformation mechanisms, and the thermal behavior of crystalline materials, particularly in pharmaceutical and materials applications, where polymorphic transitions may affect performance, processing, and long-term stability.

II. Historical

A detailed search in the Cambridge Structural Database (CSD, version 6.00, April 2025)² revealed the presence of more than 46,690 polymorphic compounds. This means that over forty-six thousand entries correspond to substances that crystallize in two or more distinct crystal structures while maintaining the same chemical composition. Such a large number highlights the ubiquity and importance of polymorphism in crystalline materials³. These polymorphic entries include organic, organometallic, and inorganic compounds, reflecting the wide range of systems where multiple solid-state forms can exist. This observation also demonstrates the advances in crystallographic techniques and the continuous growth of the database, which now allows researchers to systematically analyze structure property relationships, stability

hierarchies, and phase transformation behaviors among polymorphs. The concept of polymorphism was introduced for the first time by Martin Heinrich Klaproth in 1788 in connection with CaCO_3 represents the chemical formula of three polymorphs of calcium carbonate⁴ (Figure 2).

Aragonite (orthorhombic): high-temperature and high-pressure polymorph that forms in marine and geological environments, characterized by a denser orthorhombic structure where calcium ions are nine-coordinated by oxygen atoms.

Calcite (rhombohedral): the most stable and abundant polymorph of calcium carbonate at ambient conditions, crystallizing in the rhombohedral system with sixfold coordination of calcium and serving as the reference form in both geological and biological systems.

Vaterite (hexagonal): a rare and metastable hexagonal polymorph that forms under non-equilibrium conditions and readily transforms into calcite or aragonite, attracting interest for its role in biomineralization and potential biomedical applications.



Figure 2. Polymorphic crystalline forms of calcium carbonate (CaCO_3): Aragonite, Calcite, and Vaterite.

However, from a crystallographic perspective, the first formal definition of polymorphism is credited to Eilhard Mitscherlich (1822)⁵, who observed that certain compounds specifically arsenate, phosphate, and sulfur salts could exhibit different crystalline forms while maintaining the same chemical composition. This discovery laid the foundation for the concept of isomorphism and polymorphism in solid-state chemistry and crystallography, marking a major step in understanding the relationship between chemical composition and crystal structure.

The first example of polymorphism in an organic compound was discovered in 1832 by Friedrich Wöhler, namely benzamide (Figure 3). One hundred and seventy-five years later, the crystal structure of this historical polymorph was finally

determined in⁶ in addition detailed search in the CSD revealed the presence of 19 polymorph, of benzamide and the last one was reported in 2024 by D.N. Rainer.

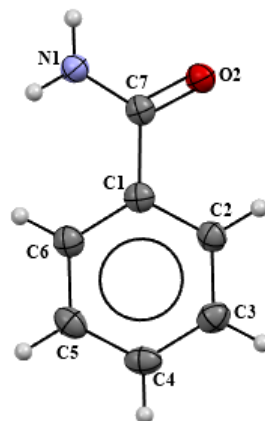


Figure 3. Molecular structure of benzamide.

Obtaining a specific polymorph under controlled and reproducible conditions is often a challenging task. Significant difficulties can arise when attempting to crystallize a desired form or reproduce results previously reported by other researchers. In many instances, even well-documented polymorphs prove elusive, despite having been successfully synthesized multiple times in the past under apparently similar conditions. Such variability often reflects the extreme sensitivity of crystallization processes to subtle factors such as temperature, solvent composition, impurities, and even the history of the sample.

III. Types of polymorphs

III. 1. Packing polymorphism

Packing polymorphism occurs when identical molecules organize themselves in distinct three-dimensional crystal lattices due solely to differences in molecular packing modes, without any significant change in the internal geometry (bond lengths, angles, or torsions) of the molecule itself. In other words, the molecular conformation remains essentially the same, but the spatial arrangement and intermolecular interactions such as hydrogen bonding, $\pi \cdots \pi$ stacking, or van der Waals forces differ between polymorphic forms. This phenomenon can lead to variations in physical properties, including melting point, solubility, density, hardness, and optical behavior, even though the chemical composition is identical. Packing polymorphism is therefore of great importance in fields such as pharmaceutical

science, materials chemistry, and crystal engineering, as small changes in molecular arrangement can result in significant differences in performance or stability.

A classic example is found in benzamide, which exhibits packing polymorphism with molecules adopting nearly identical conformations but forming different hydrogen-bond networks and crystal structures. Other compounds, such as urea and sulfur, also demonstrate polymorphism primarily arising from alternative molecular packing motifs.

III. 2. Conformational polymorphism

Conformational polymorphism occurs when a molecule can adopt different conformations (spatial arrangements of its atoms due to rotation around single bonds) in the solid state¹ leading to the formation of distinct crystal structures. Unlike packing polymorphism where the molecular conformation remains essentially the same and only the packing differs conformational polymorphs exhibit different molecular geometries within their respective lattices. These conformational differences arise because many organic molecules possess rotational flexibility around single bonds, allowing them to adopt multiple low energy conformations. When crystallization occurs, the molecular conformation that becomes part of the crystal depends on the crystallization conditions, such as temperature, solvent, rate of cooling, or presence of impurities. As a result, conformational polymorphs often display different physical and chemical properties, including melting points, densities, solubilities, and bioavailabilities. In pharmaceuticals, this can have critical implications, as conformational changes in the crystal lattice may alter how a drug dissolves or interacts biologically.

A classic example is ritonavir⁷, an antiviral drug whose second polymorph (Form II) appeared years after commercialization. This form had a different molecular conformation and lower solubility than the original (Form I), leading to drug crystallization issues and product withdrawal a landmark case in pharmaceutical crystallography. Other examples include carbamazepine and sulfur, which exhibit conformational as well as packing differences among their polymorphs.

III. 3. Pseudo-Polymorphism

Pseudo-polymorphism (also known as solvated polymorphism or solvate/hydrate formation) refers to a phenomenon in which a compound crystallizes with one or more molecules of solvent (such as water, ethanol, or methanol) incorporated into its crystal lattice. These additional solvent molecules become part of the crystal structure, altering the packing arrangement, intermolecular interactions, and physical properties of the material. Although the chemical identity of the main compound remains the same, the presence and quantity of solvent molecules lead to the formation of distinct crystalline phases. For example, when the included solvent is water, the resulting crystals are known as hydrates; when another solvent is involved, they are called solvates.

Pseudo-polymorphism is often considered a special case of polymorphism, but it is technically different because the chemical composition of the crystals is not identical; it includes additional solvent molecules. Nevertheless, pseudo-polymorphs can show behavior similar to true polymorphs, such as solid-state transformations, changes in stability, and variations in solubility, melting point, and density.

This phenomenon is of particular importance in pharmaceutical chemistry, as solvates or hydrates can exhibit different dissolution rates and stabilities compared to the anhydrous form, influencing drug formulation and storage. For instance, ampicillin trihydrate, caffeine monohydrate, and theophylline monohydrate are classic examples where pseudo-polymorphism significantly affects pharmaceutical performance.

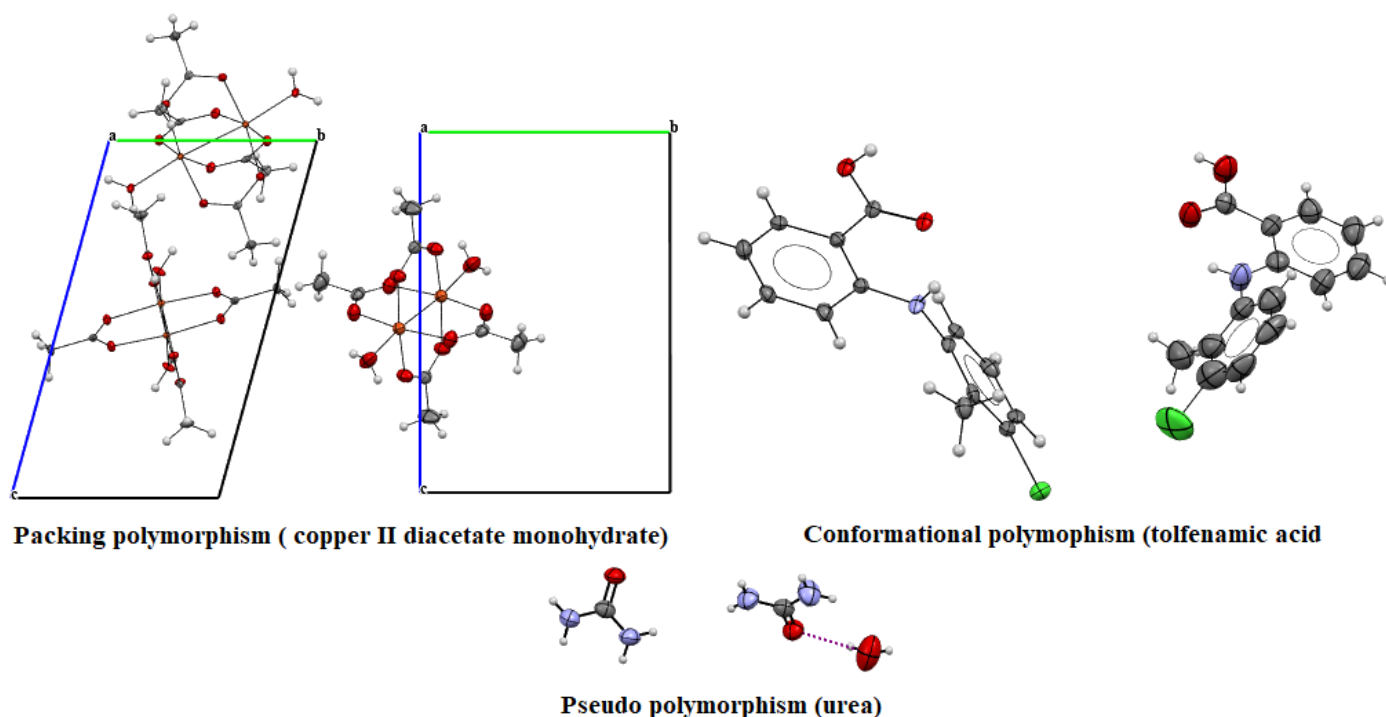


Figure 4. Different types of polymorphism

In addition, polymorphic crystallization often follows Ostwald's rule of stages, which states that metastable polymorphs tend to crystallize preferentially before the thermodynamically most stable form. This behavior reflects kinetic control during nucleation and growth processes and explains why fewer stable polymorphs are frequently observed during initial crystallization experiments.

IV. The importance of studying polymorphism

The significance of studying polymorphism, from both scientific and industrial perspectives, is clearly demonstrated by the continuous rise in the number of related publications. In 1987, only about 1,500 polymorphic structures were documented, while by June 1, 2003, this number had increased to 9,384, accounting for approximately 3% of all chemical compounds recorded in the Cambridge Crystallographic Database.⁸

Polymorphs are investigated across various disciplines including chemistry, materials science, and pharmaceutical research because of their differences in physical and physicochemical properties. Indeed, polymorphic forms of a substance may exhibit significant variations in physical and thermodynamic characteristics (such as density, refractive index, melting point, solubility, hygroscopicity, and thermal or electrical

conductivity), as well as in spectroscopic, kinetic, surface, mechanical, and chemical behaviors. These differences can influence parameters such as dissolution rate, stability, surface area, crystal habit, hardness, compressibility, thermal expansion, and chemical or photochemical reactivity. Consequently, controlling the solid-state form of a compound is essential for ensuring the desired performance of a chemical, material, or pharmaceutical product. Such control is particularly critical in fields directly impacting everyday life for example, in medicine, where polymorphism affects drug efficacy and stability, or in materials science, where it influences the functional properties of structural and transport materials⁹. On a fundamental level, the study of polymorphism deepens our comprehension of molecular packing and intermolecular interactions, which are central to crystal engineering. Ultimately, advances in experimental and computational methods continue to enhance our ability to predict and control polymorphic behavior, bridging the gap between solid-state chemistry and practical industrial innovation.

V. Conclusion

Polymorphism is a fundamental phenomenon in solid-state chemistry, illustrating how a single compound can crystallize in multiple structural forms with distinct physical and physicochemical properties. Variations in molecular packing, conformation, or solvation can significantly affect stability, solubility, mechanical behavior, and reactivity, making polymorphism a key factor in materials performance^{9, 10}. The high number of polymorphic entries reported in crystallographic databases further confirms the widespread nature of this phenomenon⁸.

From an applied perspective, polymorphism is particularly critical in pharmaceutical and materials sciences, where controlling the solid-state form is essential to ensure product reliability and functionality¹¹. Consequently, understanding and controlling polymorphic behavior remains a major challenge in crystal engineering, driving continuous advances in experimental and computational approaches.

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Chapter II.
*Structural, Spectroscopic
and Electronic
Investigation of a New
Polymorph of Copper (II)
Diacetate Monohydrate*

I. Introduction.

Copper diacetate monohydrate, commonly written as $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, is a coordination compound belonging to the family of copper (II) carboxylates. It consists of divalent copper ions coordinated by acetate ligands, with one molecule of water incorporated into the crystal structure. This compound is typically blue-green in color and crystallizes in well-defined hydrated forms, making it a useful model system in coordination chemistry and solid-state studies¹. Structurally, copper diacetate monohydrate is characterized by a coordination environment in which the copper (II) center exhibits a distorted octahedral or square pyramidal geometry, influenced by the Jahn–Teller effect commonly observed in d^9 metal ions. The acetate ligands may act as bridging or chelating groups, contributing to extended supramolecular networks through metal–ligand coordination and hydrogen bonding involving the water molecule². These structural features play a crucial role in determining the compound's thermal stability, magnetic behavior, and spectroscopic properties.

Copper acetate hydrates have attracted significant interest due to their relevance in various applications, including catalysis, pigments, fungicides, and precursors for copper-based materials. From a fundamental perspective, copper diacetate monohydrate is also of interest as a candidate for polymorphism and hydration–dehydration studies, since changes in hydration state can lead to structural transformations affecting its physical and chemical properties. As such, this compound serves as an important system for investigating structureproperty relationships in coordination compounds and crystalline materials.

II. Interest and use of metal acetate molecule.

Metal acetates (salts in which a metal cation is associated with the acetate anion, $(\text{CH}_3\text{COO}^-)$) are widely used in many scientific, industrial and technological contexts because of their beneficial chemical properties such as solubility, ease of decomposition, and diverse coordination chemistry. Some of their key interests and applications are:

- **Precursor for catalysts and nanomaterials**

Metal acetates are often used as starting materials (precursors) for preparing metal-oxide nanomaterials, bimetallic catalysts, and supported metal particles. For example, gold-palladium bimetallic catalyst particles have been prepared by physical mixing of Au and Pd acetates followed by heat treatment, yielding highly active catalysts for oxidation reactions and hydrogen peroxide formation³.

- **Additives in optoelectronic materials**

In perovskite solar cells, metal acetates are used as additives to improve film formation and to passivate defects (trap states), leading to enhanced efficiency and stability of the perovskite layer⁴.

- **Thermal decomposition for oxides / ceramic materials**

Because many metal acetates decompose cleanly under heat (releasing volatile by-products like acetic acid, CO₂, etc.), they serve as cheap, controllable precursors for obtaining metal oxides or ceramic materials with fine morphology. They allow good homogeneity and tunability of final materials via control of the decomposition and heat-treatment parameters (temperature, atmosphere, rate)⁵. Copper diacetate is a versatile coordination compound widely employed in chemistry due to its strong catalytic and coordination properties. It serves as a precursor for the synthesis of various copper-based catalysts and nanomaterials, owing to its ability to decompose cleanly into copper oxide under mild thermal conditions. In organic synthesis, copper acetate acts as an efficient oxidizing and coupling catalyst, particularly in C–H activation and oxidative coupling reactions involving aromatic and heteroaromatic compounds⁶. Furthermore, its well-defined paddle-wheel structure makes it an ideal model compound for studying metal–metal interactions and the fundamental principles of coordination chemistry and polymorphism⁷.

III. Polymorphs of copper diacetate.

Copper diacetate exists in different forms, including anhydrous copper (II) diacetate (dark green crystalline) and copper (II) diacetate monohydrate (blue-green crystalline) (Figure 5). Both are crystalline solids, but they differ in color and water content.

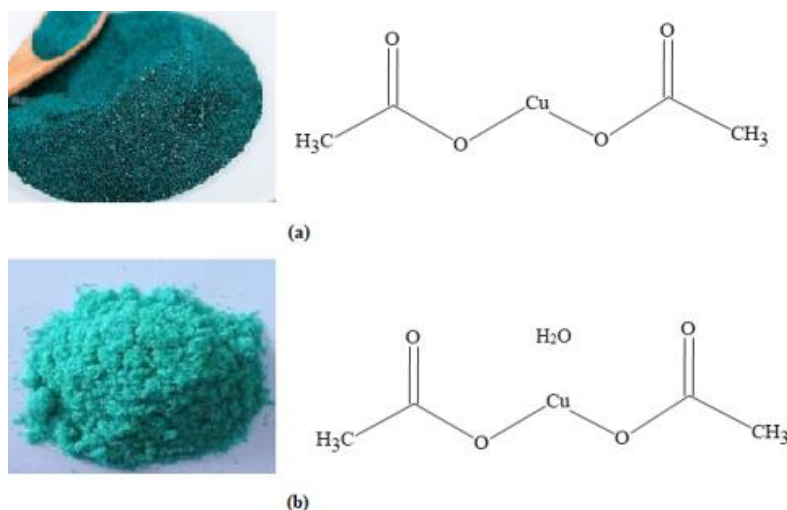


Figure 5. Copper diacetate forms: (a) anhydrous copper (II) diacetate, (b) monohydrate copper (II) diacetate.

The copper (II) diacetate monohydrate $[\text{Cu} (\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$ (Figure 6) is well known for its paddle-wheel dimeric arrangement, in which two copper (II) centers are bridged by four acetate ligands, forming a $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4$ core with a weak axial Cu–Cu interaction.

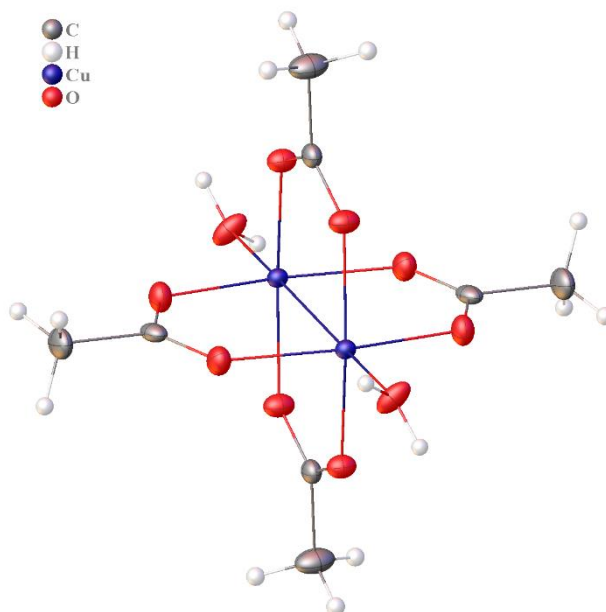


Figure 6. Molecule of diaquatetraacetatodicopper (II).

Copper diacetate monohydrate is soluble in water and alcohols and serves as a versatile precursor in the synthesis of copper-based materials and as a catalyst in organic oxidation reactions. From a solid-state chemistry perspective, copper diacetate is a representative example of a compound exhibiting polymorphism, where

the same chemical composition can crystallize in distinct forms with different crystal symmetries and packing arrangements.

The known polymorphs of copper (II) diacetate monohydrate differ mainly in their space groups, hydrogen-bonding networks, and coordination environments, which lead to observable variations in stability, color, and reactivity. This structural diversity makes copper diacetate an instructive model for understanding metal–ligand interactions and the influence of crystallographic parameters on physical properties in coordination compounds.

A systematic survey of the Cambridge Structural Database (CSD, version 6.00, April 2025)⁸ revealed the existence of 245 structures with the $\text{Cu}_2(\text{AcO})_4$ fragment, 23 of them are packing polymorphic structures of $[\text{Cu}_2(\mu\text{-OOCCH}_3)_4 \cdot 2\text{H}_2\text{O}]$ (Figure 7).

Chapter II: Structural, Spectroscopic and Electronic Investigation of a New Polymorph of Copper(II) Diacetate Monohydrate

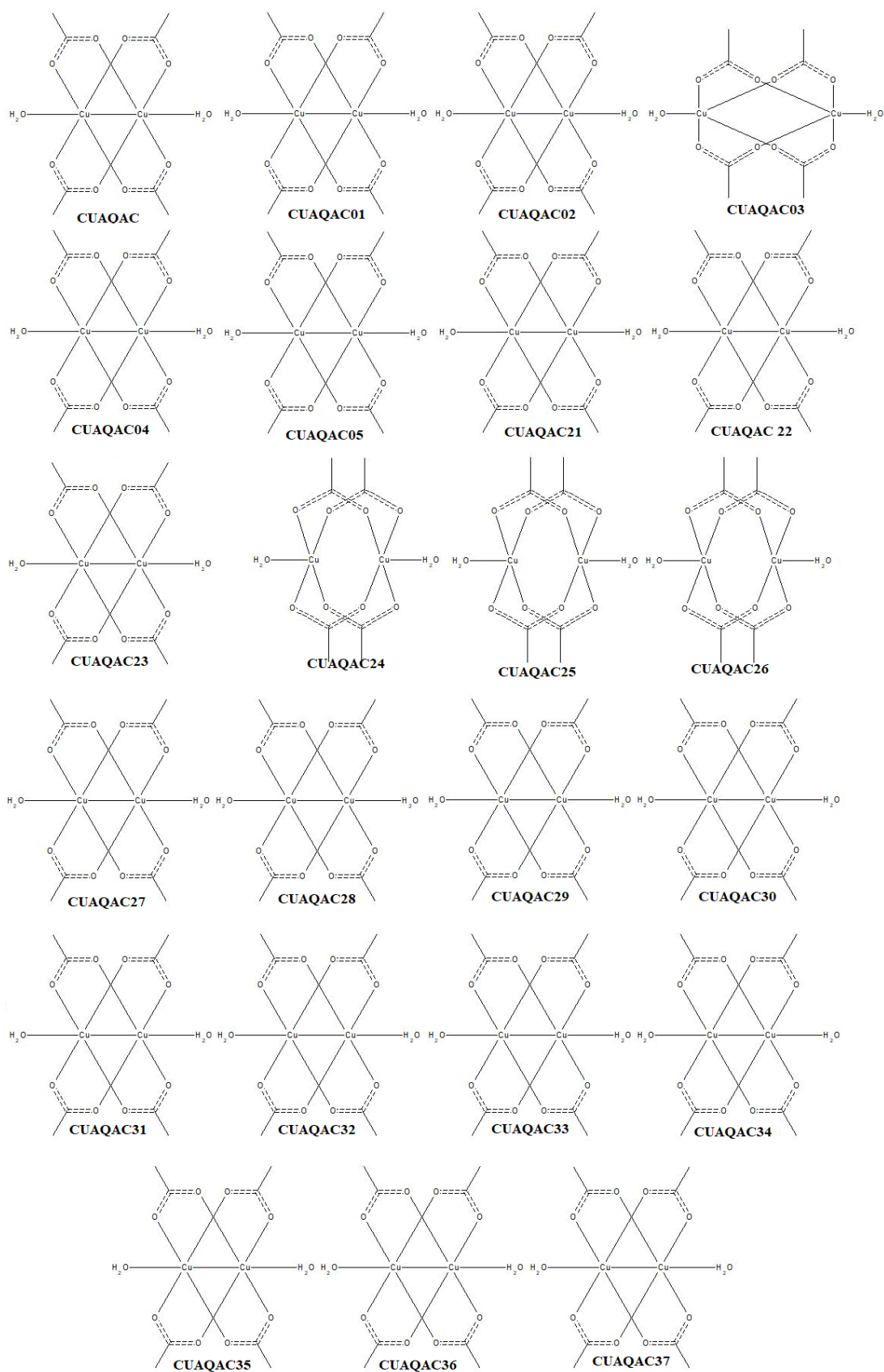


Figure 7. The crystal structure diagrams of diaquatetraacetatodicopper(II) packing polymorphs are available in the CSD.

Chapter II: Structural, Spectroscopic and Electronic Investigation of a New Polymorph of Copper(II) Diacetate Monohydrate

The crystal structure of the $[\text{Cu}_2(\mu\text{-OOCCH}_3)_4\cdot 2\text{H}_2\text{O}]$ polymorph was first determined by J. N. van Niekerk and F. R. L. Schoening in 1953 [9], and later by P. de Meester et al. in 1973¹⁰. The structural analysis of $[\text{Cu}_2(\mu\text{-OOCCH}_3)_4\cdot 2\text{H}_2\text{O}]$ has since been re-examined by several research groups¹¹⁻¹⁹. The most recent study, conducted in 2024 by P. G. Waddell, M. R. Probert, and N. T. Johnson²⁰ provided updated insights into its structure.

All 23 polymorphs of $[\text{Cu}_2(\mu\text{-OOCCH}_3)_4\cdot 2\text{H}_2\text{O}]$ crystallize in centrosymmetric space groups with a monoclinic system, while only the newly identified polymorph crystallizes in a centrosymmetric space group with a triclinic system (Table 1).

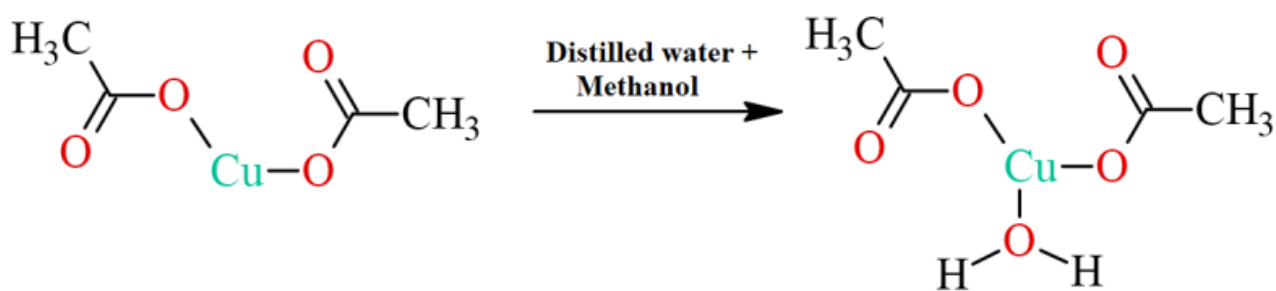
Table 1. Crystallographic data of copper (II) diacetate monohydrate polymorphs available in the CSD.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Space groupe, System
P1	7.804	7.804	12.975	99.00	101.525	114	P$\bar{1}$(Triclinic)
CUAQAC22	13.167	8.571	13.849	90	117.024	90	C 2/c (monoclinic)
CUAQAC31	13.145	8.545	13.785	90	116.880	90	C 2/c (monoclinic)
CUAQAC01	13.188	8.580	13.877	90	117.025	90	C 2/c (monoclinic)
CUAQAC05	13.096	8.511	13.753	90	116.885	90	C 2/c (monoclinic)
CUAQAC23	13.094	8.510	13.747	90	116.876	90	C 2/c (monoclinic)
CUAQAC36	13.166	8.564	13.858	90	116.924	90	C 2/c (monoclinic)
CUAQAC27	13.098	8.512	13.751	90	116.879	90	C 2/c (monoclinic)
CUAQAC28	13.083	8.502	13.731	90	116.865	90	C 2/c (monoclinic)
CUAQAC29	13.064	8.503	13.716	90	116.850	90	C 2/c (monoclinic)
CUAQAC	13.15	8.52	13.90	90	117	90	C 2/c (monoclinic)
CUAQAC02	13.168	8.564	13.858	90	117.02	90	C 2/c (monoclinic)
CUAQAC03	13.167	8.563	13.862	90	117.019	90	C 2/c (monoclinic)
CUAQAC04	13.129	8.533	13.803	90	116.91	90	C 2/c (monoclinic)
CUAQAC21	13.167	8.563	13.862	90	117.019	90	C 2/c (monoclinic)
CUAQAC24	13.177	8.571	13.871	90	117.007	90	C 2/c (monoclinic)
CUAQAC25	13.153	8.583	13.843	90	116.925	90	C 2/c (monoclinic)
CUAQAC26	13.174	8.569	13.867	90	117.026	90	C 2/c (monoclinic)
CUAQAC30	13.156	8.560	13.856	90	117.080	90	P 21/c (monoclinic)
CUAQAC32	13.084	8.503	14.050	90	119.308	90	C 2/c (monoclinic)
CUAQAC33	13.096	8.511	13.753	90	116.885	90	C 2/c (monoclinic)
CUAQAC34	13.076	8.499	13.726	90	116.864	90	C 2/c (monoclinic)
CUAQAC35	12.972	8.436	13.617	90	116.861	90	C 2/c (monoclinic)
CUAQAC37	13.096	8.506	13.758	90	116.887	90	C 2/c (monoclinic)

III. Experimental methods

III. 1. Experimental procedure.

A weighed amount of copper (II) diacetate was dissolved under stirring in a 1:1 (v/v) mixture of distilled water and methanol at room temperature to obtain a homogeneous blue solution. Slow evaporation of the solvent at ambient conditions afforded well-formed blue-green crystals, which were isolated by filtration, washed with cold methanol.



Scheme 1. Reaction scheme of the synthesis of the new polymorph P1.

III. 2. Single-crystal X-ray diffraction analysis.

A Bruker APEX II diffractometer equipped with a CCD area detector was used to perform the single crystal diffraction observations of **P1** at 100 K utilizing graphite monochromatized *MoK α* radiation, $\lambda = 0.71073$ Å. The *SHELXT* program was used to solve the structures using the intrinsic-phasic approach²¹, and then refined using the *SHELXL* program²² which was included into the Olex2 1.3 software package²³, against all reflections and F^2 . All non-H atoms were refined in an anisotropic manner. (Table 2) summarizes the data collection and structure refining features of **P1**, which revealed hydrogen atoms in the differential density in Fourier Maps.

Table 2. Structural data and recording conditions for copper (II) diacetate monohydrate polymorph: **P1**.

Crystal data	
Refined formula	(CuC ₄ H ₈ O ₅) ₂
Mr	402.96
Temperature (K)	100
Crystal system, Space group (no.)	Triclinic, <i>P</i> -1
<i>a</i> (Å), <i>b</i> (Å), <i>c</i> (Å)	7.8049(17), 7.8042(6), 12.975(2)
α (°), β (°), γ (°)	99.00, 101.525(16), 114.00
Volume (Å ³)	682.04(19)
Z	2
ρ_{calc} (g/cm ³)	1.962
μ (mm ⁻¹)	3.165
Radiation	Mo <i>K</i> _α (λ = 0.71073)
Crystal size (mm ³)	0.180 × 0.180 × 0.080
Data collection	
2 θ range (°)	2.964– 36.364
F (000)	408
Index ranges	−13 ≤ <i>h</i> ≤ 13, −13 ≤ <i>k</i> ≤ 13, −21 ≤ <i>l</i> ≤ 21
<i>T</i> _{min} – <i>T</i> _{max}	0.5731–0.7471
Reflections collected, Independent reflections, Observed reflections with [<i>I</i> > 2σ(<i>I</i>)]	32422, 6394, 6122
<i>R</i> _{int} , <i>R</i> _{sigma}	0.0367, 0.0247
Refinement	
Final <i>R</i> indexes [<i>F</i> ² > 2σ (<i>F</i> ²)], Final <i>R</i> indexes [all data], Goodness-of-fit on <i>F</i> ²	[<i>R</i> = 0.0262, <i>R</i> _w = 0.1025], [<i>R</i> = 0.0339, <i>R</i> _w = 0.1249], 1.251

III. 3. FTIR spectroscopic characterization of copper (II) diacetate monohydrate.

The FTIR spectrum of copper (II) diacetate monohydrate (Figure 8) exhibits characteristic absorption bands consistent with the coordination of acetate ligands to

Cu^{2+} ions and the presence of lattice water molecules. A broad absorption band observed in the $3600\text{--}3200\text{ cm}^{-1}$ region is attributed to O–H stretching vibrations of coordinated and hydrogen-bonded water molecules, indicating strong intermolecular hydrogen bonding within the crystal lattice. The bands appearing in the $3000\text{--}2800\text{ cm}^{-1}$ region correspond to C–H stretching vibrations of the methyl groups of the acetate ligands. Strong absorptions in the $1600\text{--}1550\text{ cm}^{-1}$ and $1450\text{--}1400\text{ cm}^{-1}$ regions are assigned to the asymmetric (ν_{as}) and symmetric (ν_{s}) stretching vibrations of the carboxylate (COO^-) groups, respectively. The separation between these two bands ($\Delta\nu$) suggests a bridging bidentate coordination mode of the acetate ligands to the copper (II) centers, which is characteristic of copper (II) acetate complexes. Additional bands in the $1350\text{--}1000\text{ cm}^{-1}$ region are attributed to C–O stretching and CH_3 bending vibrations of the acetate groups. The low-wavenumber region below 700 cm^{-1} shows bands associated with Cu–O stretching vibrations, confirming metal–ligand coordination.

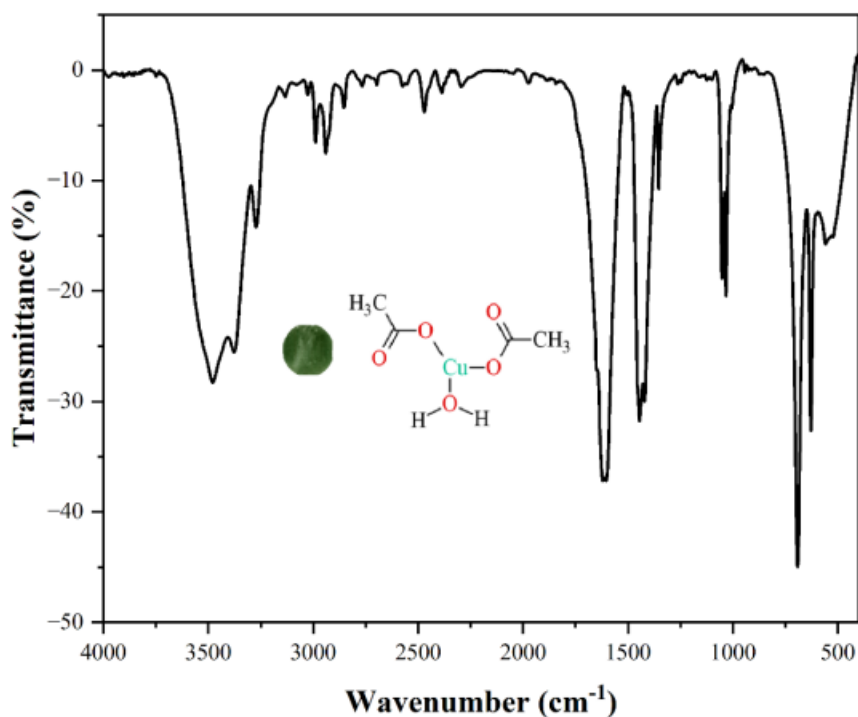


Figure 8. FTIR spectrum of copper (II) diacetate monohydrate.

Table 3. FTIR wavenumber assignments of copper (II) diacetate monohydrate polymorph: **P1** and corresponding vibrational modes.

Wavenumber (cm ⁻¹)	Assignment	Origin
3600–3200	Broad O–H stretching	Coordinated and hydrogen-bonded water molecules
3000–2850	C–H stretching	Methyl (–CH ₃) groups of acetate ligands
~1600–1550	v _{as} (COO ⁻) asymmetric stretching	Carboxylate groups coordinated to Cu ²⁺
~1450–1400	v _s (COO ⁻) symmetric stretching	Carboxylate groups of acetate
~1350–1300	CH ₃ bending (δ CH ₃)	Acetate ligands
~1250–1050	C–O stretching	Acetate groups
~1050–900	C–C stretching	Acetate backbone
~800–700	O–C–O bending	Carboxylate group deformation
~650–500	Cu–O stretching vibrations	Metal–oxygen coordination bonds

IV. Description of the structure.

P1 a binuclear complex contains two clusters of [Cu₂(μ-OOCCH₃)₄·2H₂O] with paddle-wheel geometry (Figure 9) bonded by O–H···O, **P1** crystallizes in the triclinic system with the centrosymmetric space group $P\bar{1}$. The asymmetric unit consists of two halves structurally independent of two distinct copper diacetate molecules., with each Cu atom further coordinated to a water molecule in axial position. The metal-metal lengths are 2.613 Å in the first cluster and 2.612 Å in the second cluster; these modest distances imply that **P1** exhibits high electronic coupling.

As expected for a d⁹ metal center, the Jahn–Teller effect²⁴ induces a distorted octahedral environment around Cu, characterized by equatorial Cu–O bond lengths with an average of Cu–O = 1.968 Å and axial Cu–O bond lengths with an average of Cu–O = 2.146 Å, where the equatorial O–Cu–O bond angles extend an average of 89.48° and the axial O–Cu–O bond angles extend an average of 95.43°, each copper achieves square pyramidal.

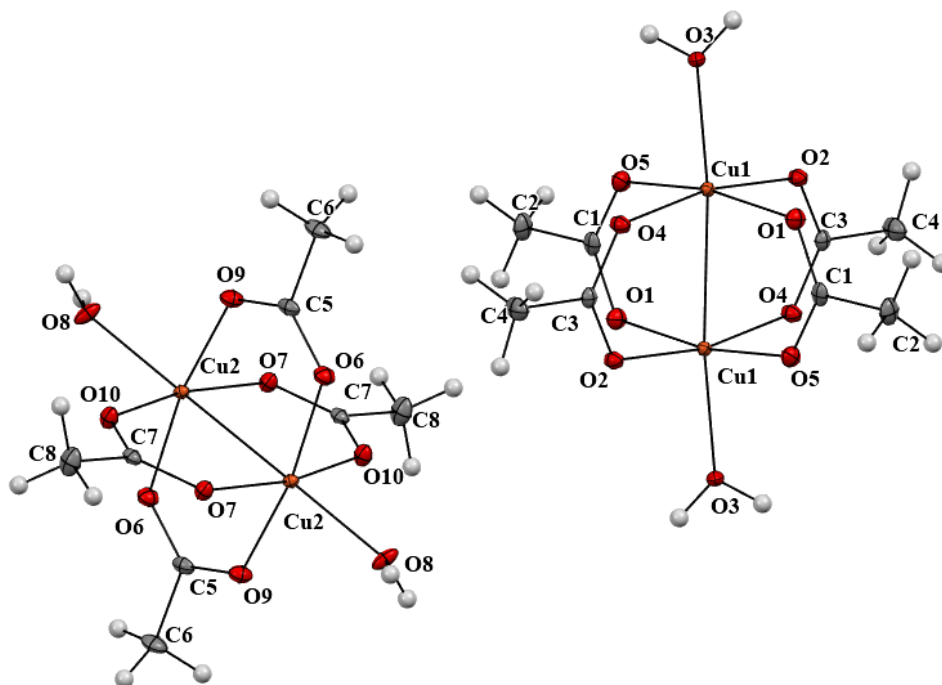


Figure 9. Perspective view of diaquatetraacetatodicopper (II) polymorph: **P1** with atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius.

In contrast, the monoclinic polymorph ($C2/c$) **P2** contains one cluster of $[\text{Cu}_2(\mu\text{-OOCCH}_3)_4 \cdot 2\text{H}_2\text{O}]$ (Figure 10 a) with paddle-wheel geometry where the asymmetric unit is a half of this cluster, its Cu–Cu distance is 2.619 Å, the equatorial Cu–O bond lengths (≈ 1.976 Å) with O–Cu–O bond angles ($\approx 89.45^\circ$), the axial Cu–O bond lengths (≈ 2.156 Å), with O–Cu–O bond angles ($\approx 95.62^\circ$). The second monoclinic polymorph ($P2_1/c$) **P3**, contains one cluster (Figure 10 b) features a complete $[\text{Cu}_2(\mu\text{-OOCCH}_3)_4 \cdot 2\text{H}_2\text{O}]$ in the asymmetric unit with paddle-wheel geometry, its Cu–Cu distance is 2.615 Å, the equatorial Cu–O bond lengths (≈ 1.967 Å) with O–Cu–O bond angles ($\approx 89.45^\circ$), the axial Cu–O bond lengths (≈ 2.158 Å), with O–Cu–O bond angles ($\approx 95.58^\circ$).

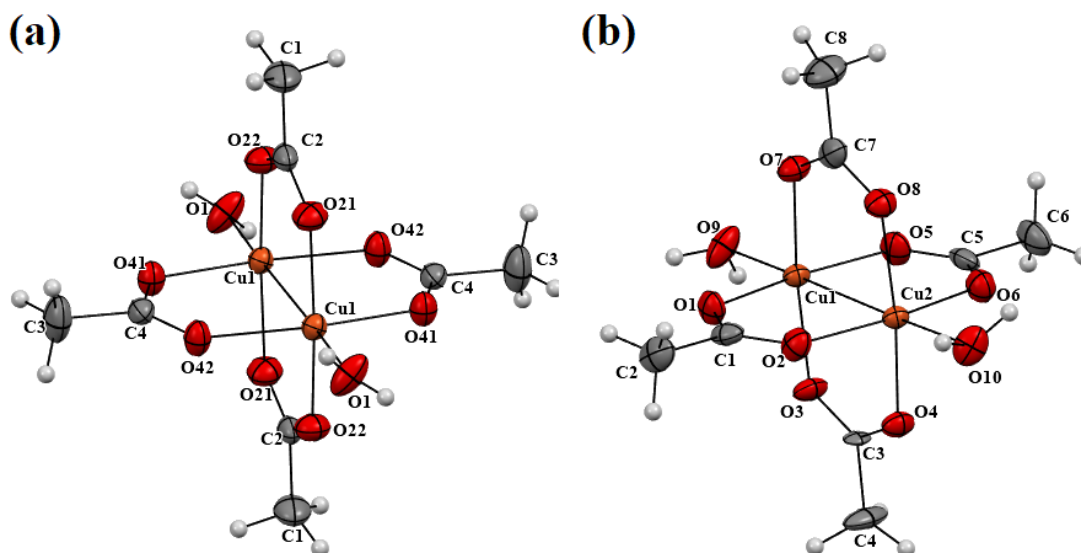


Figure 10. Perspective view of diaquatetraacetatodicopper (II) monohydrate polymorphs: **P2** and **P3** with atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius.

P1 exhibits the shortest Cu–Cu distances a direct (Cu–Cu) bond and most contracted equatorial Cu–O bonds among **P2** and **P3**, indicating the strongest local structural distortion and highest potential electronic coupling within its paddle-wheel dimers²⁵. The stacking features of the three polymorphs highlight markedly different supramolecular architectures governed by distinct hydrogen-bonding networks. In polymorph **P1**, the unit cell accommodates four molecules located at the midpoints of the edges parallel to the b-axis, together with one molecule situated at the center of the unit cell. The crystal packing is characterized by one-dimensional supramolecular chains generated by alternating binuclear motifs, which are interconnected through robust O–H $\cdots$ O hydrogen bonds, leading to the formation of dimer-based assemblies (Figure 11).

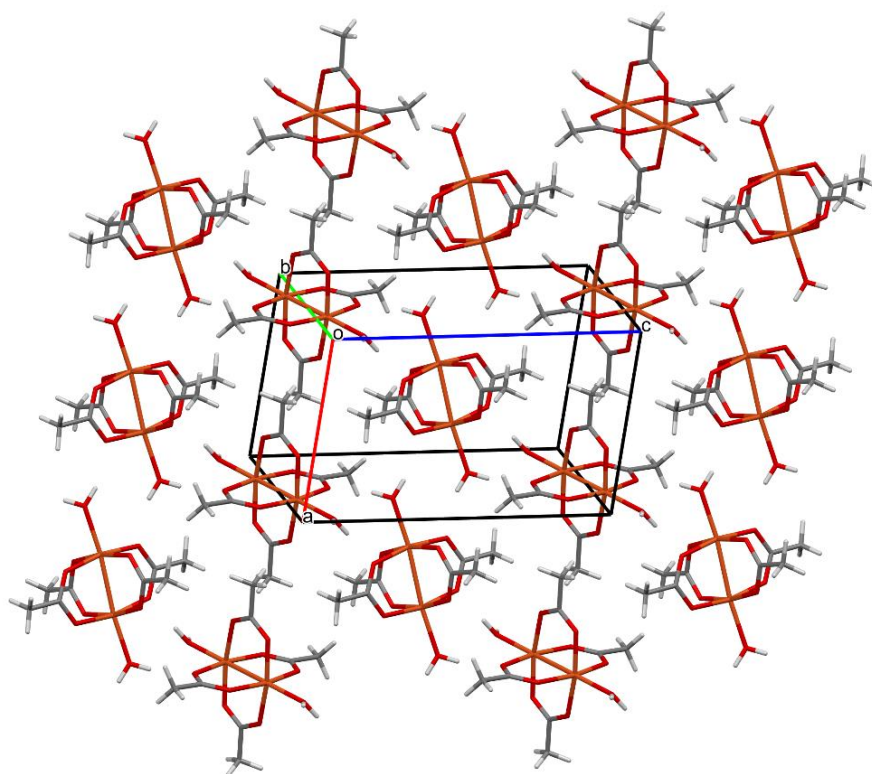


Figure 11. Crystal packing of **P1**.

In polymorph **P2** (Figure 12 a), the molecular entities occupy the vertices of the unit cell, the centers of the *c* faces, the midpoints of the edges parallel to the *c*-axis, as well as the center of the unit cell. This distinct spatial distribution gives rise to extended chain-like architectures sustained by O–H···O hydrogen-bonding interactions, resulting in a different supramolecular organization compared to **P1**.

In polymorph **P3** (Figure 12 b) the cell unit occupied by two molecules at the centre and two halves at *c* faces, these layers further stack along the *c* axis generating a three dimensional architecture maintained by O–H···Hydrogen-bonding interactions lead to a distinct supramolecular architecture in comparison to **P1**.

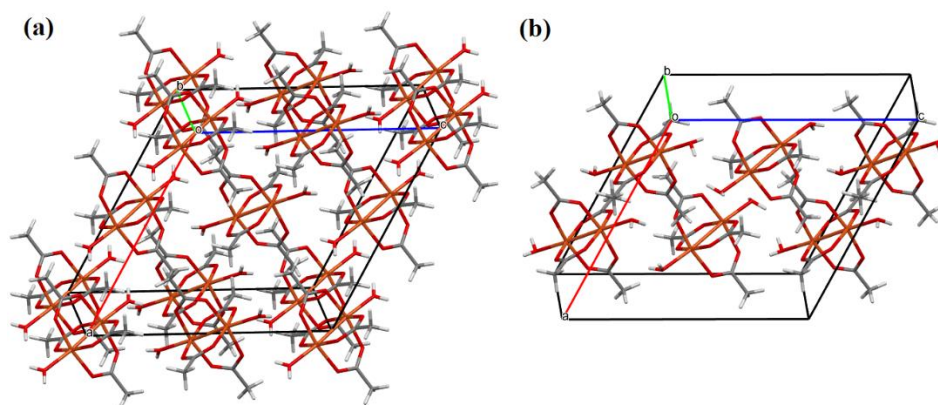


Figure 12. Crystal packing of (a) **P2**, (b) **P3**.

These variations in molecular positioning and hydrogen-bond connectivity underscore the profound impact of polymorphism on the stacking arrangement and the resulting supramolecular topology ([Figure 13](#)).

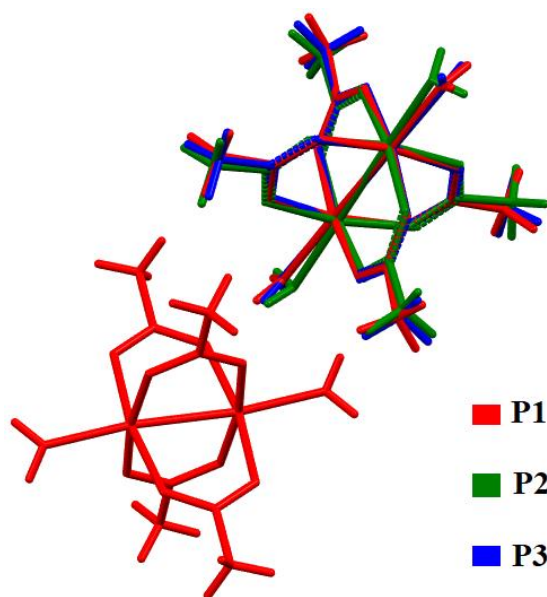


Figure 13. Superposition of the crystal structures of three polymorphs of copper (II) diacetate monohydrate **P1**, **P2** and **P3**

Moderate O–H···O interactions serve as the primary supramolecular links among adjacent $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$ units of the three polymorphs, enhancing the cohesion of the crystal lattice, this molecular association leads to the establishment of well-defined graph-set patterns ([Figure 14](#)) $R_2^2(8)$ and $R_6^6(24)$ for (**P1**), $R_2^2(8)$ for (**P2**) and $R_2^2(8)$ and $R_4^6(22)$ for (**P3**)

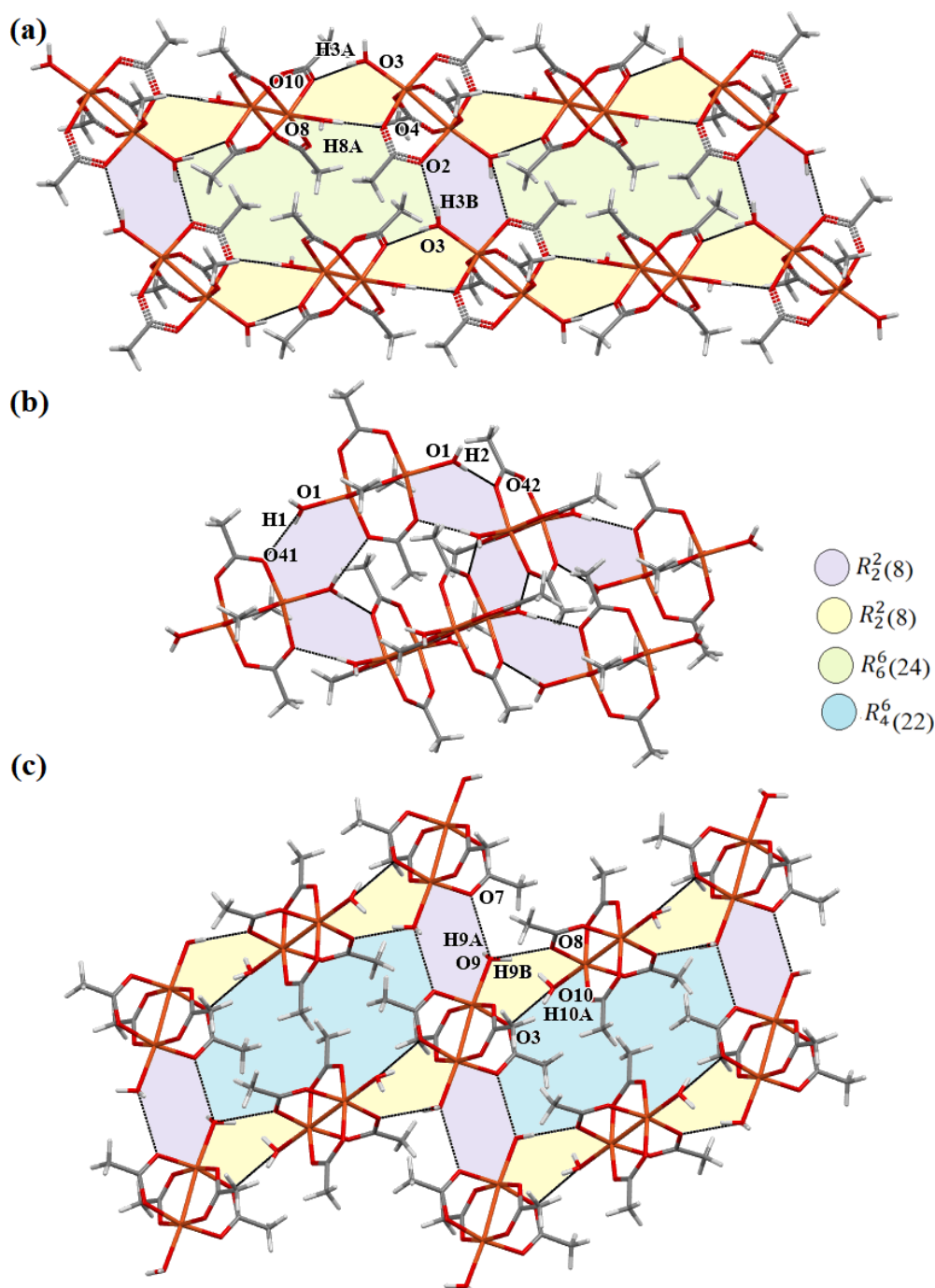


Figure 14. Supramolecular packing of (a) **P1** (b) **P2** and (c) **P3** showing O–H···O interactions forming ring motifs

(P1) features a primarily one-dimensional O–H···O hydrogen-bonding motif that propagates along the *b*-axis with four contacts (Figure 15 a). The O···O donor–acceptor separations range from 2.786 to 2.887 Å, representing the shortest O–H···O contacts among the three structures.

(P2) (Figure 15 b), the O···O distances of the two O–H···O (2.826–2.940 Å) are slightly longer than those observed in **(P1)**

(P3) (Figure 15 c) demonstrates a markedly different arrangement, characterized by three O–H···O hydrogen bonds of nearly identical length, centered around approximately 2.82 Å.

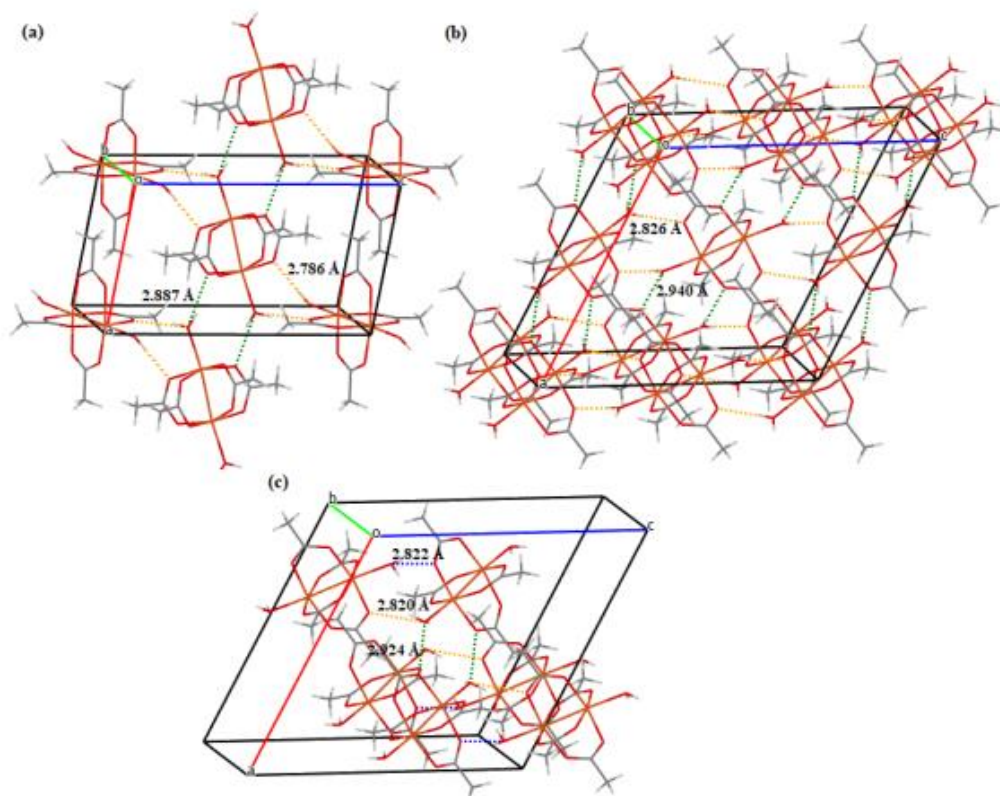


Figure 15. Dimers formed by molecules along the b-axis, and the O–H···O hydrogen bond length for **P1** (a), **P2** (b) and **P3** (c).

Table 4. Hydrogen-bond geometry (Å, °) for copper (II) diacetate monohydrate polymorphs: **P1**, **P2** and **P3**.

	D–H...A (Å)	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
(P1)	O3–H3A···O10	0.8504	1.943	2.786	170.46
	O3–H3B···O2	0.8502	2.070	2.887	161.00
	O8–H8A···O4	0.8503	1.940	2.786	170.46
	O8–H8B···O7	0.8501	2.065	2.887	161.00
(P2)	O1–H1···O41	0.740	2.223	2.940	163.38
	O1–H2···O42	0.777	2.050	2.826	175.94
(P3)	O10–H10A···O3	0.852	2.015	2.822	157.78
	O9–H9B···O8	0.851	2.033	2.820	153.47
	O9–H9A···O7	0.850	2.669	2.924	98.94

IV. 1. Morphological analysis (BFDH).

The Bravais-Friedel-Donnay-Harker (BFDH) morphology predictions²⁶ for three polymorphs of copper diacetate monohydrate $[\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}]$ (Figure 16) reveal distinct crystal habits reflecting different packing arrangements of the copper acetate dimeric units. **P1** exhibits a hexagonal-prismatic morphology dominated by (001) and (00-1) basal faces with minor (1-1-1) and (-111) prismatic faces, indicating strong in-plane bonding and restricted growth along the c-axis. **P2** displays a complex polyhedral habit with multiple well-developed faces including (002), (1-1-1), (-202), (1-10), (110), and various $(\pm 1 \pm 1 \pm 1)$ families, suggesting more isotropic intermolecular interactions and a lower-symmetry crystal system. **P3** presents a modified hexagonal morphology intermediate between (a) and (b), with prominent (100) and (-100) basal faces supplemented by significant (0-11), (-102), (0-1-1), and (01-1) truncations, reflecting altered interlayer interactions possibly due to different water molecule positions and hydrogen bonding networks. These morphological variations underscore the sensitivity of crystal habit²⁷ to subtle changes in molecular packing and intermolecular forces within polymorphic systems.

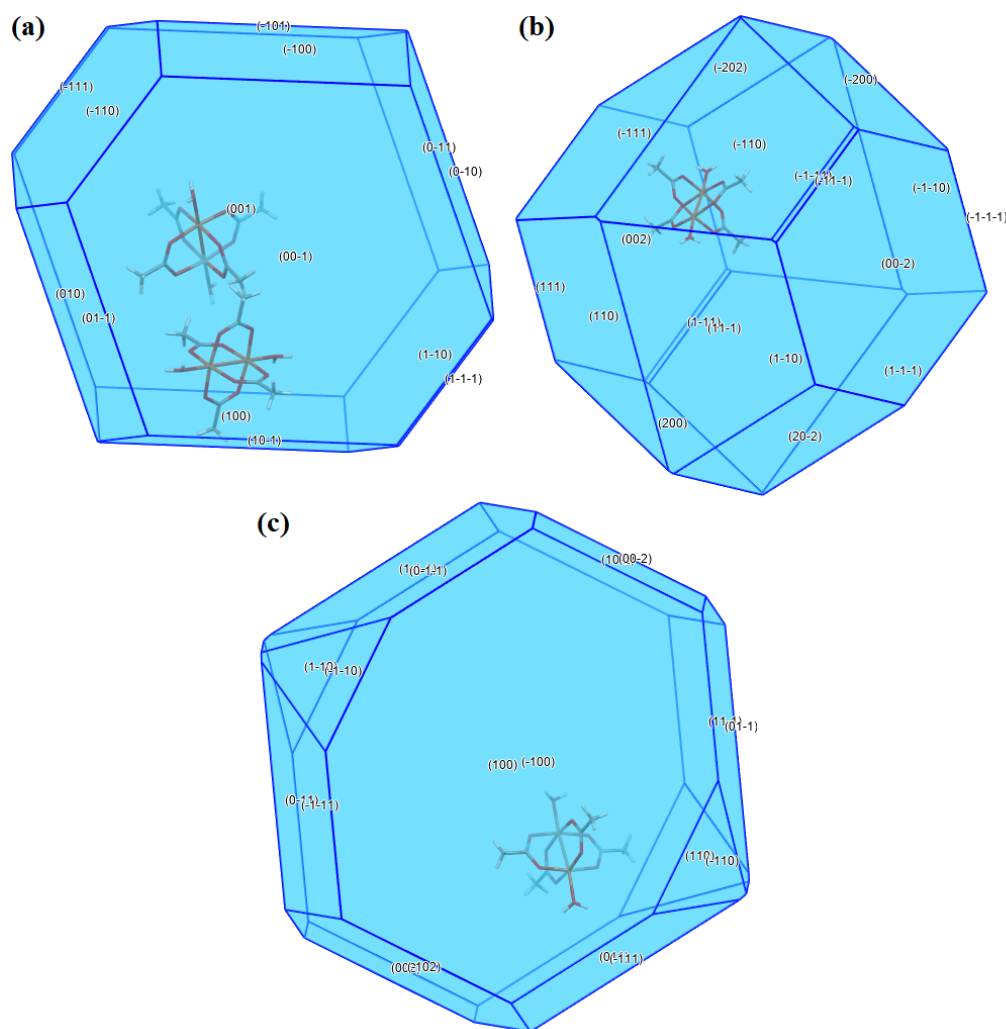


Figure 16. Predicted BFDH morphologies of (a) **P1** (b) **P2** and (c) **P3**

IV. 2. Structural porosity and pore analysis of P1.

The newly identified polymorph of copper (II) diacetate monohydrate **P1** exhibits a distinct crystal packing arrangement that gives rise to intrinsic porosity within the solid-state structure. Unlike previously reported dense polymorphs of this compound, the present structure adopts a framework-like organization in which copper (II) paddlewheel units interconnected by acetate ligands define continuous voids within the crystal lattice.

The pore architecture is illustrated in [Figure 17](#) through representations of the contact surface ([Figure 17 a](#)) and the solvent-accessible surface ([Figure 17 b](#)). The contact surface delineates the geometric void space defined by the van der Waals radii of the framework atoms and reflects the intrinsic porosity arising from inefficient packing of the coordination units. The solvent-accessible surface, calculated using a molecular

probe, represents the fraction of this void space that is accessible to guest molecules. The persistence of open channels in the solvent-accessible representation confirms that the pores are not merely crystallographic artifacts but correspond to functionally accessible voids.

Quantitative analysis of the porosity was performed using the Mercury software package. The calculations reveal a network-accessible geometric volume of $0.646 \text{ cm}^3 \text{ g}^{-1}$ and a network-accessible helium volume of $0.531 \text{ cm}^3 \text{ g}^{-1}$, indicating a substantial fraction of accessible void space within the structure. The network-accessible surface area was calculated to be $1366.97 \text{ m}^2 \text{ g}^{-1}$, further confirming the presence of an extended internal surface characteristic of porous coordination frameworks.

Pore size analysis indicates a pore limiting diameter of $4.51 \text{ \AA}$ and a maximum pore diameter of $5.64 \text{ \AA}$, consistent with the presence of narrow channels rather than large cavities. The calculated number of percolated dimensions (1) indicates a one-dimensional pore network, in agreement with the channel-like features observed in the surface representations.

Taken together, the qualitative surface visualizations and quantitative Mercury calculations demonstrate that $(\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O})$ possesses permanent, solvent-accessible porosity arising solely from its crystal packing arrangement. This behavior distinguishes it from previously reported non-porous forms of copper (II) diacetate monohydrate and supports its classification as a porous coordination framework with MOF-like characteristics, despite its relatively simple molecular composition.

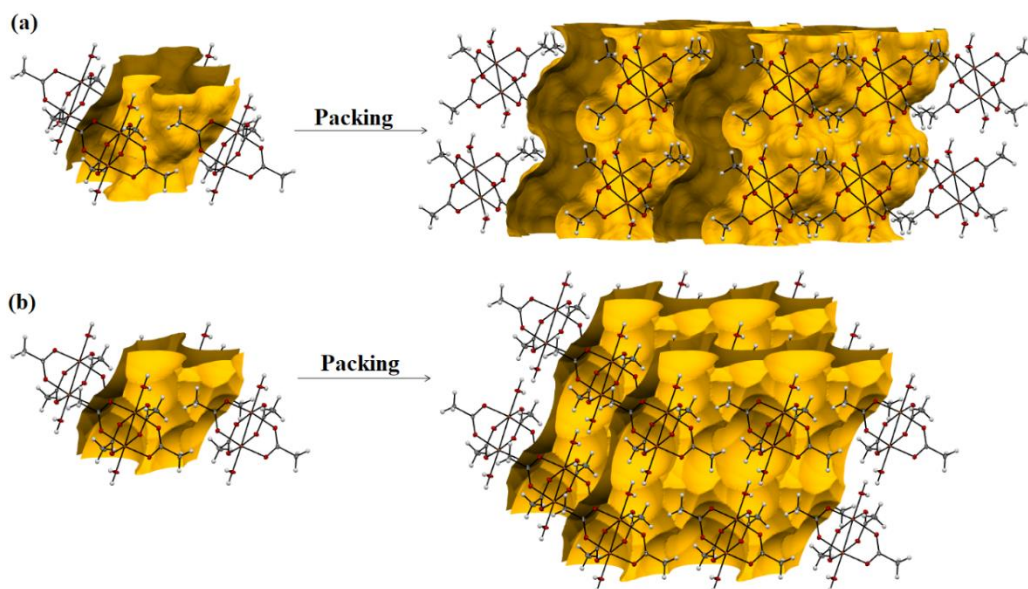


Figure 17. Porous framework architecture of copper (II) diacetate monohydrate polymorph: **P1**

This study highlights how polymorphism alone can induce framework-like porosity in classical coordination compounds, expanding the structural scope of MOF-related materials.

V. Hirshfeld surface analysis (HSA)

Hirshfeld surface (HS) analysis is a valuable technique for visualizing intermolecular interactions in crystal structures by dividing electron density into molecular fragments. This analysis provides insights into the stabilizing interactions within crystal lattices, which is vital for understanding compounds' physical and chemical behaviors. Additionally, fingerprint plots (FP) quantitatively illustrate contact distance distributions, aiding research in materials science and pharmaceuticals²⁸. A comparative HS analysis (Figure 18) using CrystalExplorer 21.5²⁹ on three polymorphs of copper (II) diacetate monohydrate revealed notable differences in intermolecular interactions and packing environments.

The d_{norm} surfaces reveal distinct hydrogen-bonding profiles : **P1** exhibits the most extensive red regions indicating numerous strong O–H $\cdots$ O interactions, **P2** shows fewer and less intense red spots reflecting a weaker hydrogen-bond network, while **P3** displays localized but intense red regions suggesting fewer yet geometrically favorable strong O–H $\cdots$ O contacts.

Shape-index surfaces reveal that **P1** exhibits pronounced red-blue features indicating well-defined directional C–H···O interactions, **P2** displays diffuse low-contrast patterns reflecting isotropic packing, and **P3** shows localized red-blue patches suggesting specific but less extensive directional contacts, with π - π stacking absent in all polymorphs.

The d_e surfaces reveal distinct packing density variations : **P1** exhibits broad blue regions indicating close external contacts and the tightest packing, **P2** shows predominantly green-yellow regions reflecting moderate intermolecular distances and the most open structure, while **P3** displays localized blue zones suggesting intermediate packing density with specific tight-packing regions.

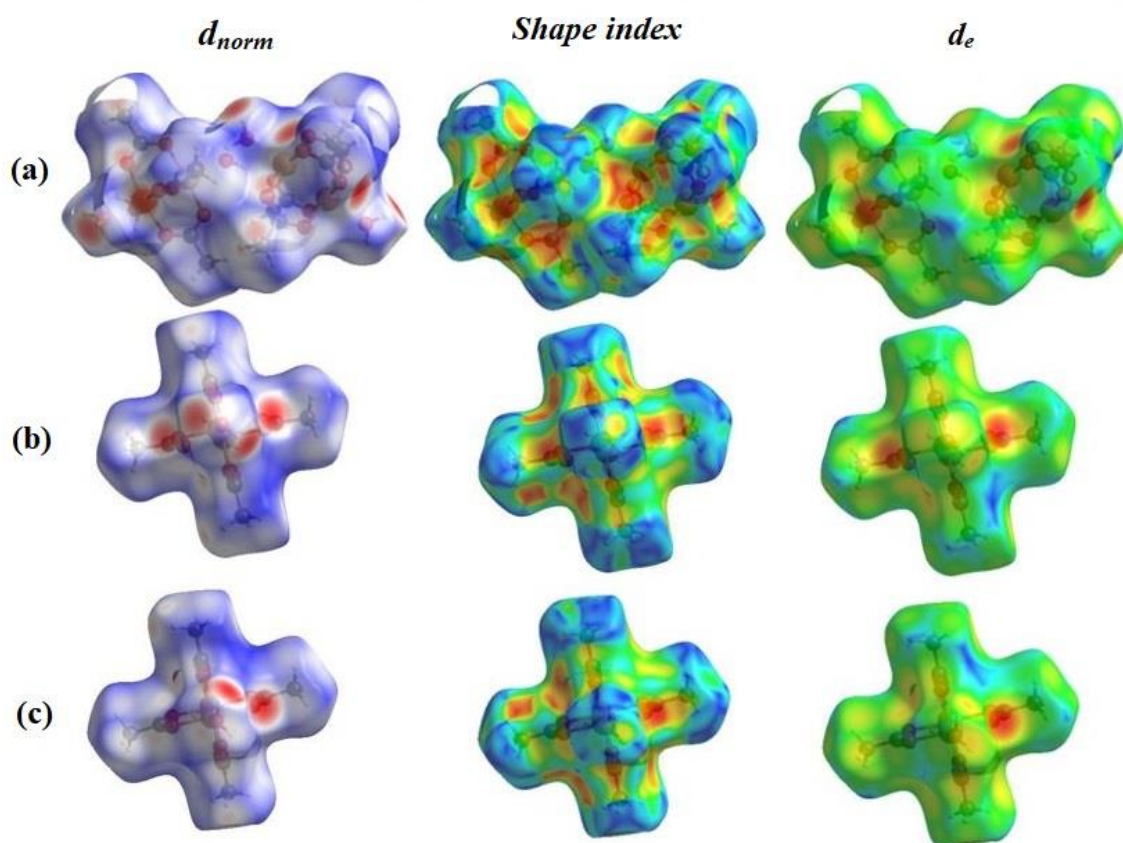


Figure 18. Hirshfeld surface analysis of polymorphs (a): **P1**, (b): **P2** and (c): **P3** of copper (II) diacetate monohydrate, showing d_{norm} , shape index, and d_e surface mappings.

The 2D fingerprint²⁸ is based on the intermolecular interactions and contacts present in the crystal structure, such as those observed in the Hirshfeld surface. This fingerprint allows a graphical visualization of the dominant intermolecular interactions and the specific contact regions within the crystal.

The 2D Hirshfeld fingerprint plots (Figure 19) show that the three polymorphs of copper (II) diacetate monohydrate differ significantly in the relative contributions of dispersive versus directional contacts. In the example dataset, **P1** exhibits a substantial H···H contribution (52.2%) together with a large O···H/H···O fraction (43.6%). **P2** is dominated by H···H contacts (54%) and shows O···H component (41.8%), **P3** occupies an intermediate position with H···H of 54.0% and O···H of 38.7%, Contributions from C···H/H···C ($\approx 3\%$ in all three polymorphs). Minor O···O percentages indicate that direct heteroatom–heteroatom or $\pi\cdots\pi$ short contacts are not the principal stabilizing interactions in any of the forms.

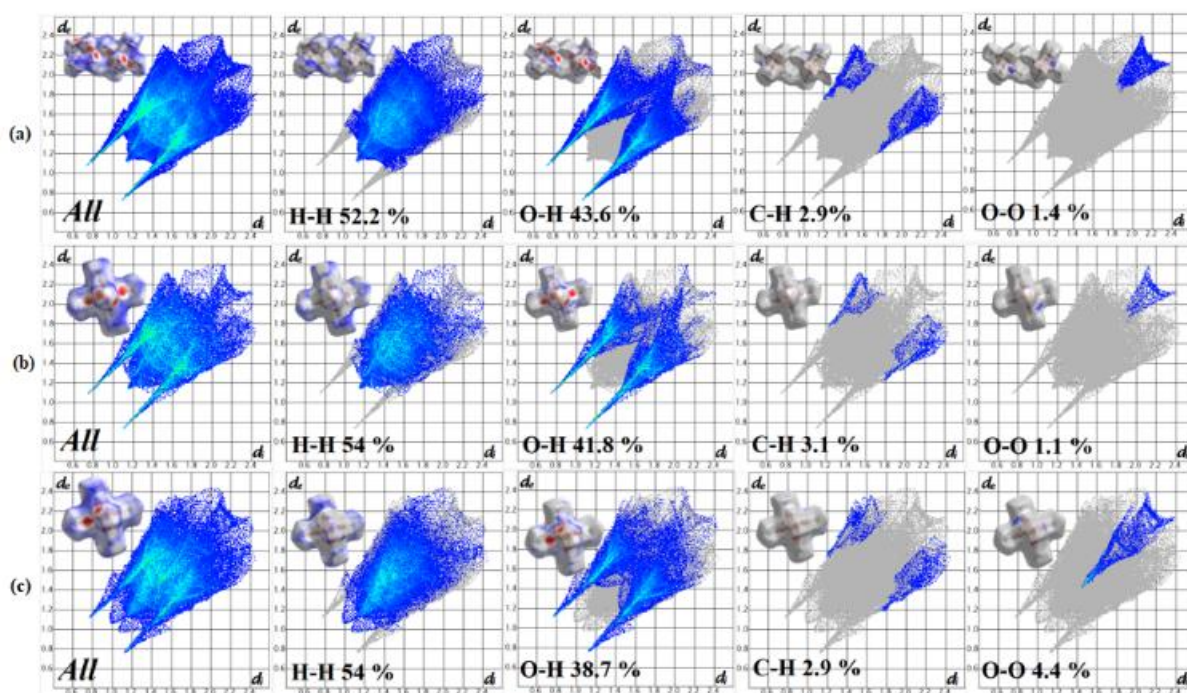


Figure 19. 2D Fingerprint plot illustrating contact contributions in three polymorphs of copper (II) diacetate monohydrate (a): **P1**, (b): **P2** and (c): **P3**

VI. Density functional theory (DFT).

Density Functional Theory (DFT)³⁰ serves as an essential framework for analyzing polymorphic stability by modeling electronic structures through the Hohenberg–Kohn theorems and Kohn–Sham formalism. It allows for the comparison of various polymorphs under identical conditions, providing insights into molecular geometries, lattice energies, and electronic structures. DFT elucidates how variations in intermolecular interactions, such as hydrogen bonding and $\pi\cdots\pi$ stacking, affect polymorph stabilization³¹. It also decomposes total crystal energy into components

that relate to molecular deformation and intermolecular forces, facilitating the understanding of energetic competition among polymorphs³². Additionally, when combined with methods like powder X-ray diffraction and thermal analysis, DFT enhances the prediction of polymorphic transitions and the establishment of structure-property relationships in solids³³.

The computational evaluations were carried out using DFT with the PBEPBE/LanL2DZ basis set^{33, 34}. The initial geometry of our polymorph, P1 and P2 was obtained from single-crystal X-ray diffraction data, and the CIF files were converted to MOL format prior to optimization. The structures were fully optimized without applying any symmetry constraints, and frequency calculations confirmed the absence of imaginary modes, indicating that the optimized structures correspond to true minima. All calculations were performed using Gaussian 09W³⁵, and GaussView 6.0 was employed for visualization³⁶. The optimized molecular structure, molecular electrostatic potential (MEP), HOMO–LUMO orbitals, and computational spectral data were generated using Gaussian. Reduced density gradient (RDG) analyses were evaluated using Gaussian, Multiwfn 3.8³⁷, and VMD 1.9.2³⁸.

VI. 1. Optimized geometric parameters.

After optimization of the molecular geometry of **P1** (Figure 20), we carried out a comparative study of the different bond lengths and bond angles calculated theoretically with the experimental data, and the results are summarized in (Table 5).

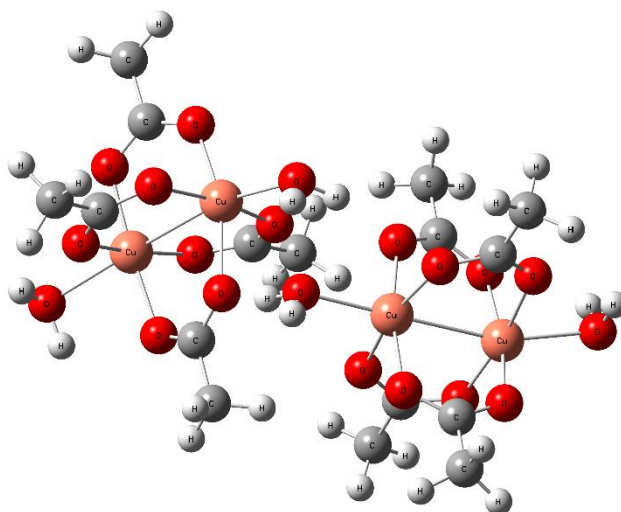


Figure 20. Optimized structure of **P1** calculated using the PBEPBE functional.

The experimental bond lengths range from 1.262 to 2.6122 Å, with an average of 1.7612 Å, while the optimized bond lengths vary from 1.3091 to 2.6888 Å,

Chapter II: Structural, Spectroscopic and Electronic Investigation of a New Polymorph of Copper(II) Diacetate Monohydrate

averaging 1.8143 Å. Experimental bond angles span 82.41 ° to 173.97 °, with an average of 112.0688°, whereas theoretical bond angles range from 82.015° to 172.6453°, yielding an average of 111.3084°. Figure 14 presents the distribution and correlation plots, showing correlation coefficients of $R^2 = 0.9998$ and $R^2 = 0.9994$ for bond lengths and angles, indicating excellent agreement between calculated and experimental values (Figure 21).

Table 5. Optimized bond lengths and bond angles for copper (II) diacetate monohydrate polymorph: **P1** calculated by DFT in comparison with SC-XRD data.

Bond length	EXP (Å)	PBEPBE (Å)	Bond length	EXP (Å)	PBEPBE (Å)
Cu1—Cu1 ⁱ	2.6128 (7)	2.7266	Cu2—Cu2 ⁱⁱ	2.6122 (4)	2.6888
Cu1—O2	1.9867 (12)	2.1417	Cu2—O8	2.1438 (12)	2.2519
Cu1—O3	2.1449 (13)	2.1424	Cu2—O7	1.9869 (12)	2.0618
Cu1—O5 ⁱ	1.9574 (12)	2.0215	Cu2—O10 ⁱⁱ	1.9920 (12)	2.0089
Cu1—O4 ⁱ	1.9918 (12)	2.0367	Cu2—O6	1.9460 (12)	2.0309
Cu1—O1	1.9440 (11)	2.0256	Cu2—O9 ⁱⁱ	1.9572 (12)	1.9984
O2—C3	1.262 (2)	1.3091	O7—C7	1.265 (2)	1.2998
O5—Cu1 ⁱ	1.9574 (11)	2.0215	O10—Cu2 ⁱⁱ	1.9919 (12)	2.0366
O5—C1	1.263 (2)	1.3021	O10—C7	1.267 (2)	1.3123
O4—Cu1 ⁱ	1.9918 (12)	2.027	O6—C5	1.266 (2)	1.3066
O4—C3	1.269 (2)	1.3004	O9—Cu2 ⁱⁱ	1.9572 (12)	2.0379
O1—C1	1.264 (2)	1.3094	O9—C5	1.263 (2)	1.3046
C4—C3	1.505 (2)	1.5262	C6—C5	1.507 (2)	1.5263
C2—C1	1.506 (2)	1.5259	C8—C7	1.505 (2)	1.5202
Bond angles	Exp (°)	PBEPBE (°)	Bond angles	Exp (°)	PBEPBE (°)
O2—Cu1—Cu1 ⁱ	86.72 (4)	78.5973	O8—Cu2—Cu2 ⁱⁱ	173.92 (3)	172.6248
O2—Cu1—O3	98.28 (5)	89.5931	O7—Cu2—Cu2 ⁱⁱ	86.77 (3)	85.9516
O2—Cu1—O4 ⁱ	168.99 (5)	167.9087	O7—Cu2—O8	98.27 (5)	89.5022
O3—Cu1—Cu1 ⁱ	173.97 (3)	172.6453	O7—Cu2—O10 ⁱⁱ	169.01 (5)	168.9765
O5 ⁱ —Cu1—Cu1 ⁱ	83.05 (4)	84.3843	O10 ⁱⁱ —Cu2—Cu2 ⁱⁱ	82.41 (4)	83.5163
O5 ⁱ —Cu1—O2	91.09 (5)	86.3154	O10 ⁱⁱ —Cu2—O8	92.65 (5)	93.4454
O5 ⁱ —Cu1—O3	93.44 (5)	98.0521	O6—Cu2—Cu2 ⁱⁱ	86.23 (4)	83.4168
O5 ⁱ —Cu1—O4 ⁱ	89.52 (5)	89.7572	O6—Cu2—O8	97.36 (5)	93.8512
O4 ⁱ —Cu1—Cu1 ⁱ	82.44 (4)	82.015	O6—Cu2—O7	87.15 (5)	91.133
O4 ⁱ —Cu1—O3	92.65 (5)	93.4454	O6—Cu2—O10 ⁱⁱ	90.18 (5)	88.7064
O1—Cu1—Cu1 ⁱ	86.22 (4)	83.4165	O6—Cu2—O9 ⁱⁱ	169.25 (5)	170.3458
O1—Cu1—O2	87.16 (5)	91.12	O9 ⁱⁱ —Cu2—Cu2 ⁱⁱ	83.07 (4)	84.3876
O1—Cu1—O3	97.35 (5)	93.8506	O9 ⁱⁱ —Cu2—O8	93.38 (5)	92.4823
O1—Cu1—O5 ⁱ	169.21 (5)	168.7439	O9 ⁱⁱ —Cu2—O7	91.18 (5)	90.7043
O1—Cu1—O4 ⁱ	90.18 (5)	88.7043	O9 ⁱⁱ —Cu2—O10 ⁱⁱ	89.47 (5)	88.7689

C3—O2—Cu1	120.94 (10)	120.8568	C7—O7—Cu2	120.86 (10)	120.8765
C1—O5—Cu1 ⁱ	124.03 (11)	122.5908	C7—O10—Cu2 ⁱⁱ	125.55 (10)	122.9087
C3—O4—Cu1 ⁱ	125.43 (10)	122.8808	C5—O6—Cu2	120.94 (10)	121.0987
C1—O1—Cu1	121.03 (11)	121.5184	C5—O9—Cu2 ⁱⁱ	124.10 (11)	125.3967
O2—C3—O4	124.29 (15)	126.3267	O6—C5—C6	117.28 (15)	116.7654
O2—C3—C4	118.79 (14)	116.0271	O9—C5—O6	125.58 (15)	125.9376
O4—C3—C4	116.92 (14)	117.6446	O9—C5—C6	117.13 (15)	116.6446
O5—C1—O1	125.60 (15)	125.9386	O7—C7—O10	124.21 (14)	124.8808
O5—C1—C2	117.06 (15)	117.1839	O7—C7—C8	118.72 (14)	119.7276
O1—C1—C2	117.34 (15)	116.8677	O10—C7—C8	117.07 (14)	116.9876

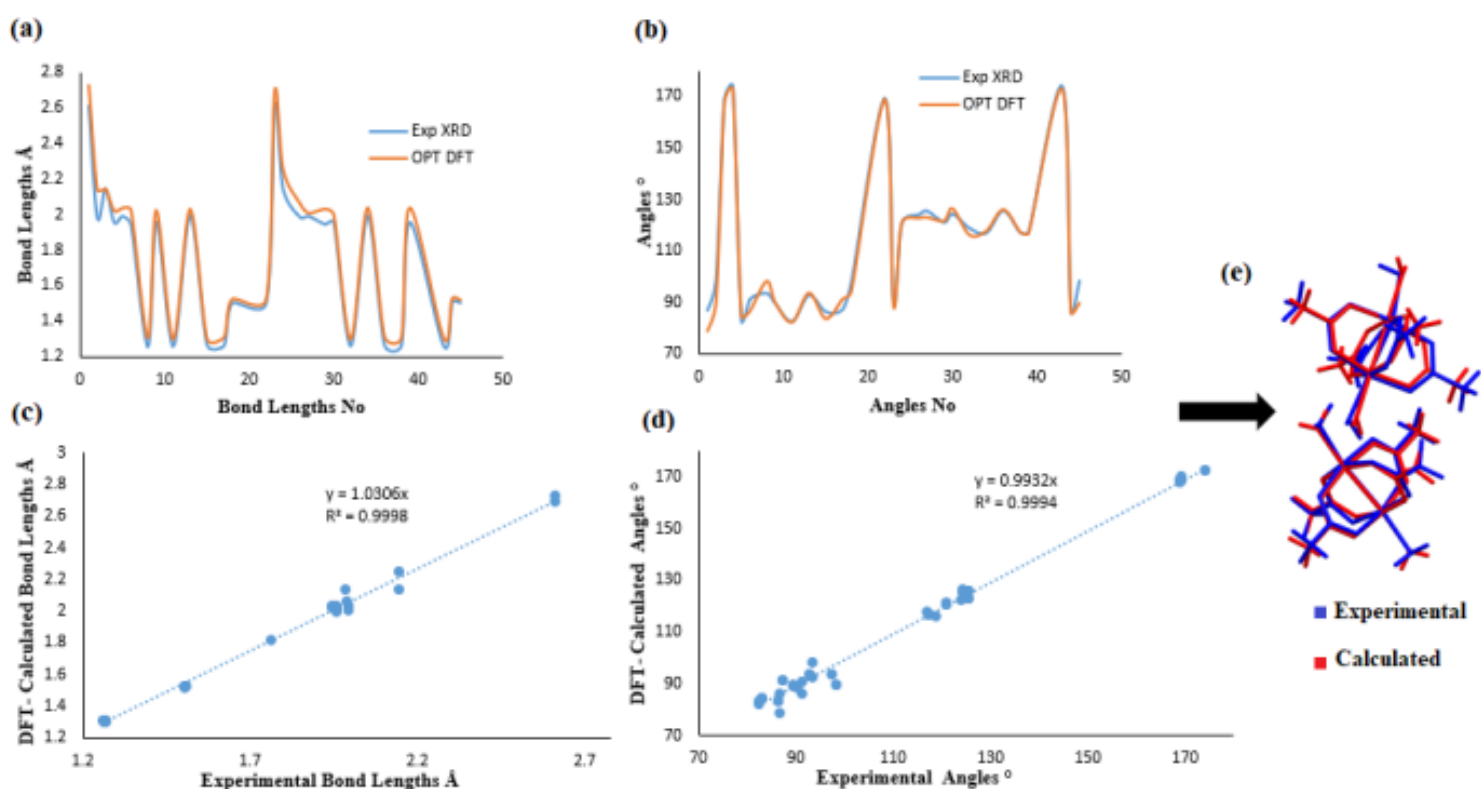


Figure 21. Comparison between experimental (SC-XRD) and DFT-optimized geometrical parameters for our polymorph (a) bond lengths, (b) bond angles, (c–d) regression plots showing near-unity correlation), and (e) superposition of experimental (blue) and calculated (red) molecular structures.

VI. 2. Frontier molecular orbitals (FMOs) and energy gap.

Frontier molecular orbital analysis (Figure 22) reveals a clear stability hierarchy (**P2** > **P3** > **P1**) based on HOMO-LUMO gaps (**P2**: 0.7224 eV, **P3**: 0.4055 eV, **P1**: 0.3347 eV), where the HOMO is localized on the Cu²⁺ center and coordinating oxygen atoms in all polymorphs, but the critical distinction lies in

LUMO delocalization: **P2** exhibits the most localized LUMO on a single acetate group yielding the largest gap and highest kinetic stability, **P1** displays the most delocalized LUMO across adjacent molecules via intermolecular interactions resulting in the smallest gap and highest reactivity, while **P3** shows intermediate LUMO delocalization, demonstrating that crystal packing and intermolecular contacts modulate LUMO energy and govern polymorph stability.

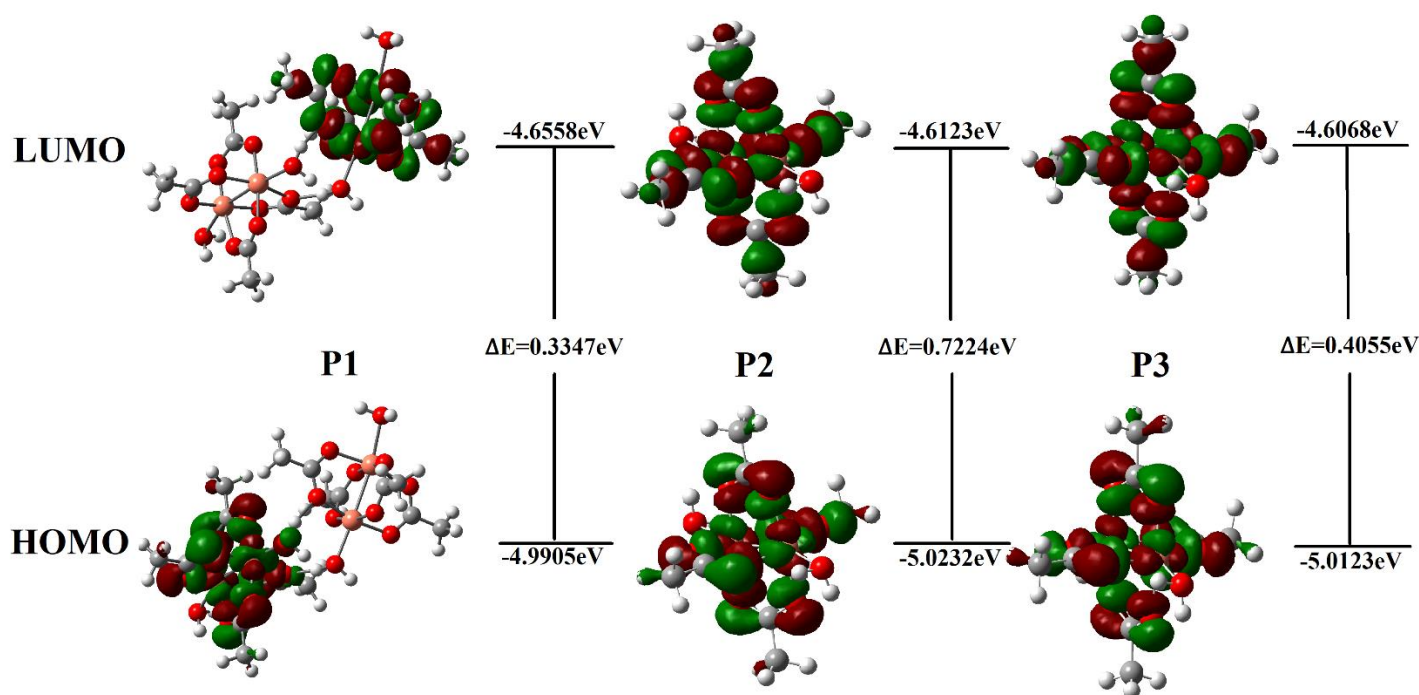


Figure 22. HOMO and LUMO energy levels and electron density distributions of **P1**, **P2** and **P3**.

VI. 3. Analysis of molecular electrostatic potential (MEP).

Molecular electrostatic potential (MEP) (Figure 23), which maps electron-rich (negative) and electron-deficient (positive)³⁹ regions on a molecule's surface to predict hydrogen bonding and $\pi \cdots \pi$ stacking⁴⁰, reveals that **P3** exhibits a significantly more negative MEP value (-7.270×10^2) compared to **P1** (-6.268×10^2) and **P2** (-6.371×10^2), indicating substantially greater electron density and stronger electrostatic-driven intermolecular interactions that likely arise from distinct coordination geometry, acetate ligand orientation, or a more extensive hydrogen-bonding network, ultimately distinguishing **P3** through enhanced lattice energy, physical stability, and altered dissolution behavior.

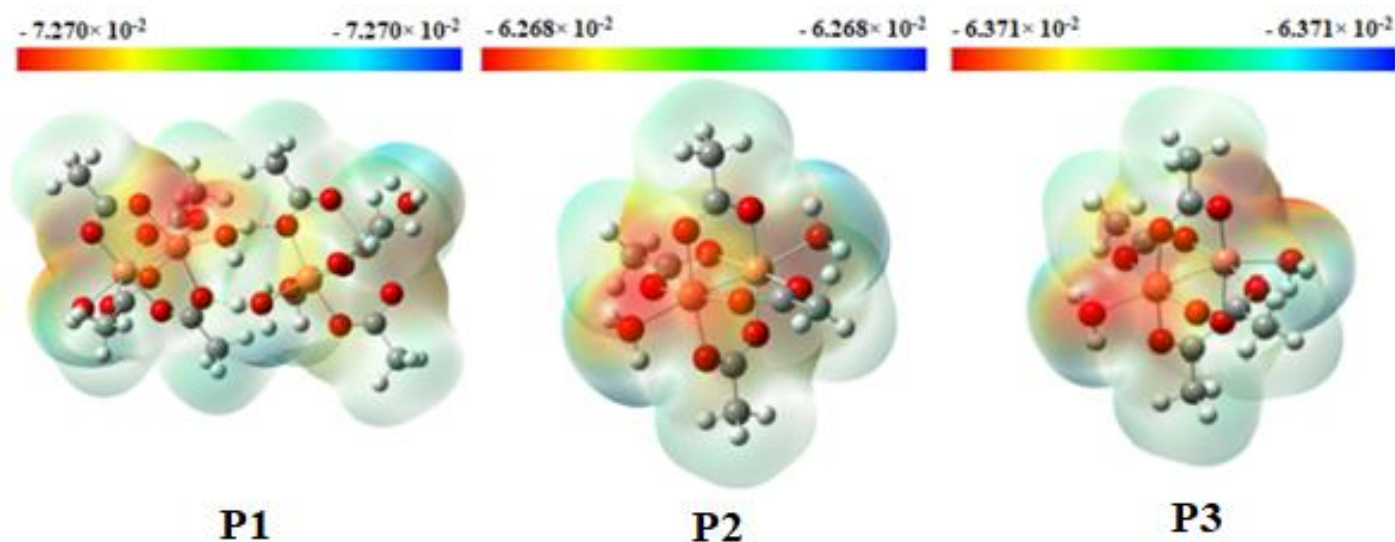


Figure 23. 3D MEP surfaces of the three polymorphs of copper (II) diacetate monohydrate.

VI. 4. Analysis of Mulliken atomic charges.

Mulliken atomic charges, which quantify electron distribution and predict atomic reactivity and intermolecular interaction sites⁴² by partitioning electron density based on atomic orbitals⁴¹, reveal distinct electronic structures among the polymorphs (Figure 24): **P1** exhibits the most pronounced charge separation (± 0.783) indicating stronger polarization and more efficient charge transfer between copper and acetate ligands due to unique coordination geometry, while **P2** and **P3** display remarkably similar reduced charge magnitudes (± 0.745 and ± 0.743 , respectively) suggesting analogous electronic environments and metal-ligand interaction strengths, thereby providing a quantum-chemical basis for understanding their structure-property relationships and stability differences.

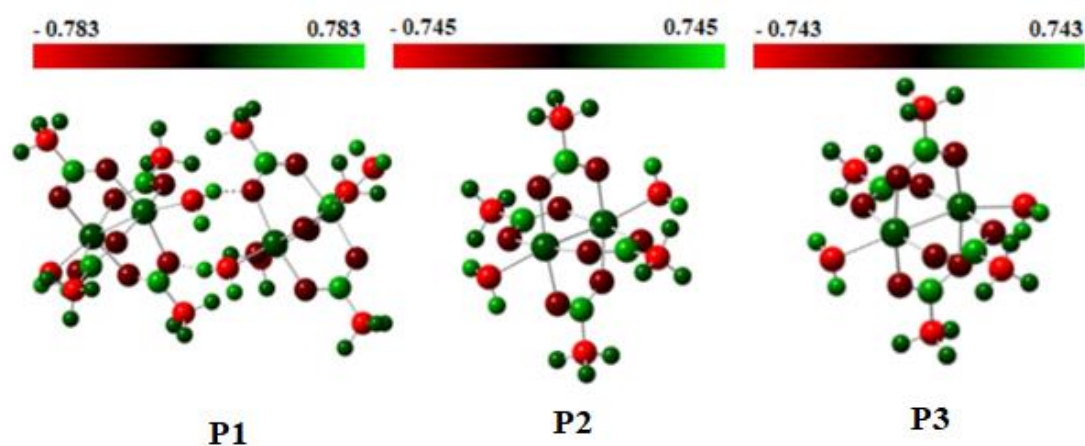


Figure 24. Mulliken charge distribution across polymorphic forms of copper (II) diacetate monohydrate.

VI. 5. Reduced density gradient (RDG) analysis of noncovalent interactions (NCI).

Reduced Density Gradient (RDG) analysis⁴² was performed using Multiwfn 3.8 and visualized with VMD 1.9.2 to investigate the noncovalent interactions within our polymorph

Reduced Density Gradient (RDG) analysis (Figure 25), which maps noncovalent interactions⁴³ by visualizing low-gradient isosurfaces colored by $\text{sign}(\lambda_2)\rho$ to reveal hydrogen bonds (blue), van der Waals forces (green), and steric repulsion (red)⁴⁴, demonstrates distinct interaction networks among the polymorphs: **P1** exhibits extensive green isosurfaces indicating dominant van der Waals interactions with moderately strong hydrogen bonds (small blue discs) supporting dense packing, **P2** displays more prominent intense blue isosurfaces reflecting stronger localized O–H···O hydrogen bonds with balanced dispersion, while **P3** shows significant red isosurfaces near copper centers indicating strong steric repulsion and strained geometries with fragmented attractive interactions, revealing that **P1** and **P2** achieve stability through robust hydrogen bonding and dispersion networks whereas **P3**'s instability arises from unfavorable steric clashes that distinguish its crystallization pathway.

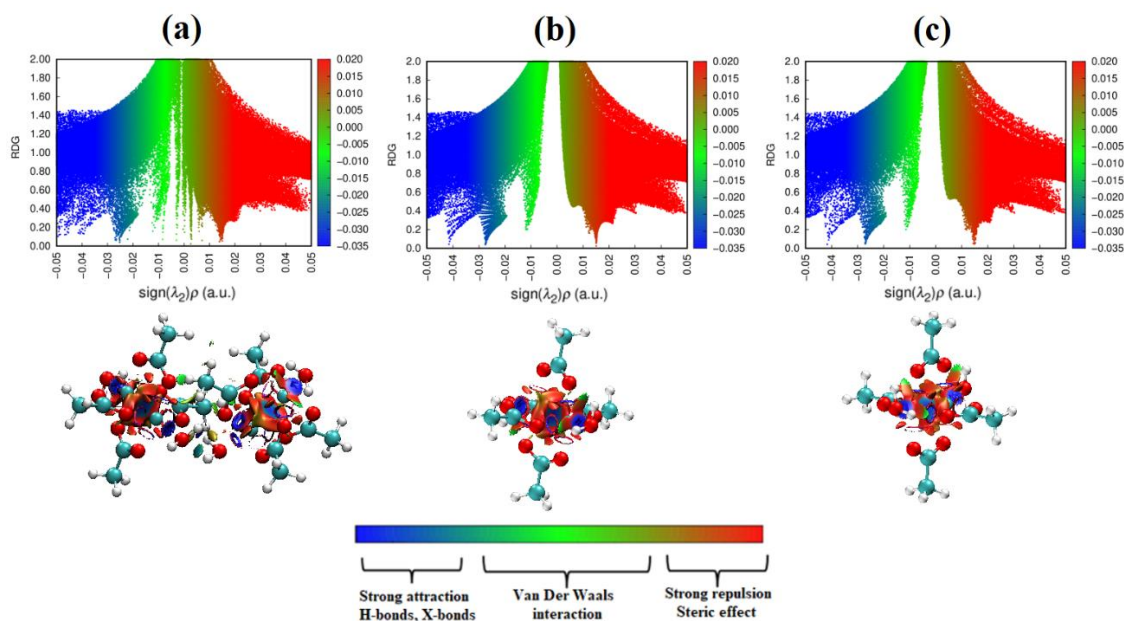


Figure 25. Reduced density gradient (RDG) and noncovalent interaction (NCI) analysis of copper (II) diacetate monohydrate polymorphs with (a) **P1** (b) **P2** and (c) **P3**.

VII. Conclusion.

This chapter explores the experimental and theoretical aspects of copper (II) diacetate monohydrate, focusing on its polymorphism and the identification of a new triclinic polymorphic form. This compound serves as a model for investigating structure–property relationships in coordination compounds due to its paddle-wheel $\text{Cu}_2(\text{OAc})_4$ core and varied crystallization responses. A survey identified 23 known monoclinic polymorphs, while the new triclinic polymorph differs in crystallographic structure and packing. Single-crystal X-ray diffraction validated its unique hydrogen-bonding topology, leading to distinct structural properties and increased porosity. Density Functional Theory calculations confirm the electronic characteristics of this new form, including lower kinetic stability and enhanced reactivity. The study illustrates how variations in packing and bonding influence the properties of copper(II) diacetate monohydrate, contributing to the understanding of metal–acetate polymorphism and its potential applications in controlled crystallization and material functionality.

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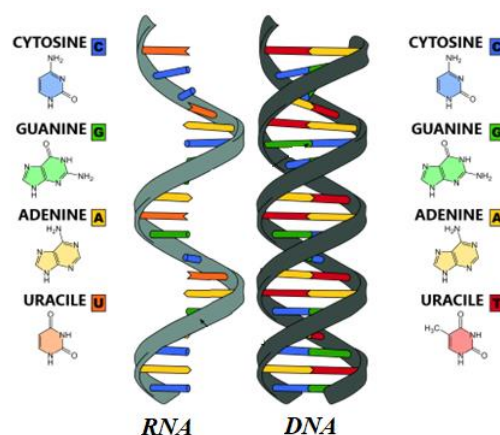
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Chapter III.

Structural, Spectroscopic and Electronic Investigation of a New Polymorph of Cytosinium Gallate

I. Introduction.

Cytosine, one of the five canonical nucleobases, is a pyrimidine base essential for the storage and transmission of genetic information in DNA and RNA. It pairs with guanine through hydrogen bonds, contributing to nucleic acids' structural stability and genetic fidelity. Chemically, cytosine has a heterocyclic aromatic ring with two nitrogen atoms and can act as both a hydrogen-bond donor and acceptor^{1,2} due to its exocyclic amino group and carbonyl function. Under acidic conditions, it can form a protonated form known as the cytosinium cation³, enhancing its hydrogen-bonding capability and allowing the formation of stable salts and co-crystals. Cytosine's polymorphic behavior in solid-state interactions is significant for understanding structure property relationships and non-covalent interactions in molecular crystals, with compounds like cytosinium gallate illustrating the complexity of these interactions and their potential applications in biomimetic systems and pharmaceutical materials.



II. Polymorphs of cytosinium gallate

Nitrogenous bases, the pyrimidine and purine components of nucleic acids, are fundamental to genetic storage and transmission through their specific hydrogen-bonding patterns⁴. This study focuses on the pyrimidine base cytosine ($C_4H_5N_3O$), whose molecular recognition via three hydrogen bonds with guanine is critical for duplex DNA stability⁵. The chemical reactivity and structural role of cytosine are profoundly influenced by its protonation state. Under acidic conditions, the most basic site, the N2 ring nitrogen, is protonated to form the cytosinium monocation ($[C_4H_6N_3O]^+$)⁶.

Cytosinium gallate is an organic salt formed through an acid-base reaction between the nucleobase cytosine and gallic acid. In this compound, cytosine exists as the cytosinium cation, protonated at the N2 site, which is paired with the gallate anion to form a complex hydrogen-bonded network in the solid state.

While a singular structure of cytosinium gallate named as [(H-1GA)(HCYT)]⁶ has been previously reported in the Cambridge Structural Database (CSD) (version 6.00, April 2025)⁷ the compound synthesized in this work (**CG1**) exhibits a distinct crystal packing, as evidenced by its fundamentally different unit cell parameters. This new phase is therefore identified as a polymorph of the known cytosinium gallate structure (Table 6).

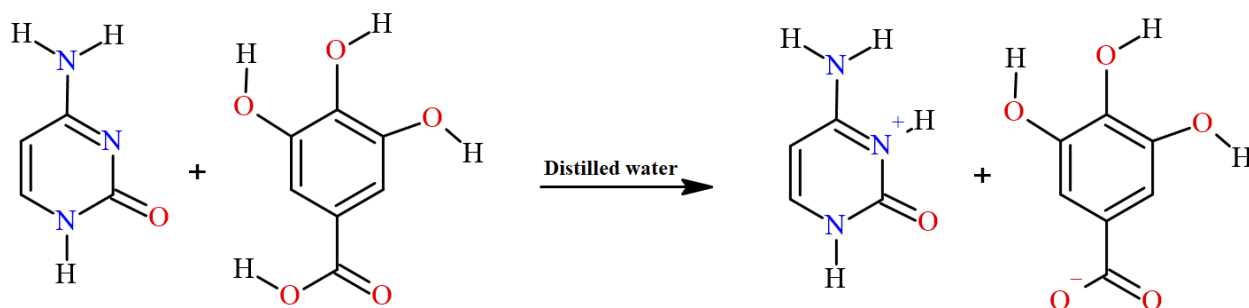
Table 6. Crystallographic data of cytosinium gallate polymorphs.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Space groupe, System
(CG1)	7.5592 (18)	6.5229 (13)	12.015 (3)	90	107.361(9)	90	<i>P</i> 2 ₁ (monoclinic)
QEYZIH	7.693 (1)	6.497 (<1)	12.016 (1)	90	107.39 (<1)	90	<i>P</i> 2 ₁ (monoclinic)

III. Experimental methods

III. 1. Experimental procedure

The molecular hybrid compound cytosinium gallate, [C₄H₆N₃O]⁺[C₇H₅O₅]⁻ (**CG1**), was synthesized via a straightforward acid-base reaction. Equimolar quantities (1:1) of cytosine and gallic acid were dissolved in distilled water under stirring at ambient temperature. Colourless, needle shaped single crystals of the product were obtained after approximately three days via slow evaporation of the solvent.



Scheme 2. Synthetic route to the new polymorph of cytosinium gallate (**CG1**).

III. 2. Single-crystal X-ray diffraction analysis

A single-crystal X-ray diffraction study of (**CG1**) was performed at 200 K. Data collection was carried out on a Bruker D8 VENTURE system featuring a PHOTON III detector, using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$

Å). The crystal structure was solved by direct methods using the *SHELXT* program⁸, and then refined using the *SHELXL* program⁹, which was included into the *Olex2 1.3* software package¹⁰. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from the difference Fourier maps and included in the refinement. (Table 7) summarizes the crystallographic data collection and refinement parameters for (CG1).

Table 7. Structural data and recording conditions for cytosinium gallate polymorph: (CG1)

Crystal data	
Refined formula	(C ₄ H ₆ N ₃ O ⁺ , C ₇ H ₅ O ₅ ⁻ ,)
Mr	281.23
Temperature (K)	200
Crystal system, Space group (no.)	Monoclinic, <i>P2₁</i> (No. 4, non-centrosymmetric)
<i>a</i> (Å), <i>b</i> (Å), <i>c</i> (Å)	7.5592(18), 6.5229(13), 12.015(3)
β (°)	107.361(9)
Volume (Å ³)	565.445
Z	2
ρ_{calc} (g/cm ³), μ (mm ⁻¹)	1.652, 0.137
Radiation	Mo <i>K</i> _α (λ = 0.71073)
Crystal size (mm ³)	0.150 × 0.180 × 0.200
Data collection	
2 θ range (°)	2.823– 26.196
F(000)	292
Index ranges	−9 ≤ <i>h</i> ≤ 9, −8 ≤ <i>k</i> ≤ 8, −14 ≤ <i>l</i> ≤ 14
<i>T</i> _{min} – <i>T</i> _{max}	0.7058–0.7454
Reflections collected, Independent reflections, Observed reflections with [<i>I</i> > 2σ(<i>I</i>)]	18569, 2293, 2201
<i>R</i> _{int} , <i>R</i> _{sigma}	0.0456, 0.0251
Refinement	
Final <i>R</i> indexes [<i>F</i> ² > 2σ (<i>F</i> ²)], Final <i>R</i> indexes [all data]	[<i>R</i> = 0.0301, <i>R</i> _w = 0.0779], [<i>R</i> = 0.0316, <i>R</i> _w = 0.0797]

Goodness-of-fit on F^2	1.051
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III. 3. FTIR spectroscopic characterization of cytosinium gallate

The FTIR spectrum (Figure 26) of cytosinium gallate exhibits several characteristic absorption bands. A broad and intense absorption band observed in the 3600–3000 cm^{-1} region is attributed to the overlapping stretching vibrations of O–H groups from the gallate moiety and N–H groups of cytosinium, indicating the presence of strong intermolecular hydrogen bonding. The absorption bands appearing in the 1700–1600 cm^{-1} range correspond to the C=O stretching vibrations of the carboxyl group of gallate and the carbonyl group of cytosine; the observed shifts and changes in intensity compared to the free components suggest proton transfer and ionic interactions between the two species. Additional bands in the 1650–1500 cm^{-1} region are assigned to C=N and C=C stretching vibrations of the heterocyclic and aromatic rings, confirming the structural integrity of both cytosine and gallate units within the complex. The bands located between 1450 and 1300 cm^{-1} are associated with C–N stretching and O–H bending vibrations, further supporting the involvement of amino and hydroxyl functional groups in intermolecular interactions. Strong absorption bands in the 1250–1000 cm^{-1} region are attributed to C–O stretching vibrations of the phenolic groups of gallate, while the bands below 1000 cm^{-1} correspond to out-of-plane bending vibrations of aromatic C–H bonds, characteristic of substituted aromatic rings.

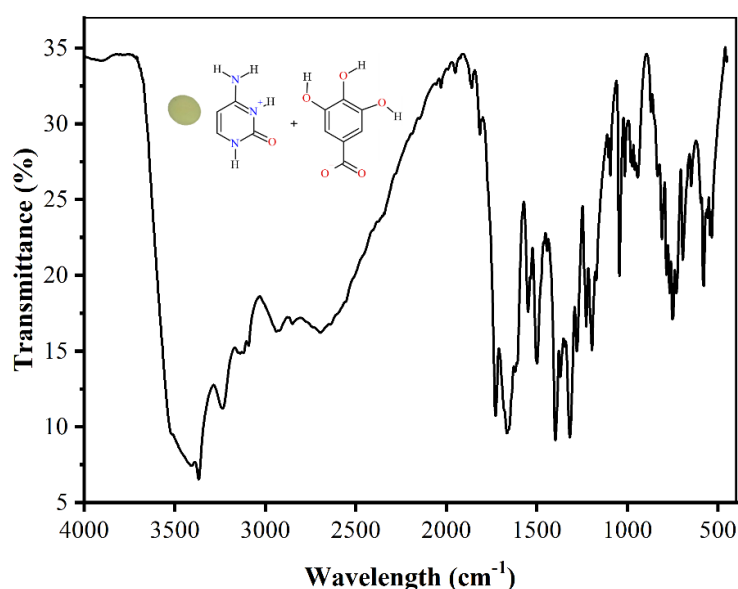


Figure 26. FTIR spectrum of cytosinium gallate.

Table 8. FTIR wavenumber assignments of cytosinium gallate and corresponding vibrational modes.

Wavenumber (cm ⁻¹)	Assignment	Origin
3600–3000	Broad O–H and N–H stretching vibrations	Phenolic O–H (gallate) and N–H (cytosinium); hydrogen bonding
~3350–3200	N–H stretching	Protonated amino groups of cytosinium
~1710–1680	C=O stretching	Carboxyl group of gallate
~1660–1620	C=O stretching	Carbonyl group of cytosine
~1600–1550	C=C and C=N stretching	Aromatic ring (gallate) and heterocyclic ring (cytosine)
~1500–1450	N–H bending / C–N stretching	Cytosinium moiety
~1420–1380	O–H bending	Phenolic groups of gallate
~1300–1250	C–N stretching	Cytosinium
~1250–1000	C–O stretching	Phenolic C–O bonds of gallate
~900–700	Aromatic C–H out of plane bending	Substituted aromatic ring (gallate)
~700–500	Ring deformation vibrations	Aromatic and heterocyclic structures

VI. Description of the structure

The crystal structure of the new polymorph (**CG1**) reveals that the asymmetric unit consists of a discrete cytosinium cation and a gallate anion ([Figure 27 a](#)), which form a stable heterosynthon through hydrogen-bonding network.

Due to the internal configuration and alignment of the various OH groups, GA⁻ assumes an M₁PM₂ orientation¹¹

In contrast to the previously characterized polymorph [(H-1GA)(HCYT)] (**CG2**) [5], the crystal structure of this form reveals that the cytosinium cations and gallate anions do not engage in direct hydrogen bonding with each other ([Figure 27 b](#)). Instead, the components form separate.

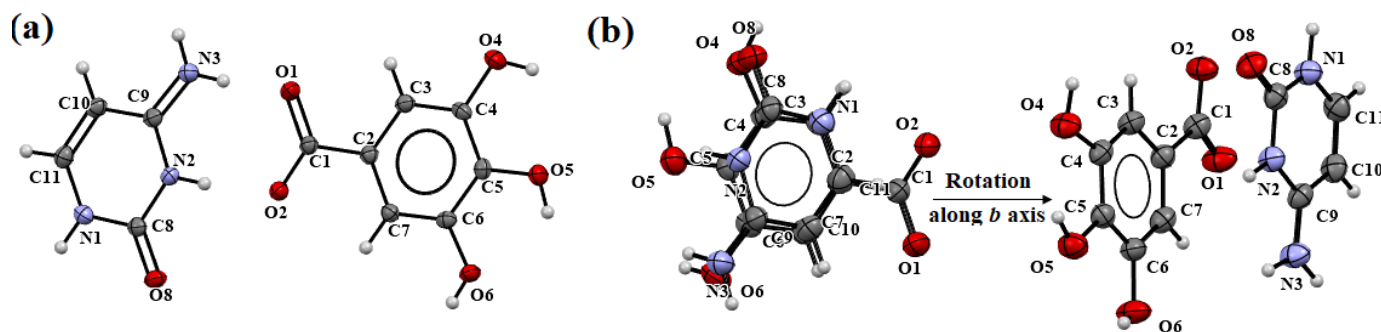


Figure 27. Asymmetric units of the two polymorphs with (a) (CG1) and (b) (CG2) along *b* axis.

The cytosinium and gallate ions in (CG1) individually constitute planar units (Figure 28 a), the dihedral angle between their least-squares planes is 4.31° , signifying a coplanar geometry, while in (CG2) the two plans of cytosinium and gallate ions (Figure 28 b) are strictly parallel, with an interplanar distance of $3.993 \text{ \AA}$, indicative of $\pi \cdots \pi$ stacking interactions.

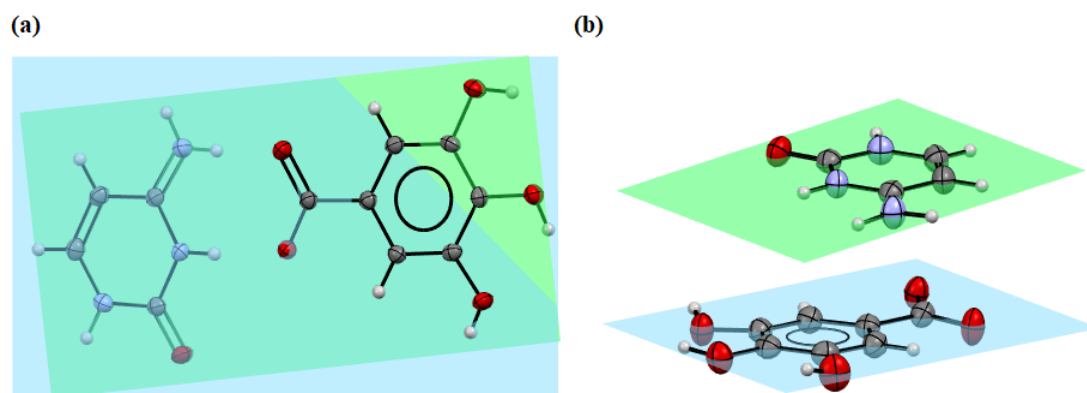


Figure 28. Coplanar geometry in (CG1) (a) and parallel planes in (CG2) (b) between cytosinium and gallate ions of asymmetric unit.

Crystal packing of the two polymorphs of cytosinium gallate (CG1) and (CG2) (Figure 29) seen along the *a*, *b*, and *c* crystallographic axes. Despite both structures comprising identical molecular components, they exhibit variations in packing arrangement.

In the crystal packing of (CG1) (Figure 29 a), gallate anions and cytosinium cations are alternatively arranged along the *ac* plane, exhibiting a significant difference in molecular orientation relative to (CG2) (Figure 29 b).

When observed along the *cb* axis, the molecules exhibit a zigzag configuration, with anions and cations alternating in a systematic order.

A significant structural difference between the two polymorphs is emphasized by orange circles: in **(CG1)**, the locations of cations and anions are effectively interchanged compared to **(CG2)**. This exchange results in variations in molecule orientation and hydrogen-bonding configurations between the two phases.

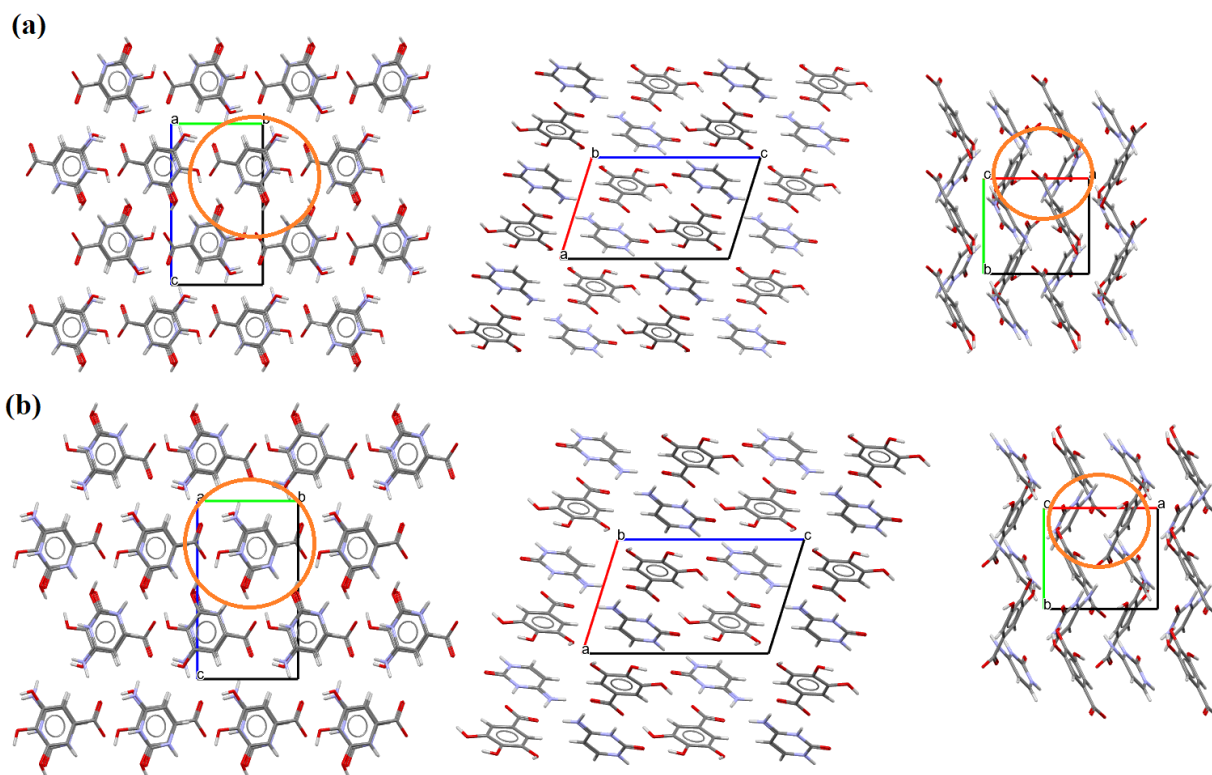


Figure 29. Crystal packing and arrangements of cytosinium gallate in (a) **(CG1)** and (b) **(CG2)**.

The alterations in molecular positioning, orientation, and hydrogen-bond connectivity, as illustrated in the superposition of the two structures ([Figure 30](#)), underscore the substantial impact of polymorphism on stacking configurations and the resulting supramolecular architecture; in this case, the polymorphism of the two compounds is categorized as packing polymorphs.

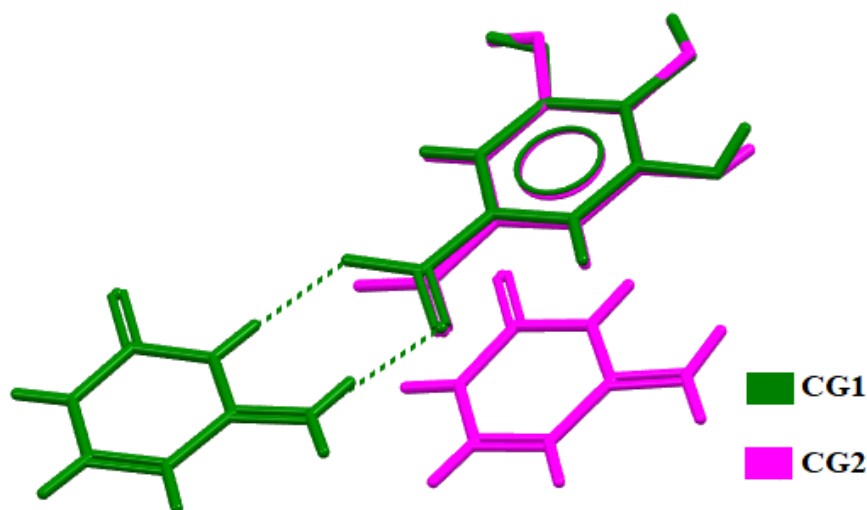


Figure 30. Superposition of the crystal structures of two polymorphs of cytosinium gallate (CG1) and (CG2)

The two polymorphs of cytosinium gallate exhibit distinct hydrogen-bonding (Figure 31) patterns that play a key role in stabilizing their respective crystal structures. In both forms, the supramolecular assembly is governed primarily by N–H $\cdots$ O and O–H $\cdots$ O hydrogen bonds involving the cytosinium cation and the gallate anion; however, notable differences are observed in the number, geometry, and organization of these interactions.

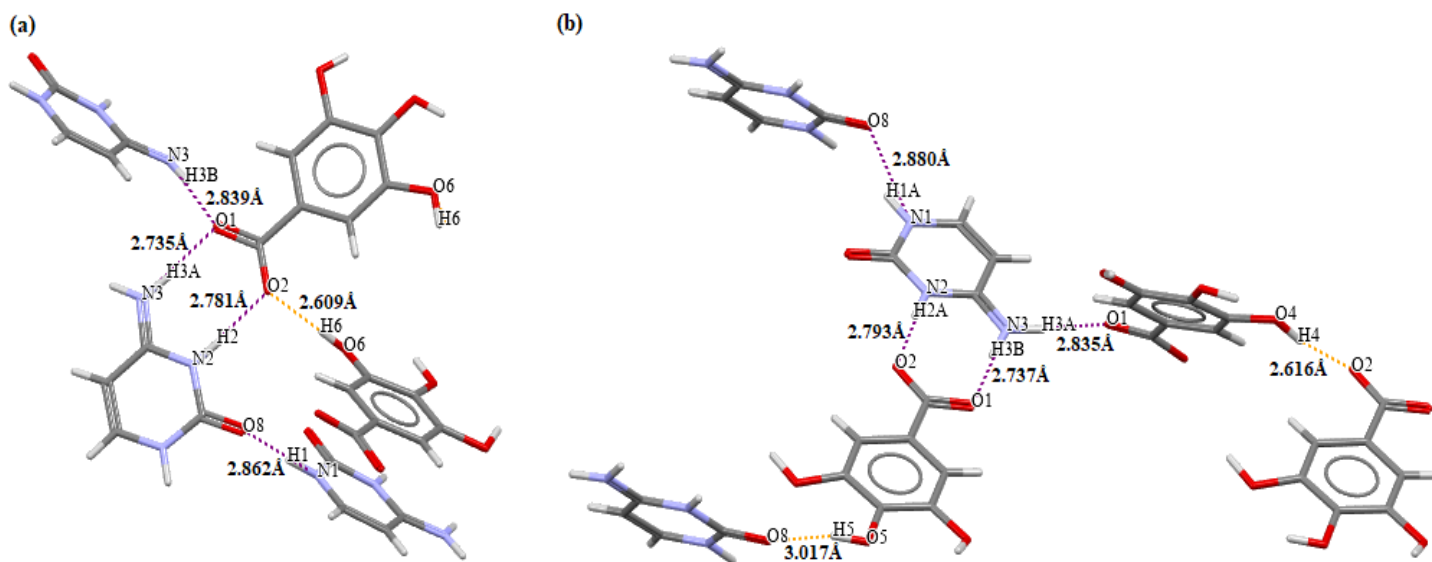


Figure 31. Hydrogen-bonding interactions in cytosinium gallate polymorphs: (a) (CG1) and (b) (CG2).

In (CG1), the cytosinium cations and gallate anions are linked through a dense and cooperative hydrogen-bonding network. Several short N–H $\cdots$ O hydrogen bonds, with donor–acceptor distances in the range of approximately 2.60–2.86 Å, indicative of

relatively strong interactions and O–H···O bond with distance of 2.61 Å. The cytosinium cation participates simultaneously as a hydrogen-bond donor and acceptor, forming multiple contacts with neighboring gallate anions. This leads to the formation of a graph set motifs $R_2^2(8)$, $R_3^3(10)$ and $R_9^9(50)$ (Figure 32 a)

By contrast, **(CG2)** displays a more extended and less densely interconnected hydrogen-bonding scheme. Although N–H···O and O–H···O interactions are still present, the donor–acceptor distances are generally longer, ranging from approximately 2.74 to 3.02 Å. The hydrogen bonds This leads to the formation of a graph set motifs $R_2^2(8)$ and $R_2^3(10)$. (Figure 32 b)

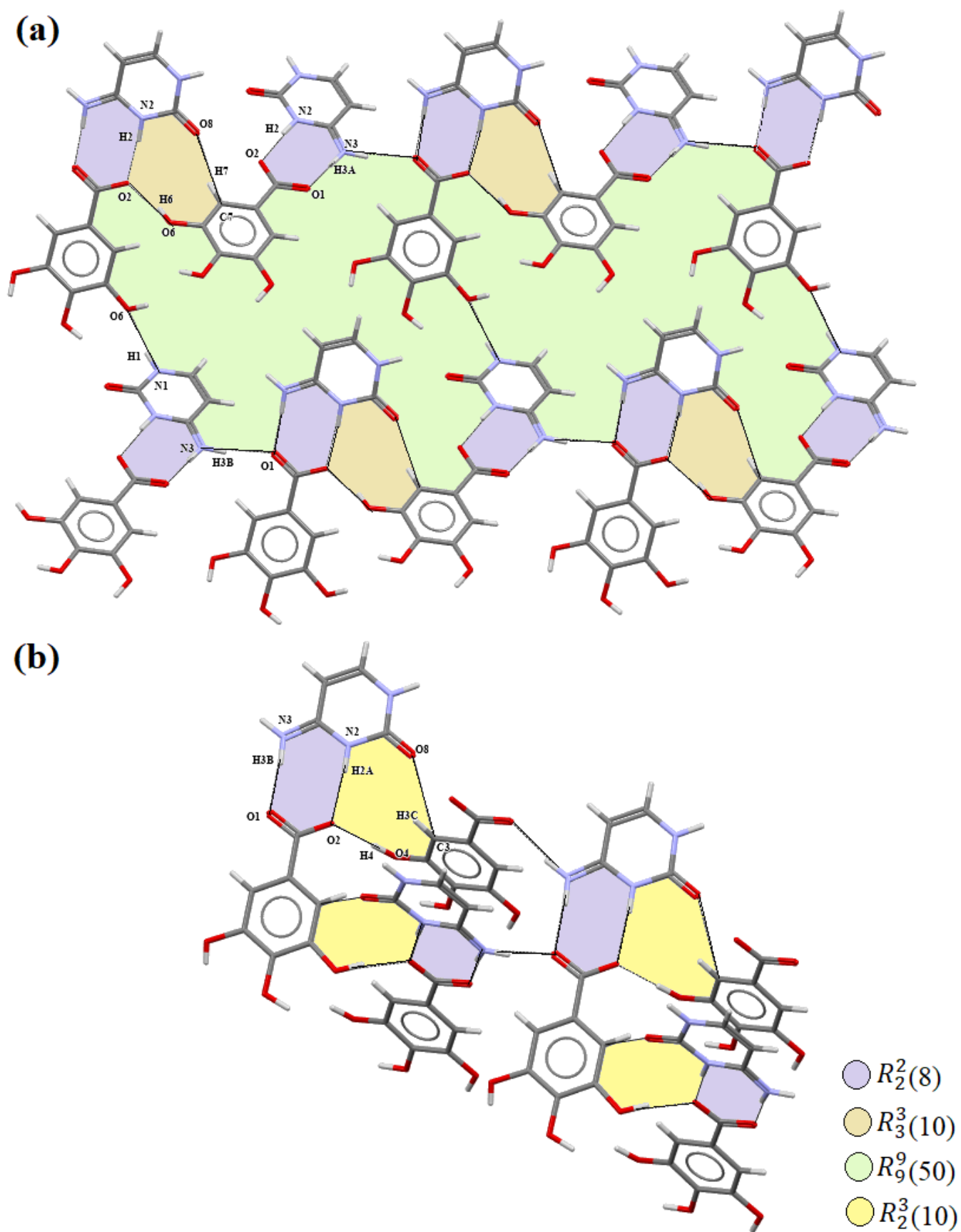


Figure 32. Supramolecular packing of (a) (CG1) and (b) (CG2) showing O—H···O interactions forming ring motifs

Table 9. Hydrogen-bond geometry (Å, °) of cytosinium gallate polymorphs: (a) (CG1) and (b) (CG2).

	<i>D</i> —H··· <i>A</i>	<i>D</i> —H (Å)	H··· <i>A</i> (Å)	<i>D</i> ··· <i>A</i> (Å)	<i>D</i> —H··· <i>A</i> (°)
(CG1)	N1—H1···O8 ⁱⁱ	0.92(3)	2.001	2.87	156.1
	N2—H2···O2 ⁱⁱⁱ	0.90(3)	1.887	2.78	174.12
	N3—H3A···O1 ^{iv}	0.88	1.973	2.74	170.41
	N3—H3B···O1 ⁱⁱⁱ	0.88	1.864	2.84	167.82
	O6—H6···O2 ⁱ	0.84	1.808	2.61	159.02
(CG2)	O4—H4···O2 ⁱ	0.93 (4)	1.70 (4)	2.616 (3)	168 (3)
	O5—H5···O8 ⁱ	0.94 (4)	2.15 (4)	3.017 (3)	154 (3)
	N1—H1A···O8 ⁱⁱ	0.96 (3)	1.99 (4)	2.880 (3)	155 (3)
	N2—H2A···O2 ⁱⁱⁱ	0.88 (4)	1.92 (4)	2.793 (3)	175 (3)
	N3—H3A···O1 ^{iv}	0.96 (4)	1.89 (4)	2.835 (3)	169 (3)
	N3—H3B···O1 ⁱⁱⁱ	0.93 (4)	1.82 (4)	2.738 (4)	172 (3)

Symmetry code(s): (i) -x+1, y-1/2, -z+1; (ii) -x, y+1/2, -z+1; (iii) x, y-1, z; (iv) -x+1, y-1/2, -z+2.

In the crystal packing cytosinium cations and gallate anions are interconnected through $\pi\cdots\pi$ stacking (Figure 33) these contacts are between phenyl rings of gallate anions and rings of cytosinium cations (centroid-centroid = 3.916Å for (CG1) and centroid- centroid= 3.993Å for (CG2))

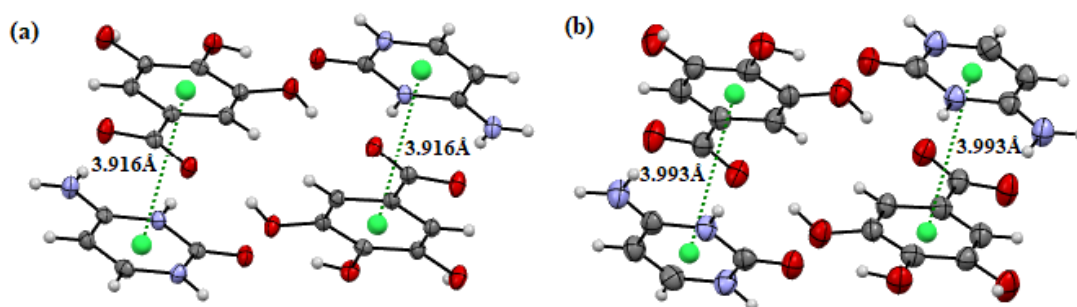


Figure 33. $\pi\cdots\pi$ Stacking interactions in cytosinium gallate polymorphs : (a) (CG1) and (b) (CG2)

VI. 1. Morphological analysis (BFDH).

The cytosinium gallate polymorphs' (CG1) and (CG2) projected morphologies (Figure 34) show a strong prismatic habit and a high degree of structural congruence. The internal lattice structure more especially, the relative spatial coordinates of the molecular entities within the unit cell is the main source of morphological divergence. The dominance of the (001) and (00-1) basal planes in both crystalline phases essentially control the habitus, with supplementary growth contributions from the

(100), (10-1), (0-1-1), (0-11), (-1-10), and (1-10) facets with the minor (-1-11) and (1-1-1).

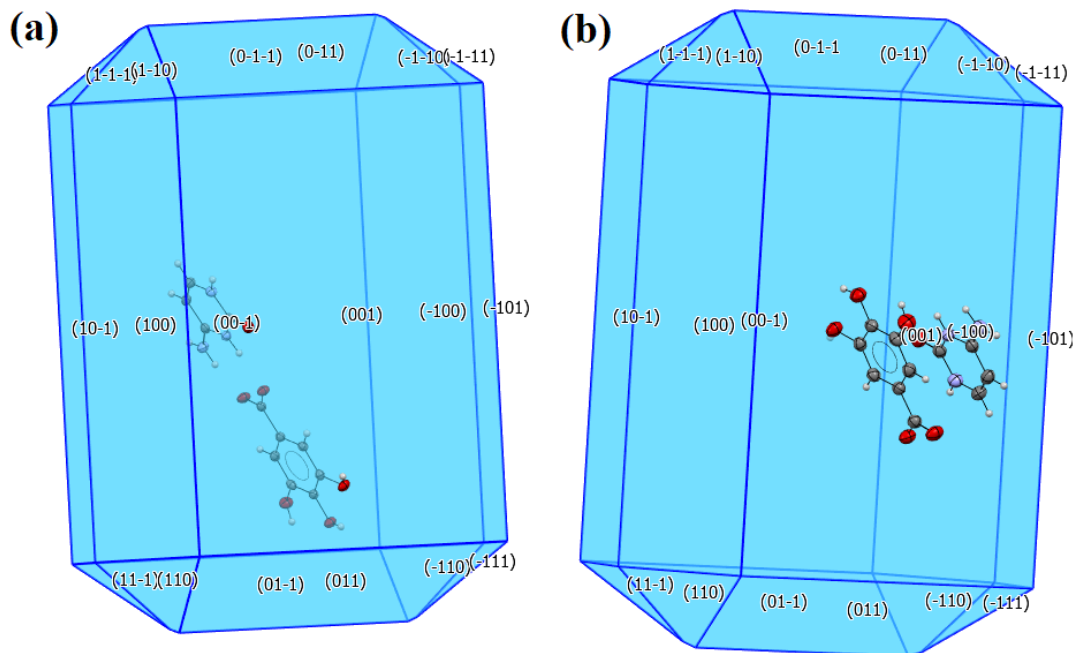


Figure 34. Predicted BFDH morphologies of cytosinium gallate polymorphs: (a) (CG1) (b) (CG2)

V. Hirshfeld surface analysis (HSA).

The d_{norm} surfaces of two polymorphs reveal distinct red regions, indicating close intermolecular contacts linked to strong hydrogen bonds (N–H $\cdots$ O and O–H $\cdots$ O) between cytosinium cations and gallate anions. **(CG1)** shows a higher density and intensity of red spots, suggesting more numerous strong interactions. In contrast, **(CG2)** has fewer, localized red areas, indicating weaker and less frequent contacts.

The shape index surfaces reveal insights into $\pi\cdots\pi$ stacking, particularly with **(CG1)** showing clear alternating red and blue triangular patches indicative of strong $\pi\cdots\pi$ interactions between aromatic rings. This symmetrical arrangement suggests efficient face-to-face stacking that aids lattice stabilization. In contrast, **(CG2)** exhibits less extensive and asymmetric red–blue patterns, indicating weaker $\pi\cdots\pi$ stacking and a diminished contribution to its stabilization compared to **(CG1)**.

The d_e surfaces illustrate the variation in molecular environments, with **(CG1)** demonstrating distinct short external contacts due to its dense hydrogen bonding and stacking interactions. In contrast, **(CG2)** exhibits smoother d_e surfaces characterized by larger green regions, indicating longer intermolecular separations and lower packing efficiency.

In comparison to **(CG2)**, which shows weaker intermolecular contacts and lower packing density, the Hirshfeld surface analysis shows that **(CG1)** achieves better structural stability through more numerous and stronger hydrogen bonds, enhanced π - π stacking interactions, and higher packing efficiency.

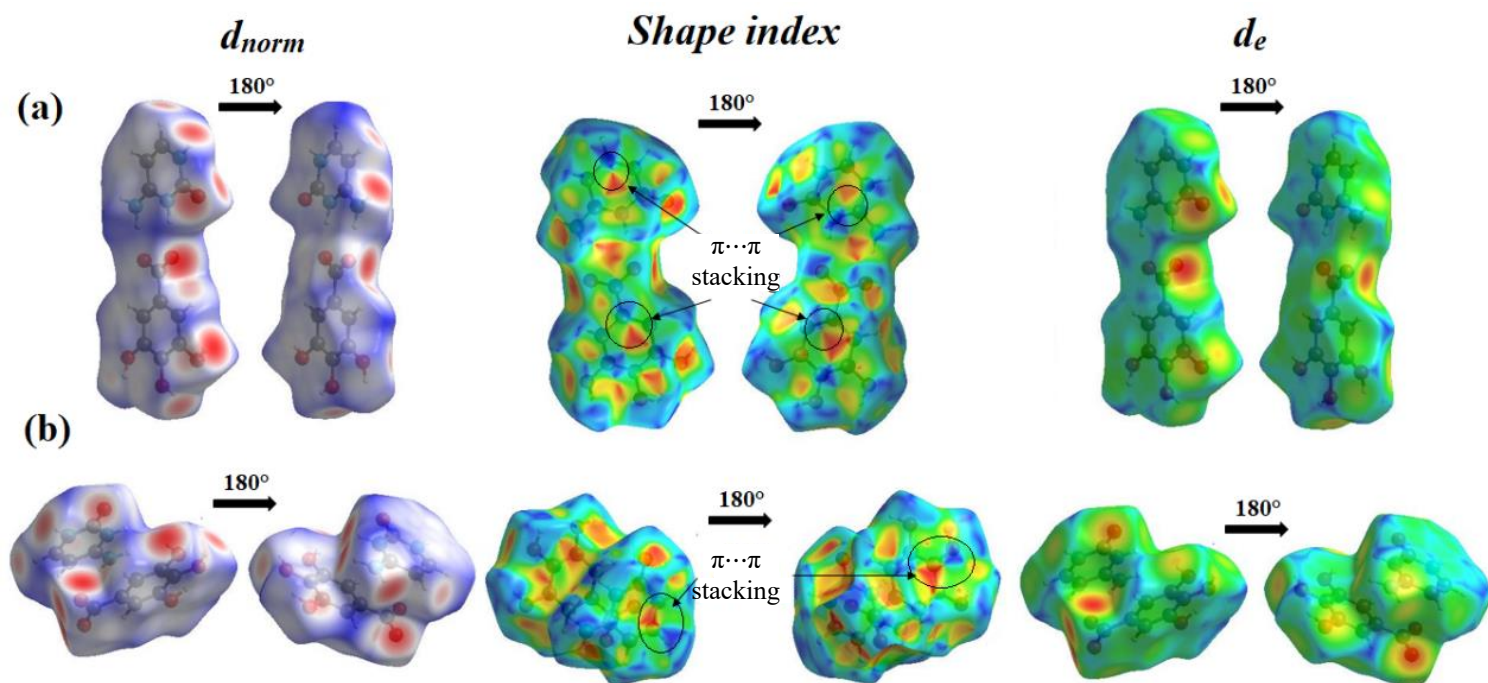


Figure 35. Hirshfeld surface analysis of cytosinium gallate polymorphs (a) **(CG1)** and (b) **(CG2)**, showing d_{norm} , shape index, and d_e surface mappings.

The 2D Hirshfeld fingerprint plots (Figure 36) of the two cytosinium gallate polymorphs reveals a fundamental and compensatory redistribution of intermolecular interaction, directly elucidating the origin of their structural divergence. **(CG1)** is characterized by a balance of moderate hydrogen bonding, evidenced by O—H contacts constituting 40.1% of the surface, and dominant van der Waals close-packing, signified by the substantial combined contribution of H—H (27.9%), H—C (10%) and C—C (7.4%) interactions. In stark contrast, the supramolecular architecture of **(CG2)** is overwhelmingly driven by an extensive and robust hydrogen-bond network, with O—H contacts escalating to 51.7% of all interactions. Demonstrating a compensatory trade-off between hydrogen bonding intensity and dispersive interactions that dictates their distinct supramolecular architectures.

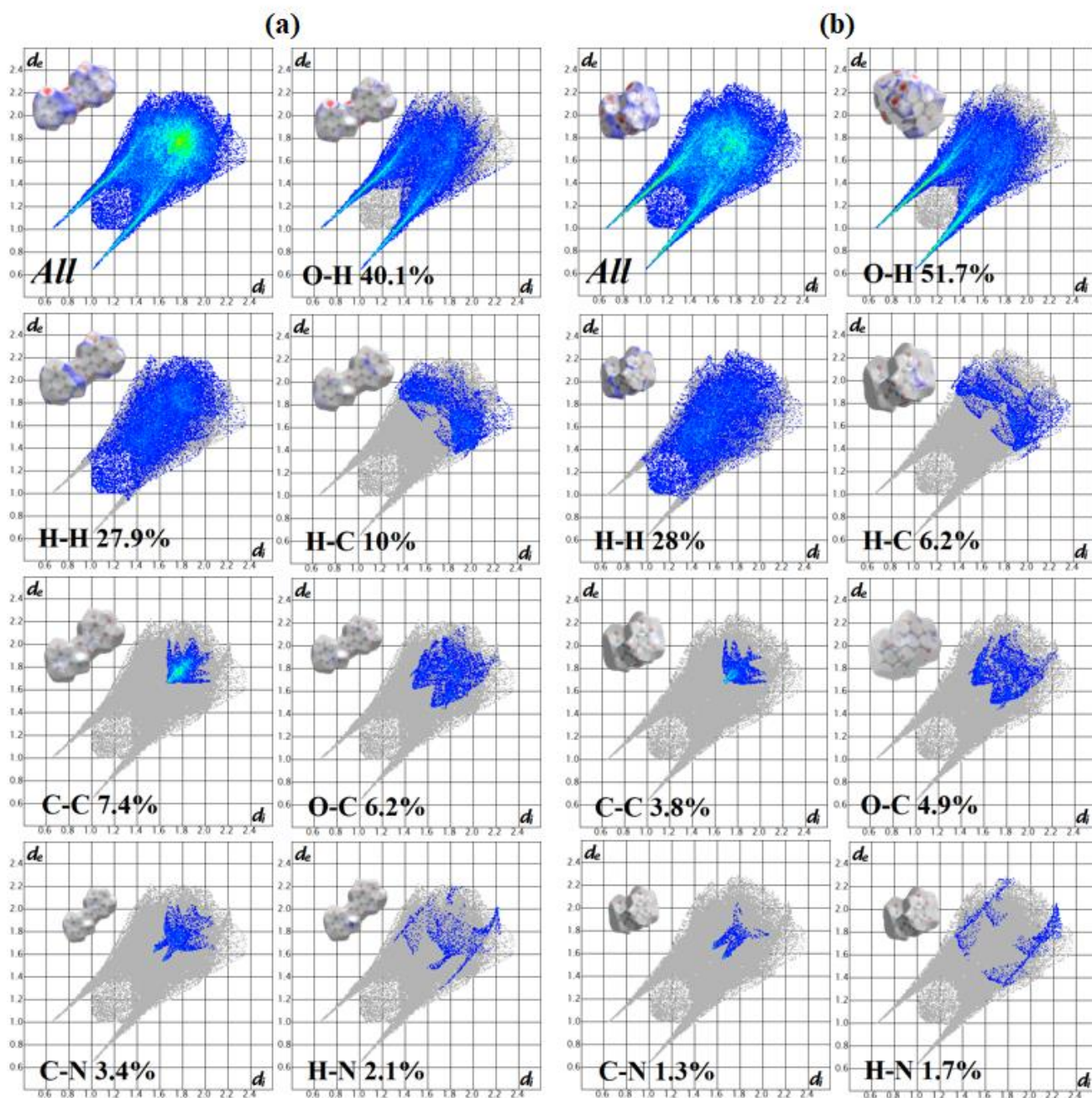


Figure 36. 2D Fingerprint plot illustrating contact contributions in cytosinium gallate polymorphs (a) (CG1) and (b) (CG2).

VI. Density functional theory (DFT)

Geometry optimizations were performed in the gas phase using density functional theory (DFT) with the B3LYP functional and the 6-311+G (d, p) basis set.

The computational methodology, including geometry optimization procedures, frequency calculations, and software has been comprehensively described in the previous chapter.

VI. 1. Optimized geometric parameters

After optimization of the molecular geometry of **(CG1)** (Figure 37), we carried out a comparative study of the different bond lengths and bond angles calculated theoretically with the experimental data, and the results are summarized in Table II.10.

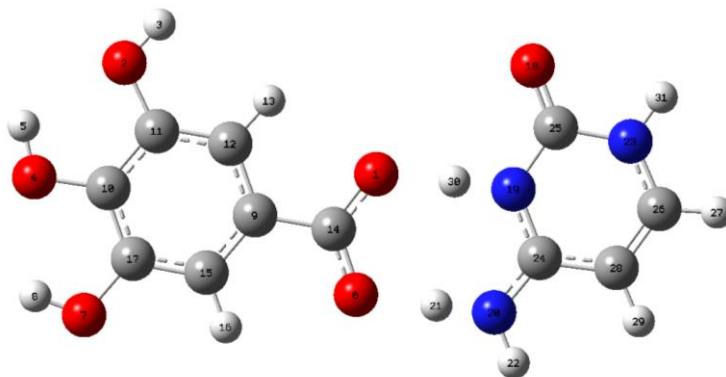


Figure 37. Optimized structure of the new polymorph of cytosinium gallate (**CG1**) calculated using the B3LYP functional.

The experimental bond lengths range from 1.23 to 1.503 Å, with an average of 1.365 Å, while the optimized bond lengths vary from 1.2354 to 1.4901 Å, averaging 1.376 Å. Experimental bond angles span 114.17° to 125.51°, with an average of 120.22°, whereas theoretical bond angles range from 114.01° to 125.28°, yielding an average of 120.21°. Figure 26 presents the distribution and correlation plots, showing correlation coefficients of $R^2 = 0.999$ for both bond lengths and angles, indicating excellent agreement between calculated and experimental values.

Table 10. Optimized bond lengths and bond angles for cytosinium gallate polymorph: (**CG1**) calculated by DFT in comparison with SC-XRD data.

Bond length	EXP (Å)	B3LYP (Å)	Bond length	EXP (Å)	B3LYP (Å)
O2—C1	1.270 (3)	1.2944	N1—C11	1.368 (3)	1.3686
O8—C8	1.230 (2)	1.2354	C2—C7	1.400 (3)	1.405
O6—C6	1.360 (2)	1.4061	C2—C1	1.503 (3)	1.4901
O5—C5	1.368 (3)	1.3951	C2—C3	1.403 (3)	1.4009
O1—C1	1.266 (2)	1.2897	C5—C6	1.398 (3)	1.3931
O4—C4	1.383 (2)	1.3899	C5—C4	1.388 (3)	1.3946
N2—C9	1.363 (3)	1.368	C6—C7	1.390 (3)	1.3872
N2—C8	1.384 (3)	1.3897	C9—C10	1.425 (3)	1.4419
N3—C9	1.313 (3)	1.3234	C3—C4	1.386 (3)	1.3914

N1—C8	1.364 (3)	1.4117	C11—C10	1.343 (3)	1.3556
Bond angles	Exp (°)	B3LYP (°)	Bond angles	Exp (°)	B3LYP (°)
C9—N2—C8	124.17 (19)	124.403	C9—N2—C8	124.17 (19)	122.4954
C8—N1—C11	122.96 (18)	123.4588	C8—N1—C11	122.96 (18)	124.7093
C7—C2—C1	121.26 (18)	119.1567	C7—C2—C1	121.26 (18)	120.9676
C7—C2—C3	119.87 (18)	120.6053	C7—C2—C3	119.87 (18)	114.3231
C3—C2—C1	118.87 (17)	120.238	C3—C2—C1	118.87 (17)	117.7519
O5—C5—C6	120.92 (18)	122.2364	O5—C5—C6	120.92 (18)	123.5647
O5—C5—C4	119.05 (18)	117.5715	O5—C5—C4	119.05 (18)	118.6834
C4—C5—C6	120.0 (2)	120.1921	C4—C5—C6	120.0 (2)	119.5646
O6—C6—C5	114.17 (19)	114.0158	O6—C6—C5	114.17 (19)	120.8151
O6—C6—C7	125.51 (18)	125.2828	O4—C4—C5	121.14 (19)	119.7487
C7—C6—C5	120.26 (18)	120.7014	O4—C4—C3	118.58 (18)	120.2872
C6—C7—C2	119.62 (18)	118.9725	C3—C4—C5	120.22 (19)	119.9641
N2—C9—C10	118.21 (18)	118.393	C11—C10—C9	117.78 (19)	118.607
N3—C9—N2	119.1 (2)	119.1115			

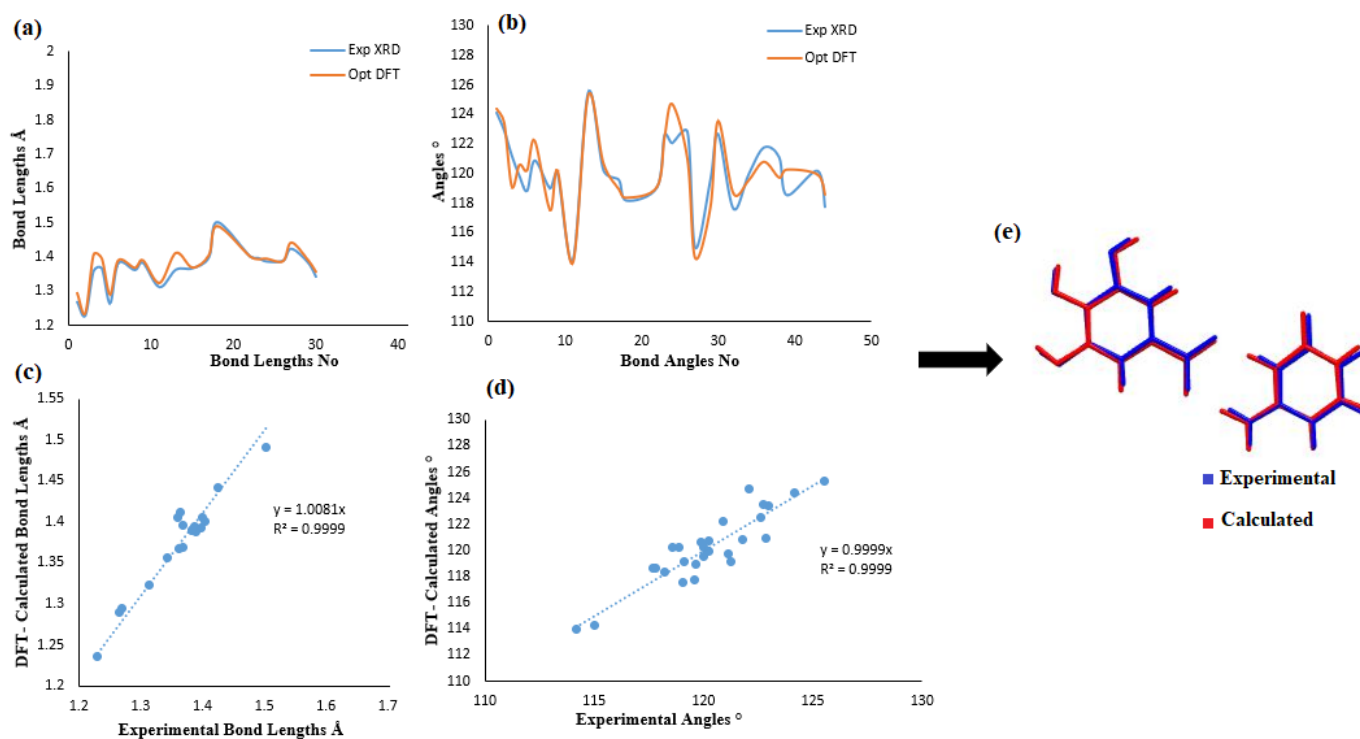


Figure 38. Comparison between experimental (SC-XRD) and DFT-optimized geometrical parameters for [CYT⁺, GA⁻] (a) bond lengths, (b) bond angles, (c–d) regression plots showing near-unity correlation), and (e) superposition of experimental (blue) and calculated (red) molecular structures.

VI. 2. Frontier molecular orbitals (FMOs) and energy gap.

(Figure 39) shows the HOMO and LUMO spatial distributions and energy levels for polymorph I and II.

In **(CG1)**, the HOMO is predominantly localized over the gallate moiety, with significant electron density distributed across the aromatic ring and the adjacent oxygen atoms. This localization indicates that the gallate anion acts as the primary electron-donating region. In contrast, the LUMO is mainly delocalized over the cytosinium cation, particularly along the heterocyclic ring system, suggesting that this moiety serves as the preferred electron-accepting site. The clear spatial separation between the HOMO and LUMO implies an intermolecular charge-transfer character upon electronic excitation. The calculated HOMO and LUMO energies for **(CG1)** are -5.685 eV and -2.284 eV, respectively, resulting in an energy gap (ΔE) of 3.401 eV.

For **(CG2)**, a similar donor–acceptor pattern is observed; however, notable differences in orbital localization are evident. The HOMO remains largely concentrated on the cytosinium unit, but with increased delocalization extending toward the hydrogen-bonding regions involving the gallate anion. The LUMO is again primarily localized on the gallate moiety, though it exhibits a more extended distribution over the molecular framework compared to **(CG1)**, reflecting differences in crystal packing and hydrogen-bonding topology. The HOMO and LUMO energies for **(CG2)** are calculated to be -5.902 eV and -1.306 eV, respectively, yielding a larger band gap of 4.596 eV.

Both polymorphs display intermolecular charge-transfer characteristics between gallate (HOMO, donor) and cytosinium (LUMO, acceptor); however, **(CG1)** exhibits enhanced electronic reactivity with a narrower band gap (3.401 eV) and distinct orbital separation, whereas **(CG2)** demonstrates superior electronic stability with a larger band gap (4.596 eV) and extended orbital delocalization, attributed to its distinctive hydrogen-bonding network.

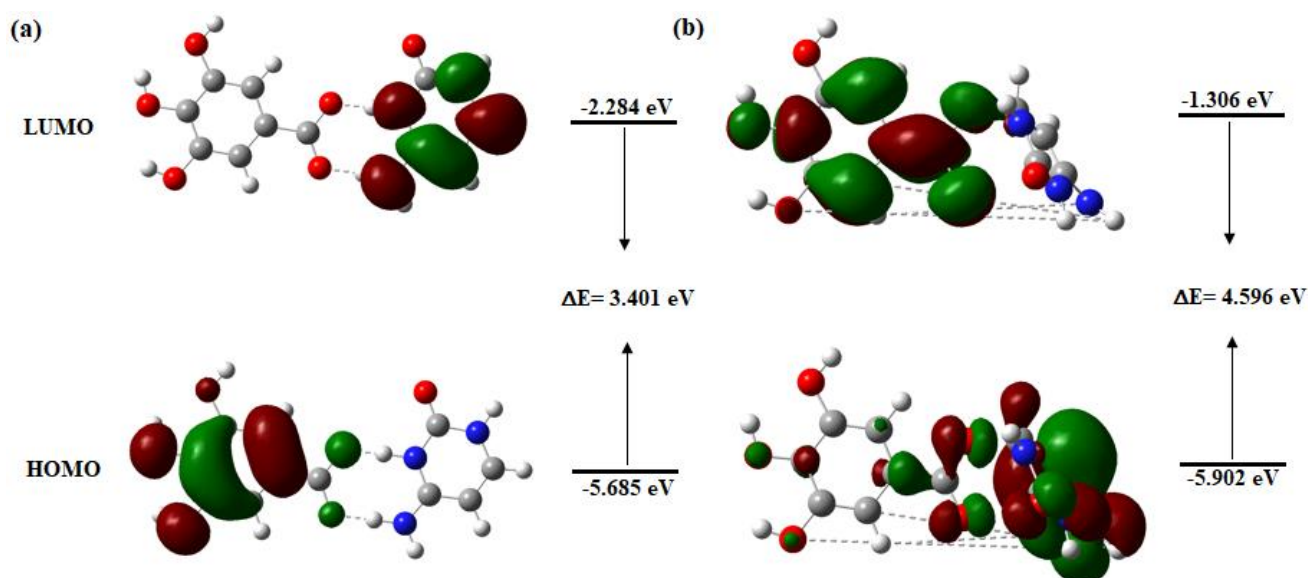


Figure 39. Comparative visualization of the HOMO and LUMO energy levels and orbital distributions for the two polymorphs of cytosinium gallate with (a) (CG1) and (b) (CG2).

VI. 3. Analysis of molecular electrostatic potential (MEP)

Molecular electrostatic potential (MEP) (Figure 40) analysis reveals that both cytosinium gallate polymorphs exhibit complementary charge distributions with electron-rich regions (red/orange) localized on gallate oxygen atoms serving as hydrogen-bond acceptors and electron-deficient regions (blue/green) on cytosinium nitrogen and hydrogen atoms acting as donors, but (CG1) displays more intense and localized negative potentials on gallate functionalities favoring stronger electrophilic interactions, whereas (CG2) shows more delocalized negative regions and extended positive potentials along hydrogen-bonding pathways, reflecting enhanced electrostatic stabilization through a more extensive hydrogen-bond network that compensates for reduced localized interaction strength.

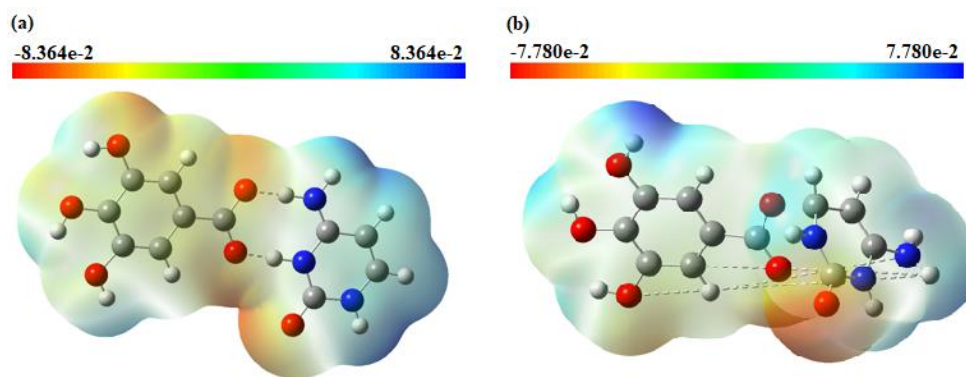


Figure 40. Molecular electrostatic potential (MEP) surfaces of the two polymorphs of cytosinium gallate with (a) (CG1) and (b) (CG2).

IV. 4. Analysis of Mulliken atomic charges

Atomic charge distribution analysis (Figure 41) demonstrates that both polymorphs exhibit complementary charge localization gallate oxygen atoms as electron-rich hydrogen-bond acceptors and cytosinium N–H groups as donors but (CG2) displays enhanced negative charges on gallate oxygens and greater positive charge delocalization across cytosinium, indicating stronger electrostatic interactions and more pronounced intermolecular charge transfer that contribute to its superior electrostatic stabilization and distinct physicochemical properties compared to (CG1).

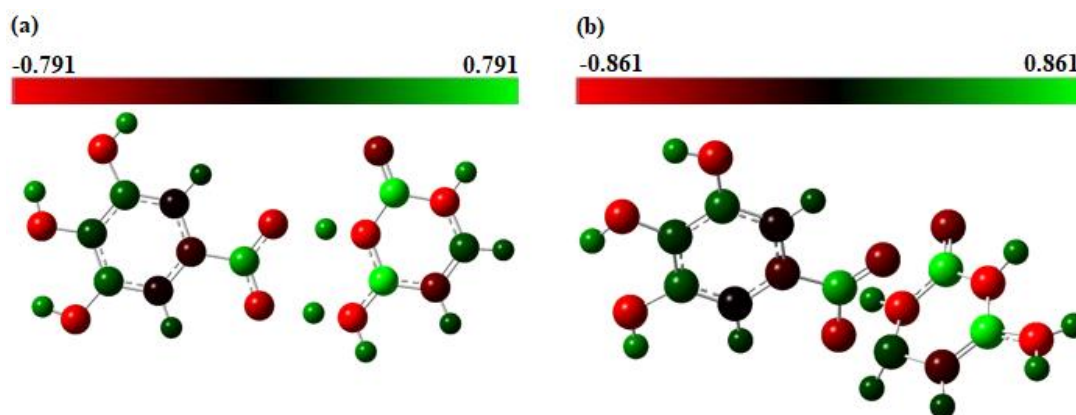


Figure 41. Mulliken Charge Distribution Across Polymorphic Forms of cytosinium gallate with (a) (CG1) and (b) (CG2).

IV. 5. Reduced density gradient (RDG) analysis of noncovalent interactions (NCI).

Reduced density gradient (RDG) and noncovalent interaction (NCI) analysis (Figure 42) reveals that both cytosinium gallate polymorphs are stabilized primarily by strong hydrogen bonding (N–H $\cdots$ O and O–H $\cdots$ O), but with distinct interaction profiles: (CG1) exhibits sharper, more intense features at negative $\text{sign}(\lambda_2)\rho$ values,

indicating stronger and more localized hydrogen-bonding networks, whereas **(CG2)** displays broader distributions near $\text{sign}(\lambda_2)\rho \approx 0$ with enhanced contributions from weak dispersive van der Waals interactions ($\pi \cdots \pi$ stacking, $\text{C-H} \cdots \pi$ contacts) and slightly increased steric repulsion, demonstrating that polymorphism arises from the differential balance between directional hydrogen bonding and dispersive interactions governing lattice stabilization.

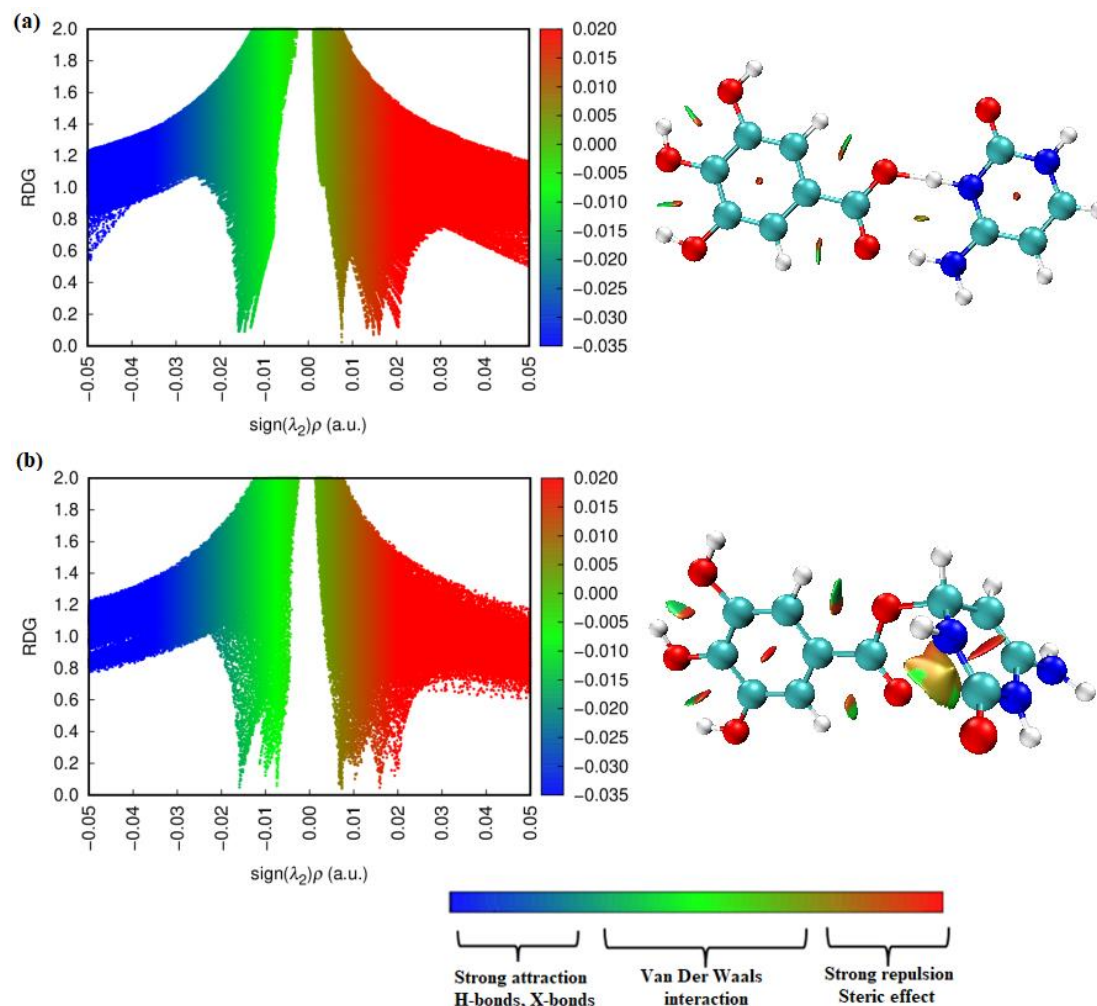


Figure 42. Reduced density gradient (RDG) and noncovalent interaction (NCI) analysis of cytosinium gallate polymorphs with (a) **(CG1)** and (b) **(CG2)**.

VII. Conclusion.

This chapter describes the structural, spectroscopic, and electronic characterization of a new polymorph of cytosinium gallate, **(CG1)** compared to the known polymorph **(CG2)**. The new form, synthesized via an acid-base reaction, crystallizes in the monoclinic $P2_1$ space group but features different unit-cell

parameters and a unique crystal packing. Structural analysis reveals that while both polymorphs are stabilized by extensive hydrogen-bonding networks, **(CG1)** has a more isotropic structure with notable contributions from hydrogen bonding and van der Waals interactions. FTIR analysis further indicates differences in hydrogen-bonding environments, while DFT calculations show that **(CG1)** has a smaller HOMO–LUMO gap, suggesting enhanced charge transfer capabilities. This research highlights how variations in crystallization conditions affect the supramolecular assembly of cytosinium gallate, with implications for the design of materials in various applications. Future studies will explore the thermodynamic stability and functional properties of these polymorphs.

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Chapter IV.
*Structural,
Spectroscopic, and
Electronic Investigation
of a New Polymorph of
(Z)-5-{[4-(
(dimethylamino)phenyl]
methylidene}-2-
sulfanylidene-1,3-
thiazolidin-4-one*

I. Introduction.

Rhodanine, or 2-thioxothiazolidin-4-one, is a versatile heterocyclic compound with a core consisting of sulfur and nitrogen¹, making it important in organic and medicinal chemistry. It belongs to the thiazolidinone family and is characterized by a thiocarbonyl group. Rhodanine derivatives have gained attention due to their biological activities, including antimicrobial, antiviral, anti-inflammatory, antidiabetic, and anticancer effects². The drug epalrestat marks its clinical application, spurring research into rhodanine-based therapeutics. Although they are considered privileged scaffolds for drug discovery³, some can interfere in assays, presenting challenges. The chapter also discusses a newly discovered polymorphic form of a rhodanine derivative, (Z)-DMAP-RDN, emphasizing the impact of structural modifications on physicochemical properties and crystallization behavior, enhancing the understanding of structure-property relationships in rhodanine systems.

II. Polymorphs of [(Z)-DMAP-RDN].

A systematic search of the Cambridge Structural Database (CSD) revealed that (Z)-5-{[4-(dimethylamino) phenyl] methylidene}-2-sulfanylidene-1,3-thiazolidin-4-one, a rhodanine derivative, has previously been reported (Table 11) to crystallize in two distinct polymorphic forms^{4, 5}. Although these polymorphs share the same molecular composition, they differ in their crystal packing arrangements and intermolecular interactions. In the present work, a third polymorphic form of this compound is identified and characterized.

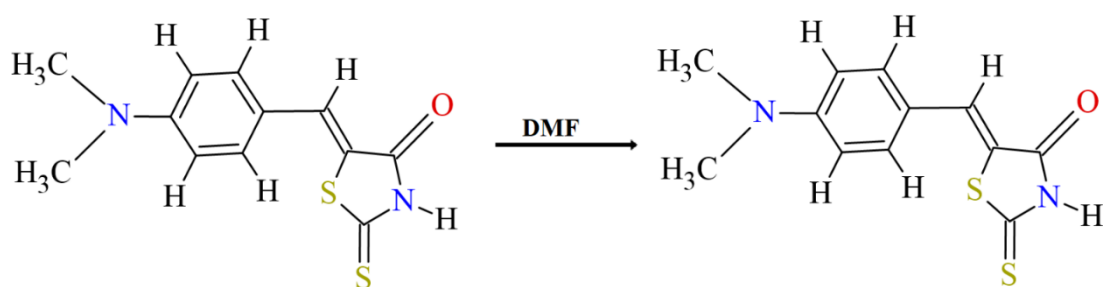
Table 11. Crystallographic data of [(Z)-DMAP-RDN] polymorphs

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Space groupe, System
P1	3.958	11.264	26.717	90	94.027	90	<i>P2₁/c</i> (monoclinic)
FEXLUT (P2)	3.936	11.248	26.67	90	93.85	90	<i>P2₁/c</i> (monoclinic)
FEXLUT01(P3)	3.937	11.244	26.714	90	93.98	90	<i>P2₁/c</i> (monoclinic)

III. Experimental methods.

III. 1. Experimental procedure.

A weighed amount of (Z)-DMAP-RDN was dissolved in N, N-dimethylformamide (DMF) under continuous stirring at room temperature to obtain a homogeneous orange solution. Slow evaporation of the solvent under ambient conditions yielded well-formed light-yellow block-shaped crystals. The resulting crystals were isolated by filtration and washed with cold DMF.



Scheme 3. Synthetic route to the new polymorph of [(Z)-DMAP-RDN].

III. 2. Single-crystal X-ray diffraction analysis.

Single-crystal X-ray diffraction data collection and structural refinement protocols for [(Z)-DMAP-RDN], including instrumentation specifications and computational methods, have been fully described in the previous chapter. (Table 12) summarizes the important parameters for collecting and refining crystallographic data.

Table 12. Structural data and recording conditions for [(Z)-DMAP-RDN].

Crystal data	
Chemical formula	C ₁₂ H ₁₂ N ₂ OS ₂
<i>M_r</i>	264.36
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	200
<i>a</i> (Å), <i>b</i> (Å), <i>c</i> (Å)	3.9585 (3), 11.2642 (9), 26.7179 (19)
β(°)	94.027 (2)
<i>V</i> (Å ³)	1188.39 (16)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ(mm ⁻¹)	0.43

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Crystal size (mm)	0.5 × 0.4 × 0.2
$T_{\min}, T_{\max}$	0.643, 0.745
Reflections collected, Independent reflections, Observed reflections with $[I > 2\sigma(I)]$	15662, 2111, 1613
$R_{\text{int}}, R_{\text{sigma}}$	0.096, 0.595
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), \text{Goodness-of-fit on } F^2$	0.049, 0.121, 1.06
No. of reflections, No. of parameters	2111, 156
$\Delta\rho_{\max}, \Delta\rho_{\min} (\text{e } \text{\AA}^{-3})$	0.34, -0.23

III. 3. FTIR spectroscopic characterization of [(Z)-DMAP-RDN].

The FTIR spectrum of [(Z)-DMAP-RDN] (Figure 43) displays characteristic vibrational bands. A broad absorption band centered in the 3400–3200 cm^{-1} region is attributed to N–H stretching vibrations, indicative of hydrogen-bonded amine or amide functionalities. The weak-to-moderate bands observed around 3050–2900 cm^{-1} correspond to aromatic and aliphatic C–H stretching modes associated with the dimethylamino and heteroaromatic fragments. A strong absorption in the 1650–1600 cm^{-1} region is assigned to C=O and C=C stretching vibrations of the conjugated heterocyclic system, reflecting the extended π -delocalization characteristic of the (Z)-configured framework. Additional intense bands between 1550 and 1450 cm^{-1} arise from aromatic ring vibrations and C–N stretching modes linked to the DMAP moiety. The fingerprint region (1400–600 cm^{-1}) exhibits multiple sharp bands corresponding to C–S, C–N, and in-plane and out-of-plane aromatic C–H bending vibrations, which are consistent with the presence of sulfur-containing heterocycles and substituted aromatic rings. Overall, the FTIR spectral features are in good agreement with the proposed structure of [(Z)-DMAP-RDN], supporting the formation of a conjugated, heteroatom-rich molecular framework stabilized by intramolecular interactions.

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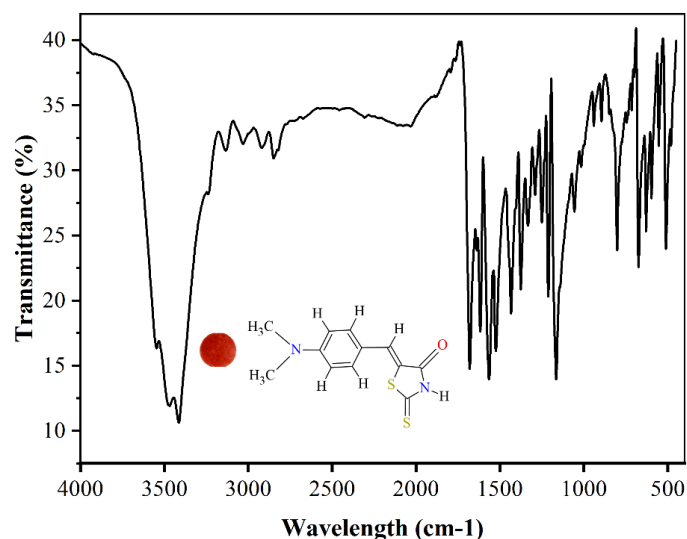


Figure 43. FTIR spectrum of [(Z)-DMAP-RDN].

Table 13. FTIR wavenumber assignments of [(Z)-DMAP-RDN] and corresponding vibrational modes.

Wavenumber (cm ⁻¹)	Assignment	Origin
3370	Broad ν(N–H) stretching	Hydrogen-bonded amine/imine N–H group
3060	ν(C–H) aromatic stretching	Aromatic C–H vibrations (heteroaromatic and DMAP rings)
2965, 2870	ν(C–H) aliphatic stretching	Methyl (–CH ₃) groups of the dimethylamino substituent
1625	ν(C=N), ν(C=C) stretching	Conjugated imine and aromatic ring vibrations
1540	ν(C=C) aromatic stretching	π-delocalized heteroaromatic ring system
1460	δ(CH ₃) bending	Methyl deformation of –N(CH ₃) ₂ groups
1335	ν(C–N) stretching	C–N vibrations of the DMAP moiety
1245	ν(C–S) stretching	Sulfur-containing heterocyclic framework
1115	ν(C–N), ν(C–S) stretching	Mixed C–N/C–S modes in the heterocycle
980	γ(C–H) out-of-plane bending	Aromatic C–H deformation
745	Ring deformation	Heteroaromatic ring bending
680	ν(C–S) bending/stretching	Thioamide-related skeletal vibration

IV. Description of the structure.

The three polymorphs **P1**, **P2** and **P3** of [(Z)-DMAP-RDN] crystallize in the monoclinic *P2₁/c* space group with an asymmetric unit containing one Schiff base-rhodanine derivative featuring (Figure 44) a 1,3-thiazolidin-4-one ring (with carbonyl at C4 and thiocarbonyl at C2) conjugated through an exocyclic methyldene linker (–

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CH=) to a para-dimethylaminophenyl group, forming an extended π -conjugated system that enhances planarity and electronic delocalization, with the electron-donating dimethylamino substituent adopting trigonal pyramidal geometry.

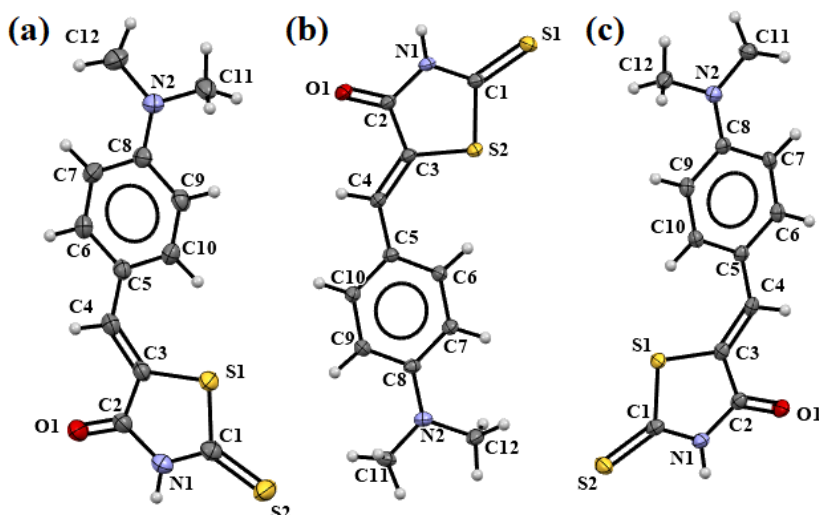


Figure 44. Asymmetric units of three polymorphs of [(Z)-DMAP-RDN] with (a) **P1**, (b) **P2** and (c) **P3** along *a* axis

The dihedral angle between the rhodanine and phenyl rings (Figure 45) exhibits minimal variation across the three polymorphs, with values of 7.02° in **P1**, 7.13° in **P2**, and 7.11° in **P3**, indicating near-planar molecular conformations that are essentially conserved despite polymorphic differences.

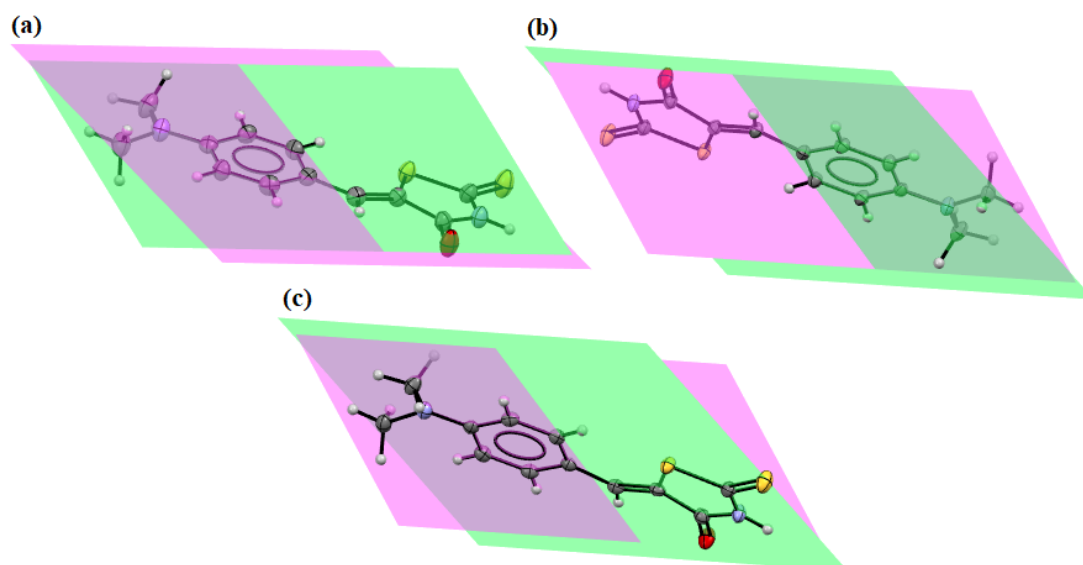


Figure 45. Coplanar geometry in [(Z)-DMAP-RDN] polymorphs : (**P1**) (a) (**P2**) (b) and (**P3**) (c) between phenyl ring and rhodanine ring in asymmetric unit.

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Comparative analysis of the crystal packing in [(Z)-DMAP-RDN] polymorphs **P1**, **P2**, and **P3** along the crystallographic axes (Figure 46) reveals distinct supramolecular architectures arising from systematic variations in molecular orientation. Along the **a axis**, molecules organize into periodic columnar arrangements with polymorph-dependent orientations reflecting divergent intermolecular contact geometries. Viewing along the **b axis** reveals layered packing motifs with quasi-parallel molecular arrays, where interlayer planarity and compactness vary progressively across **P1**, **P2**, and **P3**, indicating differential packing efficiencies. Along the **c axis**, stacking interactions dominate, generating zigzag chain architectures with distinct molecular orientations in each polymorph.

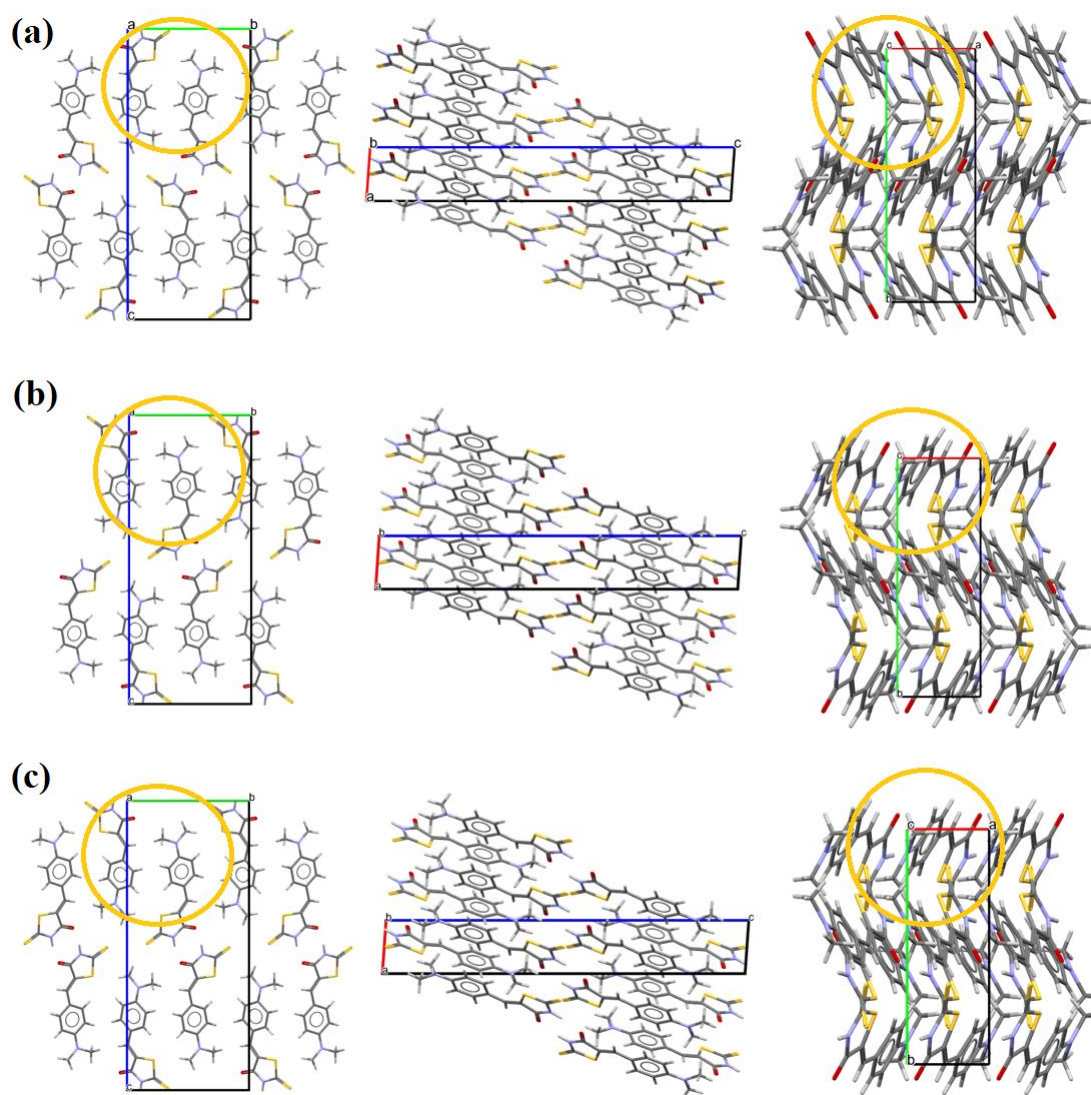


Figure 46. Packing Arrangements of three polymorphic forms of [(Z)-DMAP-RDN]: (a) **P1**, (b) **P2** and (c) **P3**.

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These axis-specific packing differences in molecules orientation in the superposition of the three polymorphs of [(Z)-DMAP-RDN] (Figure 47) demonstrate that polymorphism arises primarily from intramolecular conformational changes, thereby classifying **P1**, **P2** and **P3** as conformational polymorphs.

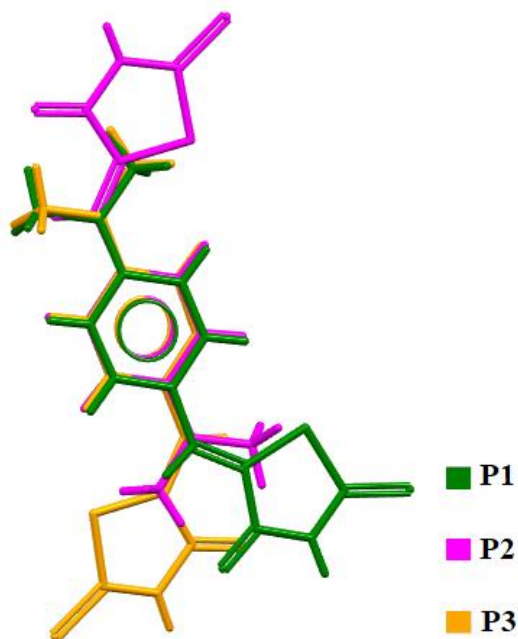


Figure 47. Superposition of crystal structures of [(Z)-DMAP-RDN] polymorphs

The hydrogen-bonding patterns observed in the three polymorphs of [(Z)-DMAP-RDN]. In all three structures **P1**, **P2** and **P3** leads to the establishment of well-defined graph-set patterns $R_2^2(8)$ (Figure 48).

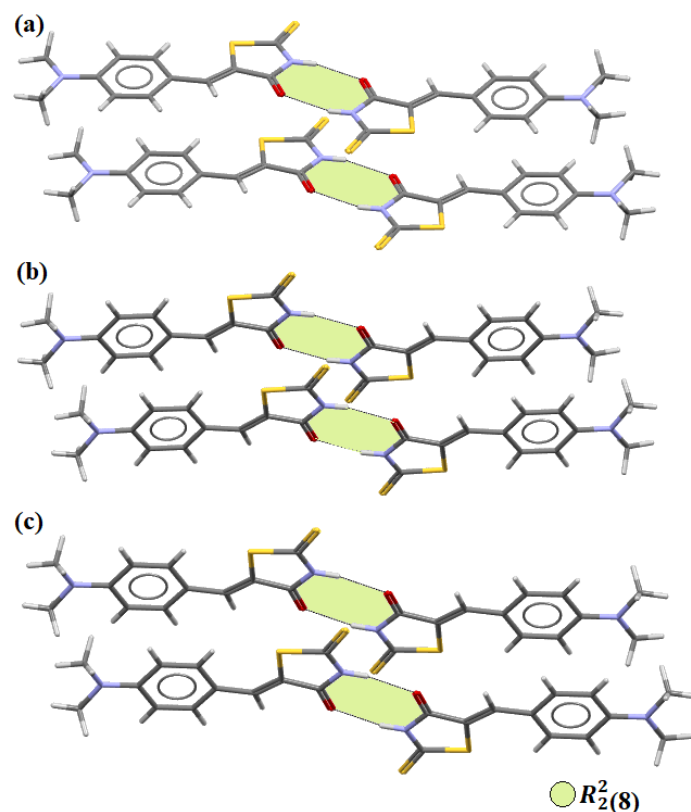


Figure 48. Supramolecular packing of [(Z)-DMAP-RDN] polymorphs with (a) **(P1)**, (b) **(P2)** and (c) **(P3)** showing N—H $\cdots$ O interactions forming ring motifs
In three polymorphs of [(Z)-DMAP-RDN] the dominant hydrogen bonds involve the N—H groups acting as donors and the oxygen (O1) as acceptors (Figure 49), forming comparable N—H $\cdots$ O interaction with D $\cdots$ A distances typically in the range of $\sim$ 2.84–2.86 Å, characteristic of moderately strong hydrogen bonds. In addition, several weak C—H $\cdots$ C and C—H $\cdots$ S interactions are consistently present, with longer contact distances ($\sim$ 2.928–4.007 Å)

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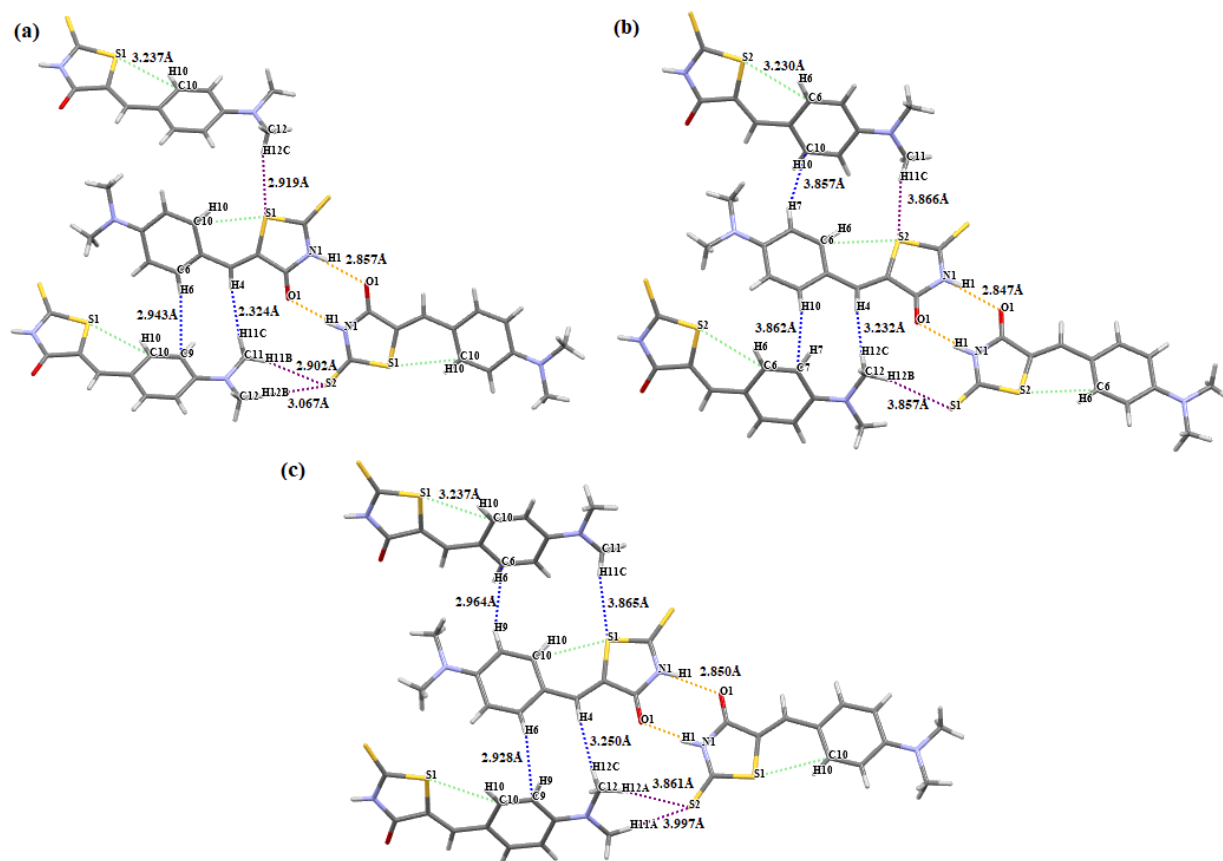


Figure 49. Hydrogen-bonding interactions in [(Z)-DMAP-RDN] polymorphs: (a) **P1**, (b) **P2** and (c) **P3**.

Table 14. Hydrogen-bond geometry (Å, °) of [(Z)-DMAP-RDN] polymorphs: (a) **P1**, (b) **P2** and (c) **P3**.

	<i>D</i> —H··· <i>A</i>	<i>D</i> —H (Å)	H··· <i>A</i> (Å)	<i>D</i> ··· <i>A</i> (Å)	<i>D</i> —H··· <i>A</i> (°)
P1	N1—H1···O1	0.881	1.996	2.857	165.47
	C10—H10···S1	0.950	2.517	3.237	132.61
	C12—H12C···S1	0.950	2.919	3.871	164.26
	C11—H11B···S2	0.980	3.067	3.861	166.60
	C12—H12B···S2	0.979	2.902	4.007	161.33
	C6—H6···C9	0.950	2.943	3.878	168.37
	C4—H4··· H11C	0.949	2.324	3.258	167.33
P2	N1—H1···O1	0.881	1.983	2.847	166.58
	C6—H6···S1	0.992	2.517	3.230	128.59
	C11—H11C···S2	0.984	2.905	3.866	165.71
	C10—H10···C7	0.960	2.914	3.862	169.22
	C12—H12C···H4	0.990	2.268	3.232	174.63
	C12—H12B···S1	0.955	2.927	3.857	164.83
	C7—H7···C10	0.992	2.916	3.857	158.85

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P3	N1—H1···O1	0.890	1.97	2.850	168
	C10—H10···S1	0.950	2.521	3.237	132.26
	C11—H11C···S1	0.980	2.908	3.865	165.38
	C6—H6···C9	0.950	2.928	2.964	168.78
	C9—H9···C6	0.950	2.964	2.928	157.89
	C12—H12C···H4	0.980	2.320	3.250	175.75
	C12—H12A···S2	0.980	2.896	3.861	168.41
	C11—H11A···S2	0.980	3.061	3.997	160.31

The three polymorphs of [(Z)-DMAP-RDN] display structurally distinct $\pi \cdots \pi$ stacking interactions (Figure 50) that systematically influence their packing architectures. **P1** exhibits slipped parallel stacking with centroid–centroid distances of 3.958 Å, indicative of moderate $\pi \cdots \pi$ interactions that stabilize uniform columnar assemblies. **P2** demonstrates enhanced $\pi \cdots \pi$ stacking with shorter, more symmetrical centroid–centroid separations of 3.936 Å, reflecting stronger aromatic overlap and improved packing efficiency relative to **P1**. **P3** presents comparable interplanar distances (3.937 Å) to **P2**, however, subtle variations in lateral ring offset produce a distinct stacking geometry and differentiated packing motif. The progressive reduction in centroid–centroid distance (**P1** > **P2** $\approx$ **P3**) correlates with enhanced $\pi \cdots \pi$ stabilization and underscores the critical role of aromatic stacking in modulating the polymorphic behavior and solid-state properties of [(Z)-DMAP-RDN].

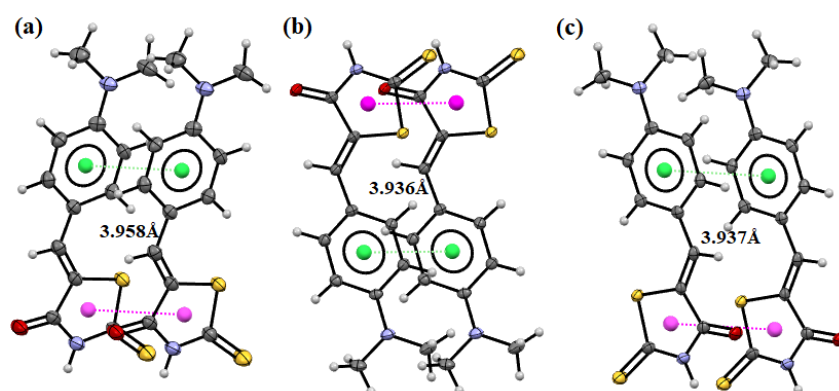


Figure 50. $\pi \cdots \pi$ Stacking interactions in the three polymorphs of [(Z)-DMAP-RDN]: (a) **P1**, (b) **P2** and (c) **P3**.

IV. 1. Morphological analysis (BFDH).

The predicted crystal morphologies of polymorphs **P1**, **P2**, and **P3** of [(Z)-DMAP-RDN] (Figure 51) are broadly similar, showing comparable prismatic habits. The main differences arise from variations in the molecular position and orientation within the crystal lattice rather than major changes in overall shape. In all three polymorphs, the morphology is mainly dominated by the (002) faces, with auxiliary growth contributions from the (011), (0-11), (100) and (10-2) facets, while planes such as (-1-11), (-110), (-111) and (-1-10) appear as minor facets contributing less to the crystal habit

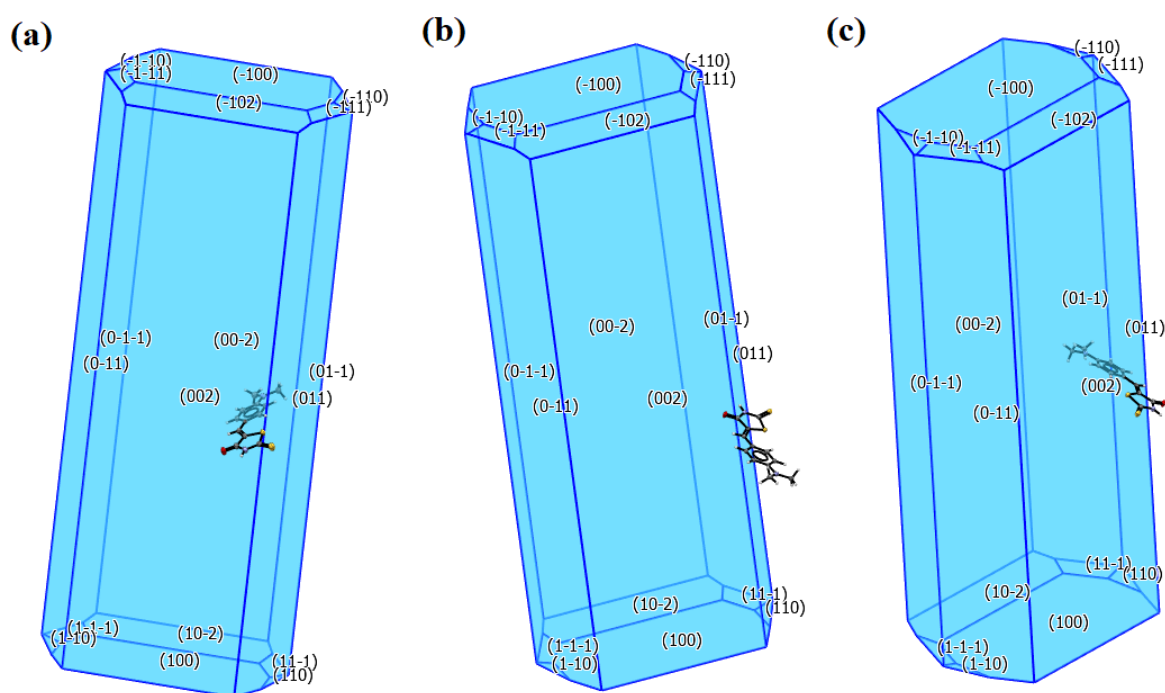


Figure 51. Predicted BFDH morphologies of [(Z)-DMAP-RDN] polymorphs: (a) (**P1**) (b) (**P2**) and (c) (**P3**)

V. Hirshfeld surface analysis (HSA).

The Hirshfeld surface analyses for the three polymorphs (Figure 52) exhibit a high degree of qualitative similarity, suggesting that they share a common set of fundamental intermolecular assembly motifs. The d_{norm} surfaces for all forms are characterized by nearly identical red regions indicative of C–H $\cdots$ S, N–H $\cdots$ O, and C–H $\cdots$ N contacts that fall below the sum of the van der Waals radii. Furthermore, the shape index surfaces consistently reveal complementary red and blue triangular

patterns, confirming the persistence of π - π stacking interactions across the crystalline phases. This structural consistency is reinforced by the d_e surfaces, which map out highly comparable intermolecular distances, reflecting a unified packing paradigm despite the subtle variations that differentiate the three polymorphic structures.

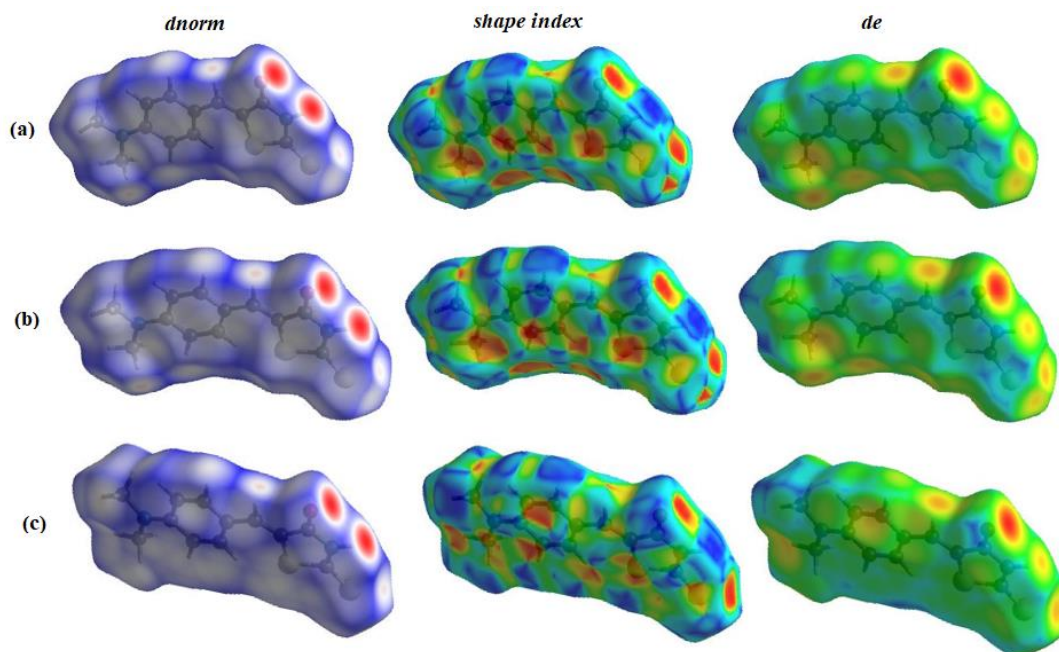


Figure 52. Hirshfeld surface analysis (d_{norm} , *Shape Index* and d_e) of three polymorphs of [(Z)-DMAP-RDN]: (a) (**P1**), (b) (**P2**) and (c) (**P3**).

The 2D Hirshfeld fingerprint plots (Figure 53) of the three polymorphs of [(Z)-DMAP-RDN] reveals distinctive patterns of intermolecular contact contributions that govern their crystal packing arrangements. The three polymorphs (**P1**, **P2**, and **P3**) of [(Z)-DMAP-RDN] exhibit remarkably consistent intermolecular contact profiles, with H $\cdots$ H contacts serving as the primary interaction at approximately 33% across all forms. Significant contributions are also observed from S $\cdots$ H interactions ($\sim$ 23%) and H $\cdots$ C contacts (15.4–16.1%), underscoring the dominant role of the hydrogen-rich structure and sulfur-containing groups in crystal packing. While minor variations exist such as P2 having the highest H $\cdots$ C percentage (16.1%) and P1 showing a marginally higher O $\cdots$ H contribution (11%) the overall distribution of contacts remains largely uniform, indicating a highly similar hierarchy of intermolecular forces in all three polymorphs.

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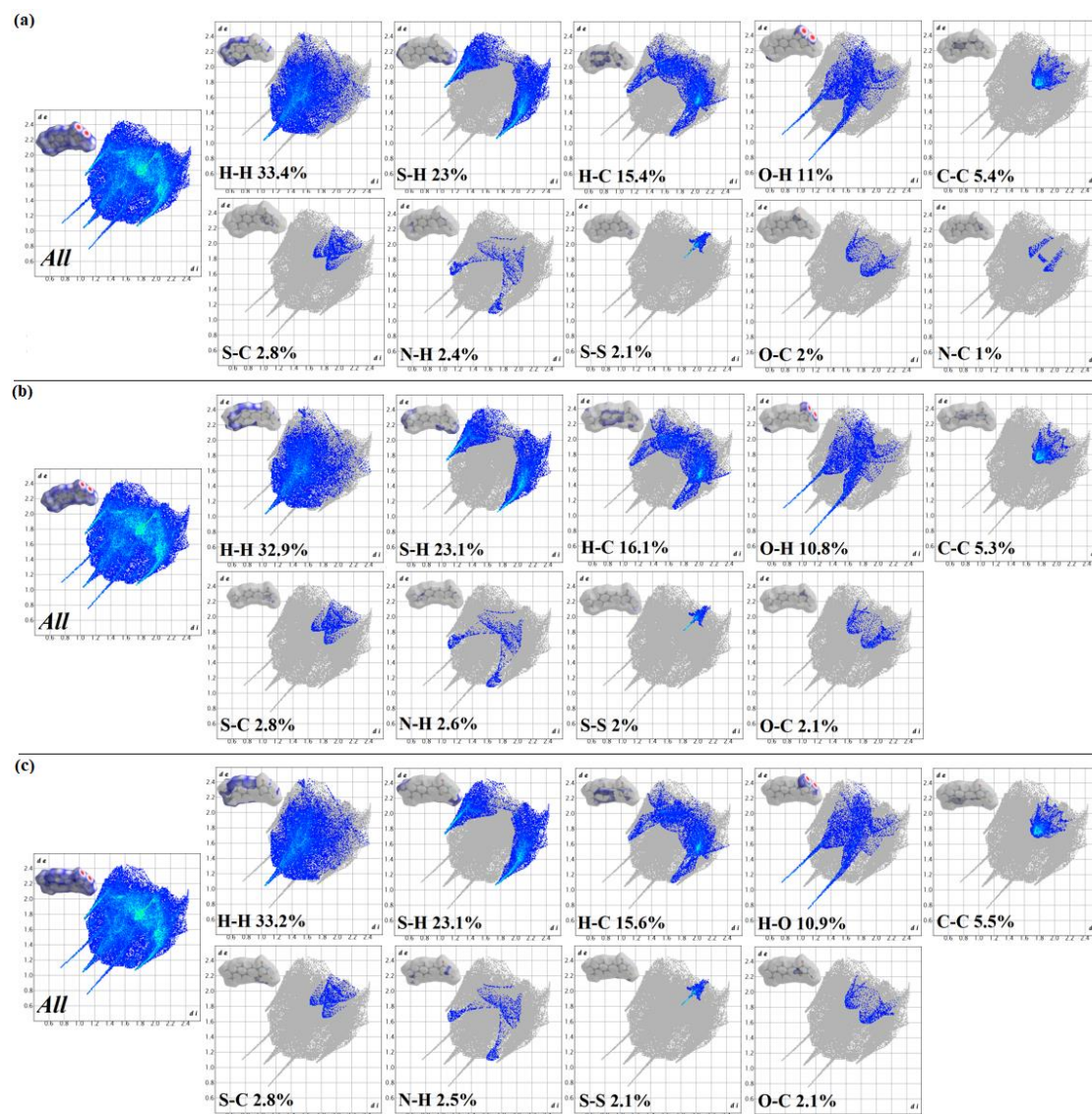


Figure 53. 2D Fingerprint plot illustrating contact contributions in [(Z)-DMAP-RDN] polymorphs: (a) (P1), (b) (P2) and (c) (P3).

VI. Density functional theory (DFT).

Density functional theory (DFT) with the B3LYP functional and the 6–311+G(d,p) basis set was used to optimize geometry in the gas phase.

VI. 1. Optimized geometric parameters.

Following the optimization of our polymorph molecular geometry [(Z)-DMAP-RDN] (Figure 54), we compared the various bond lengths and bond angles that were estimated theoretically with the experimental data. The findings are compiled in Table 15.

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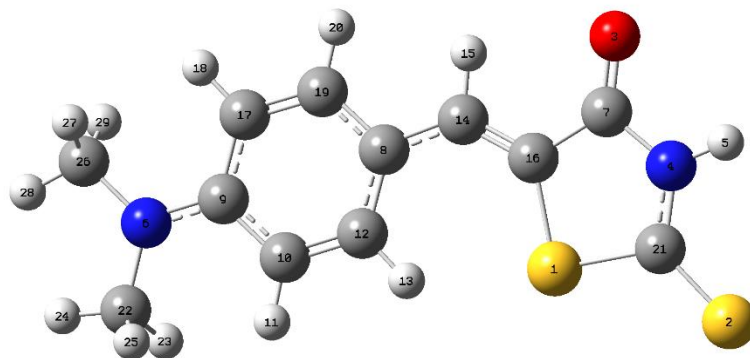


Figure 54. Optimized structure of the new polymorph of [(Z)-DMAP-RDN] calculated using the B3LYP functional.

The optimized bond lengths range from 1.2442 to 1.8453 Å, with an average of 1.466 Å, whereas the experimental bond lengths range from 1.223 to 1.756 Å, with an average of 1.445 Å. Theoretical bond angles range from 91.0712° to 132.5327°, with an average of 119.61°, while experimental bond angles range from 92.96 ° to 131.2 °, with an average of 119.56°. The distribution and correlation plots are shown in Figure 39, with correlation coefficients of $R^2 = 0.9997$ and 0.9999 bond lengths and angles, respectively, demonstrating good agreement (Figure 55) between calculated and experimental values.

Table 15. Optimized bond lengths and bond angles for [(Z)-DMAP-RDN] calculated by DFT in comparison with SC-XRD data.

Bond length	EXP (Å)	B3LYP (Å)	Bond length	EXP (Å)	B3LYP (Å)
S1—C3	1.756 (3)	1.8453	C2—C3	1.469 (4)	1.4645
S1—C1	1.755 (3)	1.838	C5—C10	1.407 (4)	1.4155
S2—C1	1.626 (3)	1.6794	C5—C4	1.439 (4)	1.4415
O1—C2	1.223 (4)	1.2442	C5—C6	1.405 (4)	1.4164
N1—C2	1.379 (4)	1.4104	C8—C9	1.417 (4)	1.4215
N1—C1	1.365 (4)	1.3654	C8—C7	1.410 (4)	1.4208
N2—C8	1.366 (4)	1.3804	C9—C10	1.370 (4)	1.3836
N2—C11	1.450 (4)	1.4658	C4—C3	1.347 (4)	1.3553
N2—C12	1.455 (4)	1.4654	C7—C6	1.367 (4)	1.3827
Bond angles	Exp (°)	B3LYP (°)	Bond angles	Exp (°)	B3LYP (°)
C1—S1—C3	92.96 (14)	91.0712	C7—C8—C9	116.9 (3)	117.2688
C1—N1—C2	118.4 (2)	120.6899	C10—C9—C8	121.0 (3)	121.271
C8—N2—C11	121.0 (2)	120.4197	C9—C10—C5	122.4 (3)	121.7801
C8—N2—C12	120.4 (3)	120.2768	C3—C4—C5	131.2 (3)	132.5327
C11—N2—C12	118.1 (2)	119.3035	C2—C3—S1	109.1 (2)	109.5047

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O1—C2—N1	123.2 (3)	122.1158	C4—C3—S1	128.5 (2)	128.8195
O1—C2—C3	126.4 (3)	127.3373	C4—C3—C2	122.3 (3)	121.6757
N1—C2—C3	110.3 (3)	110.547	C6—C7—C8	121.0 (3)	120.7276
C10—C5—C4	124.9 (3)	125.2559	C7—C6—C5	122.7 (3)	122.3631
C6—C5—C10	115.9 (3)	116.5894	S2—C1—S1	122.74 (18)	124.5953
C6—C5—C4	119.2 (3)	118.1547	N1—C1—S1	109.1 (2)	108.1872
N2—C8—C9	120.9 (3)	121.3228	N1—C1—S2	128.2 (2)	127.2176
N2—C8—C7	122.2 (3)	121.4084			

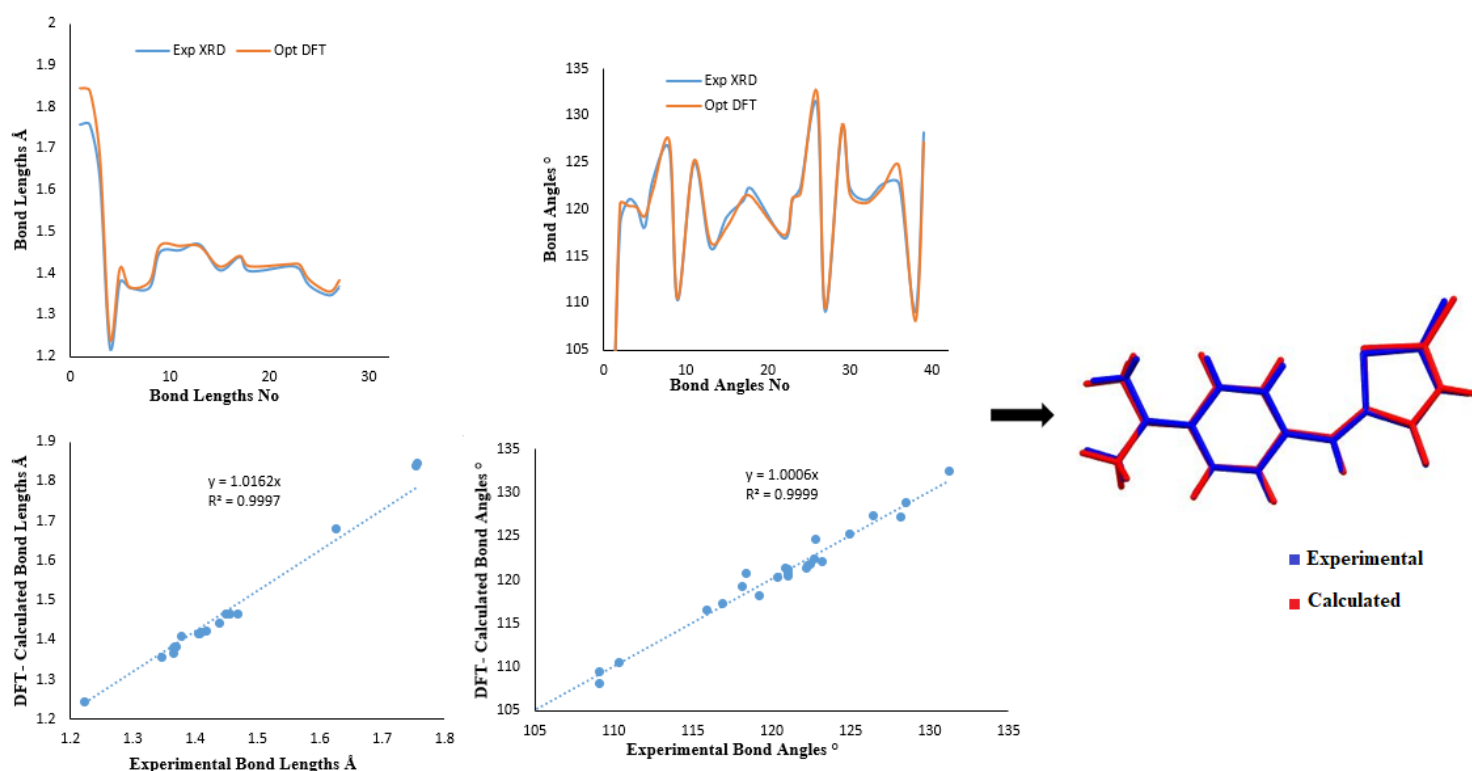


Figure 55. Comparison between experimental (SC-XRD) and DFT-optimized geometrical parameters for [(Z)-DMAP-RDN] (a) bond lengths, (b) bond angles, (c–d) regression plots showing near-unity correlation), and (e) superposition of experimental (blue) and calculated (red) molecular structures.

VI. 2. Frontier molecular orbitals (FMOs) and energy gap.

The frontier molecular orbital (FMO) analysis (Figure 56) reveals that while all three polymorphs of [(Z)-DMAP-RDN] share similar qualitative electronic characteristics, **P1** and **P2** are electronically identical with a HOMO–LUMO energy gap of 3.076 eV. In contrast, **P3** exhibits distinct energetic behavior characterized by a slight destabilization of both frontier orbitals and a wider energy gap of 3.138 eV. This larger gap in **P3** suggests a reduction in intramolecular charge-transfer efficiency

and slightly higher electronic stability compared to the more conjugated and energetically aligned frameworks of **P1** and **P2**.

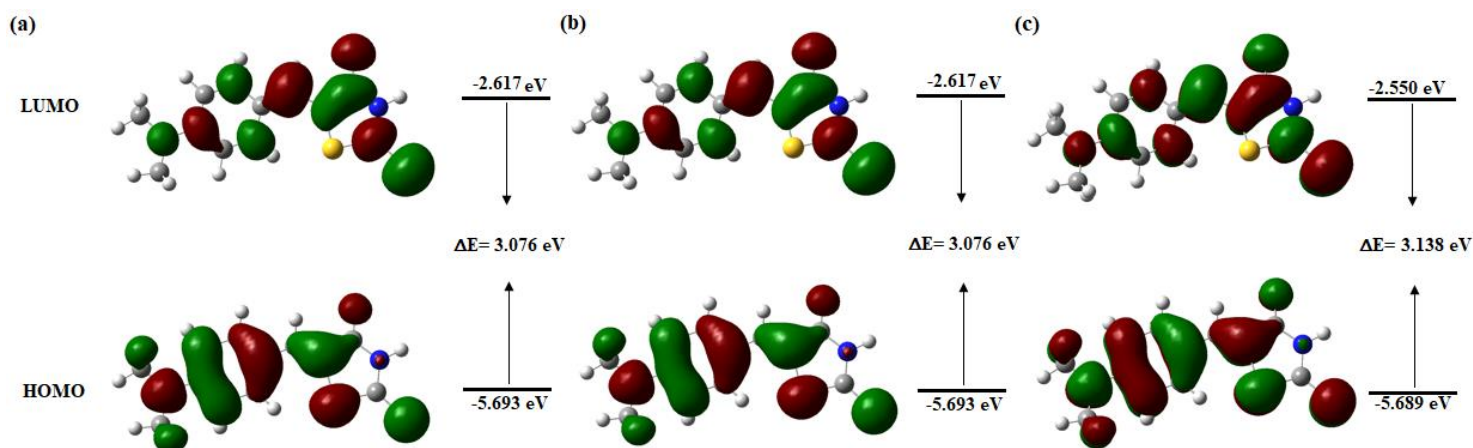


Figure 56. Comparative visualization of the HOMO and LUMO energy levels and orbital distributions for the three polymorphs of [(Z)-DMAP-RDN]: (a) **(P1)**, (b) **(P2)** and (c) **(P3)**.

VI. 3. Analysis of molecular electrostatic potential (MEP).

The three polymorphs of [(Z)-DMAP-RDN] display remarkably consistent molecular electrostatic potential (MEP) surfaces (Figure 57), reflecting nearly identical electronic environments across all forms. Negative potential regions are uniformly localized on the DMAP nitrogen and nitro-group oxygen atoms, while positive potential is concentrated on hydrogen atoms and the sulfur-containing moiety. Although minor fluctuations in intensity and spatial distribution occur due to subtle conformational and packing variations, the electrostatic ranges remain virtually identical, indicating that the polymorphic transitions do not significantly alter the molecule's intrinsic electronic characteristics or hydrogen-bond accepting capabilities.

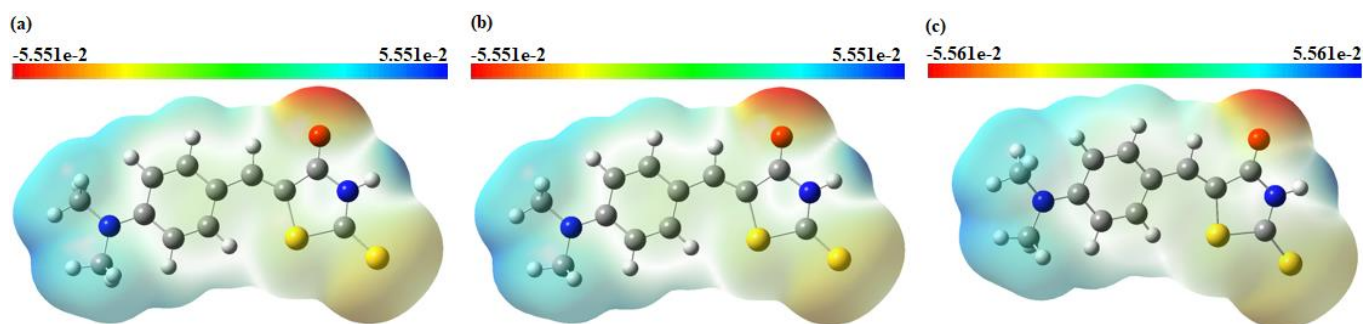


Figure 57. Molecular electrostatic potential (MEP) surfaces for the three polymorphs of [(Z)-DMAP-RDN]: (a) **(P1)**, (b) **(P2)** and (c) **(P3)**.

IV. 4. Analysis of Mulliken atomic charges.

The atomic charge distributions of the three [(Z)-DMAP-RDN] polymorphs (P1, P2, and P3) (Figure 58) are remarkably consistent, maintaining nearly identical charge ranges from approximately -0.66 to $+0.66$ e. All three forms exhibit well-preserved polarization patterns, where electronegative oxygen and nitrogen atoms carry negative partial charges while hydrogen and specific carbon atoms remain positive. This high degree of similarity across all magnitude and spatial arrangements suggests that the intramolecular electronic characteristics remain essentially unchanged by polymorphism, consequently, any variations in their macroscopic solid-state properties are likely driven by intermolecular packing effects rather than fundamental electronic redistribution.

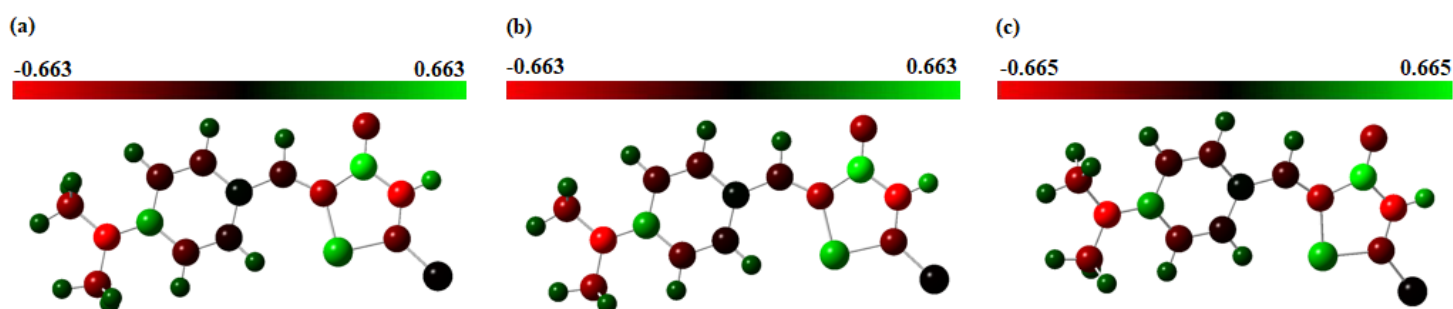


Figure 58. Mulliken charge distribution across polymorphic forms of [(Z)-DMAP-RDN]: (a) (P1), (b) (P2) and (c) (P3).

IV. 5. Reduced density gradient (RDG) analysis of noncovalent interactions (NCI).

The Reduced Density Gradient (RDG) analysis (Figure 59) reveals that the three polymorphs of [(Z)-DMAP-RDN] possess remarkably similar noncovalent interaction profiles, with nearly identical scatter plot distributions and isosurface spatial arrangements. Across all forms, attractive hydrogen bonding, van der Waals interactions, and steric repulsion regions are preserved in both location and magnitude around the molecular framework. This consistency indicates that while subtle packing differences exist, the fundamental nature and characteristics of the intermolecular

interactions remain essentially unchanged by polymorphism.

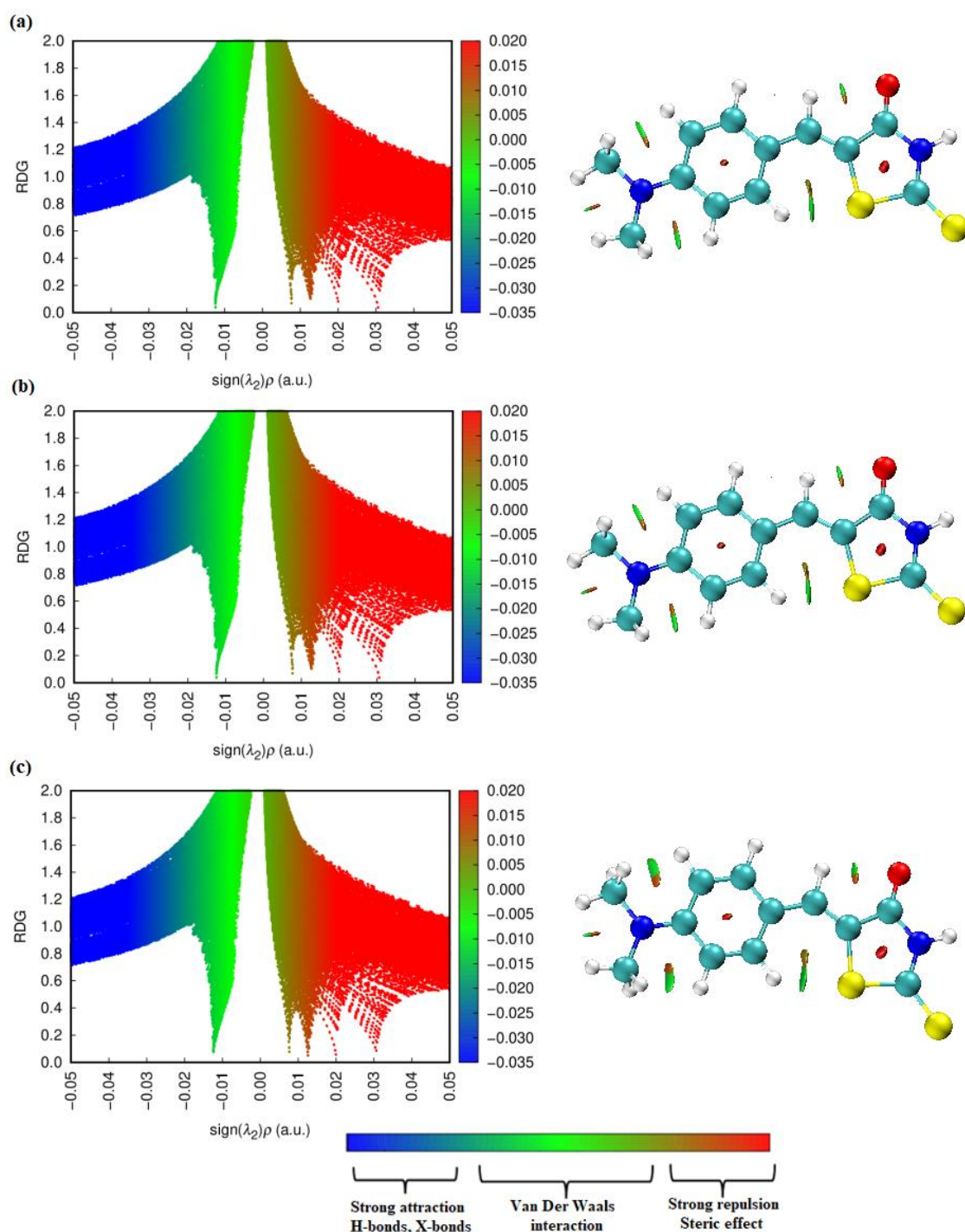


Figure 59. Reduced density gradient (RDG) and noncovalent interaction (NCI) analysis of [(Z)-DMAP-RDN] polymorphs: (a) (P1), (b) (P2) and (c) (P3).

VII. Conclusion.

In this chapter, a new polymorphic form of the rhodanine derivative (Z)-DMAP-RDN was isolated and characterized. Single-crystal X-ray diffraction indicated that the three polymorphs crystallize in the monoclinic $P2_1/c$ space group,

Chapter IV. Structural, Spectroscopic, and Electronic Investigation of a New Polymorph of (Z)-5-{[4-(dimethylamino) phenyl] methylidene}-2-sulfanylidene-1,3-thiazolidin-4-one

with differences primarily in crystal packing rather than molecular geometry. Structural analysis revealed similar hydrogen-bonding networks, with variations attributed to $\pi\cdots\pi$ stacking strength and packing efficiency. Density functional theory calculations validated experimental data, highlighting that polymorphism minimally affects the electronic structure and noncovalent interactions. This study underscores that polymorphism in [(Z)-DMAP-RDN] is primarily driven by packing effects, enhancing understanding of polymorphism in biologically relevant heterocyclic compounds.

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PART TWO: HYBRID
ORGANIC-INORGANIC
COMPOUND

*“A PhD in chemistry is the art
of turning curiosity into
compounds and caffeine into
conclusions”*



Chapter I.

Hybrid Organic- Inorganic Compound: a Bibliographic Overview

I. Introduction.

Hybrid organic–inorganic compounds represent a rapidly evolving class of materials that merge the advantageous properties of organic and inorganic components within a unified structure^{1,2}. By combining the flexibility and tunability of organic moieties with the stability and strength of inorganic units, these hybrids exhibit unique properties unattainable in solely organic or inorganic materials. They can be categorized by the nature of interactions between their components, from weakly bound systems (class I hybrids) to strongly coupled materials (class II hybrids)^{2,3}, allowing control over dimensions and functional behaviors. Their diverse physicochemical properties, including conductivity, luminescence, and catalytic activity, enhance their potential in fields such as energy storage, sensing, and biomedicine, making them key targets for advanced material design^{4,5}.

II. Classification of hybrid organic–inorganic compounds.

II.1. Class I hybrids: weak interactions

Class I hybrid organic–inorganic compounds are characterized by the association of organic and inorganic components through weak, noncovalent interactions, without the formation of direct covalent or coordination bonds between the two subunits. In these materials, each component largely preserves its intrinsic structural and electronic identity, while the cohesion and stability of the hybrid system arise from intermolecular forces. Due to the reversible and flexible nature of these interactions, Class I hybrids often exhibit rich supramolecular architectures and dynamic physicochemical behavior, making them particularly attractive for crystal engineering and functional material design^{1, 6, 7}.

Hydrogen bonding plays a central role in the formation and stabilization of Class I hybrids. It typically occurs between proton donors such as –NH or –OH groups in the organic moiety and electronegative atoms (O, N, halides) associated with the inorganic component. These hydrogen-bonding interactions can generate extended one-, two-, or three-dimensional networks that strongly influence crystal packing, structural flexibility, and properties such as proton mobility, phase transitions, and thermal behavior^{4, 7, 8}.

Electrostatic (ionic) interactions arise when organic cations and inorganic anions associate through Coulombic attraction. Such interactions are fundamental in organic–inorganic salts, where charge balance governs the assembly and overall topology of the hybrid structure. Although ionic interactions are generally stronger

than hydrogen bonds, they remain weaker than covalent bonds, thereby allowing significant structural diversity and tunable packing arrangements within the solid state^{1, 5}.

Van der Waals forces also contribute to the stabilization of Class **I** hybrids through weak dispersion interactions between closely packed molecular fragments. While individually weak, the cumulative effect of van der Waals interactions can be substantial, particularly in densely packed structures, influencing packing efficiency, polymorphism, and lattice stability^{6, 9}.

Proton-transfer salts represent a distinctive and widely investigated subclass of Class **I** hybrid compounds. These materials result from the transfer of a proton from an inorganic or organic acid to an organic base, frequently a nitrogen-containing heterocycle. The resulting organic cations and inorganic anions are held together by a combination of electrostatic interactions and hydrogen bonding, often forming extended supramolecular networks. Proton-transfer hybrids are of particular interest due to their potential proton conductivity, flexible hydrogen-bonding frameworks, and relevance to functional materials such as solid electrolytes, sensors, and supramolecular assemblies⁴.

Overall, Class **I** hybrid compounds clearly demonstrate how weak intermolecular interactions can effectively direct the organization of organic and inorganic components into stable and functional solid-state materials with tunable structural and physicochemical properties.

II.2. Class II hybrids: strong interactions

Class **II** hybrid organic–inorganic compounds are defined by the presence of strong chemical bonds linking the organic and inorganic components, most commonly covalent or coordination bonds. In contrast to Class **I** hybrids, where the two subunits largely retain their individual identities, Class **II** hybrids exhibit a high degree of electronic and structural coupling between the organic and inorganic moieties. This strong interaction results in materials with enhanced mechanical strength, thermal stability, and well-defined architectures, often accompanied by emergent physicochemical properties arising from the intimate integration of both components^{1, 7}.

Covalent bonding in Class **II** hybrids involves the formation of direct chemical bonds between organic groups and inorganic entities, such as metal oxides or metal centers. Typical examples include organically functionalized silicates, phosphonates,

and metal oxides, where organic ligands are covalently grafted onto inorganic backbones. These covalent linkages provide robust structural integrity and allow precise control over composition, functionality, and dimensionality, making such materials attractive for applications requiring long-term stability and resistance to harsh conditions^{1, 3}.

Coordination bonding represents another key interaction in Class **II** hybrid systems and arises from the coordination of organic ligands to metal ions through donor atoms such as nitrogen, oxygen, or sulfur. Nitrogen-containing bases, including pyridines, imidazoles, and amines, are particularly effective ligands due to their strong metal-binding ability. Coordination bonds enable the formation of extended architectures with tunable geometries and properties, while maintaining a balance between rigidity and flexibility in the resulting structures^{7, 10}.

Metal–ligand frameworks, including metal organic frameworks (MOFs) and coordination polymers, are among the most prominent representatives of Class **II** hybrids. These materials consist of metal ions or metal clusters interconnected by multitopic organic ligands to form one-, two-, or three-dimensional networks. The strong coordination bonds confer high structural stability, while the modular combination of metal nodes and organic linkers allows fine tuning of porosity, surface area, electronic structure, and chemical functionality. As a result, metal–ligand frameworks have attracted considerable attention for applications in gas storage and separation, catalysis, sensing, and energy-related technologies¹¹⁻¹³. Overall, Class **II** hybrid organic–inorganic compounds exemplify how strong covalent and coordination interactions can be exploited to engineer robust, multifunctional materials with precisely controlled structures and advanced physicochemical properties.

III. Structural features and design principles.

The structural diversity and functional performance of hybrid organic–inorganic compounds are governed by the deliberate selection of both organic and inorganic components, as well as by the way these building units assemble into extended architectures. Understanding the nature of each component and the principles that control their organization is essential for rational material design and for tailoring physicochemical properties^{7, 1}.

III.1. Nature of organic components.

The organic component plays a crucial role in determining flexibility, functionality, and intermolecular interactions within hybrid materials. Through appropriate molecular design, organic units can modulate structural topology, electronic distribution, and supramolecular assembly.

III.1. 1. Role of nitrogen-containing bases.

Nitrogen-containing organic bases such as pyridine, imidazole, triazole, amines, and their derivatives are among the most widely used organic building blocks in hybrid materials. Their ability to act as proton acceptors, hydrogen-bond donors (upon protonation), or coordination ligands enables strong interactions with inorganic species. These bases facilitate proton transfer, coordination bonding, and the formation of extended hydrogen-bond networks, making them particularly valuable in the construction of proton-transfer salts, coordination polymers, and metal–organic frameworks with tunable electronic and transport properties^{4, 8, 10}.

III.1. 2. Functional groups and molecular flexibility.

The presence of functional groups such as -NH_2 , -OH , -COOH , $\text{-SO}_3\text{H}$, and -SH introduces additional interaction sites that enhance hydrogen bonding, electrostatic interactions, or coordination with metal centers. Molecular flexibility, dictated by rotatable bonds and linker length, further influences framework adaptability, packing modes, and dynamic behavior such as framework breathing or phase transitions. Consequently, functionalization of organic components provides an effective strategy for fine-tuning structure property relationships in hybrid systems¹⁰.

III.2. Nature of inorganic components

The inorganic component provides structural rigidity, connectivity, and often imparts specific electronic, magnetic, or catalytic properties to hybrid materials.

III.2. 1. Metal ions and metal clusters

Metal ions serve as coordination centers that define geometry, connectivity, and dimensionality within hybrid architectures. The coordination number, oxidation state, and electronic configuration of metal ions strongly influence framework topology and stability. Metal clusters, such as secondary building units (SBUs) in MOFs, offer higher connectivity and structural robustness, enabling the construction of highly porous and stable networks with well-defined cavities and channels^{10, 11}.

III. 2. 2. Inorganic anions and frameworks

Inorganic anions, including halides, sulfates, phosphates, nitrates, and polyoxometalates, can act as counterions, hydrogen-bond acceptors, or structural linkers. These species often participate in electrostatic interactions and hydrogen bonding, contributing to the stabilization and organization of hybrid structures. Extended inorganic frameworks, when combined with organic components, further expand structural diversity and enable multifunctional behavior^{7, 14}.

III. 3. Dimensionality and architecture

The interplay between organic and inorganic building units determines the dimensionality and overall architecture of hybrid materials, which in turn governs their physicochemical properties.

III. 3. 1. Zero-dimensional (0D) hybrids

0D hybrids consist of discrete molecular or ionic units held together by weak interactions. These systems often exhibit molecular-like behavior and are useful models for studying host–guest interactions and localized properties¹.

III. 3. 2. One-dimensional (1D) chains

In 1D hybrids, organic and inorganic components assemble into chain-like structures through coordination or hydrogen bonding. Such materials may display anisotropic properties, including directional conductivity or mechanical behavior⁸.

III. 3. 3. Two-dimensional (2D) layers

2D hybrid materials are composed of layered structures stabilized by strong in-plane interactions and weaker interlayer forces. These materials often exhibit high structural anisotropy and are of interest for applications in ion exchange, catalysis, and layered electronics⁴.

III. 3. 4. Three-dimensional (3D) networks

3D hybrids, including MOFs and coordination frameworks, form fully interconnected networks with extended porosity and high structural stability. Their tunable pore sizes and chemical functionality make them particularly attractive for gas storage, separation, catalysis, and sensing applications^{10, 11}.

IV. Intermolecular interactions in hybrid compounds.

Intermolecular interactions play a fundamental role in governing the formation, stability, and functional properties of hybrid organic–inorganic compounds. Beyond the primary covalent or coordination bonds, these secondary interactions dictate supramolecular organization, crystal packing, and dynamic

behavior, thereby strongly influencing the resulting physicochemical properties and applications of hybrid materials^{1, 6, 7}.

IV. 1. Hydrogen bonding networks.

Hydrogen bonding networks are among the most important interactions in hybrid systems, particularly in materials containing heteroatoms such as nitrogen, oxygen, or sulfur. Hydrogen bonds can link organic and inorganic components into extended one-, two-, or three-dimensional networks, stabilizing the structure and enabling cooperative phenomena such as structural flexibility, phase transitions, and proton mobility. In many hybrid compounds, hydrogen bonding acts as a key structure-directing force in crystal engineering^{8, 15}.

IV. 2. Proton transfer mechanisms.

Proton transfer mechanisms are especially relevant in hybrid systems incorporating acidic inorganic species and basic organic components, such as nitrogen-containing heterocycles. Proton transfer leads to the formation of organic cations and inorganic anions that interact through a combination of electrostatic forces and hydrogen bonding. These interactions often generate continuous hydrogen-bond pathways that facilitate proton transport, making such materials attractive for applications in proton-conducting electrolytes and fuel cells^{4, 16, 17}.

IV. 3. $\pi\cdots\pi$ stacking and other noncovalent interactions.

$\pi\cdots\pi$ stacking and other noncovalent interactions including C–H $\cdots\pi$, halogen bonding, and van der Waals forces, further contribute to the stabilization and organization of hybrid structures. $\pi\cdots\pi$ interactions between aromatic organic moieties can significantly affect packing density, electronic coupling, and optical properties, while weaker dispersion forces collectively influence polymorphism and lattice stability^{7, 9}.

IV. 4. Role of supramolecular organization.

The role of supramolecular organization is central to hybrid materials, as the spatial arrangement of molecules and ions determines how local interactions propagate into long-range order. Supramolecular assembly allows the emergence of collective properties that are not predictable from individual components alone, underscoring the importance of intermolecular interactions in structure–property relationships^{8, 18}.

V. Applications of hybrid organic–inorganic compounds

Owing to their structural versatility and tunable properties, hybrid organic–inorganic compounds have found widespread applications across diverse scientific and technological fields.

V. 1. Energy-related applications.

Energy-related applications, including fuel cells and batteries, represent a major area of interest. Hybrid materials exhibiting proton or ionic conductivity are promising candidates for solid electrolytes, where hydrogen-bond networks and proton-transfer pathways enable efficient charge transport. In addition, hybrid frameworks are being explored as electrode materials and separators in energy storage devices^{5, 16}.

V. 2. Chemical sensing and detection.

Chemical sensing and detection benefit from the responsiveness of hybrid materials to external stimuli such as guest molecules, pH changes, or metal ions. Variations in luminescence, conductivity, or color upon analyte binding make hybrid compounds effective sensors with high selectivity and sensitivity^{10, 19}.

V. 3. Catalysis.

Catalysis is another important application domain, where hybrid materials combine the active sites of inorganic components with the tunability and selectivity of organic ligands. Such systems are widely used in heterogeneous catalysis, photocatalysis, and acid–base catalysis, offering improved efficiency and recyclability^{20, 21}.

V. 4. Optoelectronic devices

Optoelectronic devices exploit the electronic and photophysical properties of hybrid compounds, including tunable band gaps, charge-transfer behavior, and luminescence. These materials have been investigated for applications in light-emitting diodes, photovoltaic devices, and photodetectors^{22, 23}.

V. 5. Environmental and biomedical applications

Environmental and biomedical applications include pollutant adsorption, water purification, drug delivery, and bioimaging. The high surface area, functional diversity, and biocompatibility of certain hybrid materials make them suitable for removing contaminants, hosting therapeutic agents, or interacting selectively with biological systems^{24, 25}.

Overall, the wide range of applications of hybrid organic–inorganic compounds stems directly from their supramolecular organization and the cooperative

effects of intermolecular interactions, which enable fine control over material properties and performance.

VI. Conclusion.

This chapter provides an overview of hybrid organic-inorganic compounds, detailing their concepts, classifications, and applications. It distinguishes between Class I hybrids, characterized by weak intermolecular interactions, and Class II hybrids, which are based on strong covalent or coordination bonding. The roles of nitrogen-containing organic bases, inorganic ions or metal centers, and supramolecular interactions in determining the structure and properties of these materials are emphasized. The chapter also highlights the significance of design in tuning properties like proton conductivity and optical response, along with a wide range of applications in energy, sensing, and biomedical fields. These insights lay the groundwork for future exploration of hybrid systems with customized properties in subsequent chapters.

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Chapter II.

*Structural, Spectroscopic,
and Electronic Investigation
of a New Hybrid: N,N-
dimethyl-4-[(Z)-(4-oxo-2-
sulfanylidene-1,3-
thiazolidin-5-ylidene)
methyl]aniliniumbromide*

**Chapter II. Structural, spectroscopic, and electronic investigation of a new hybrid:
N,N-dimethyl-4-[(*Z*)-(4-oxo-2-sulfanylidene-1,3-thiazolidin-5-ylidene)methyl]
anilinium bromide**

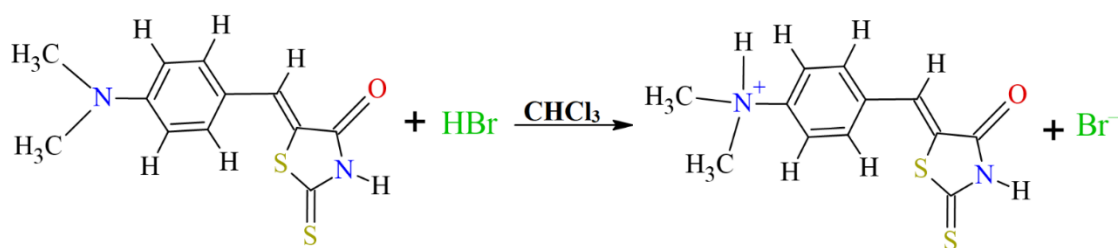
I. Introduction.

Hybrid organic–inorganic compounds based on proton transfer have gained significant interest due to their diverse structures and physicochemical properties¹⁻³. These materials form from the combination of organic molecules and inorganic species, resulting in stable crystalline architectures that exhibit tunable functionalities. Nitrogen-containing organic bases serve as ideal building blocks for these hybrids, readily accepting protons and forming strong interactions with counter anions^{4,5}. An example is the hybrid compound 5-{[4-(dimethylamino)phenyl]methylidene}-2-sulfanylidene-1,3-thiazolidin-4-one, which features a crystal structure stabilized by hydrogen bonds and other noncovalent interactions^{2,6}. These proton-transfer hybrids are promising for applications in proton conduction, molecular electronics, nonlinear optics, and chemical sensing, with properties adjustable through molecular design and interaction control^{3,7,8}.

II. Experimental methods.

II. 1. Experimental procedure.

A weighed amount of (*Z*)-DMAP-RDN was dissolved in chloroform (CHCl₃). Hydrobromic acid (HBr/33%) was then progressively added while being continuously agitated at room temperature to produce a homogenous orange solution. The solvent gradually evaporated under ambient conditions to produce well-formed yellow block-shaped crystals. The resulting crystals were filtered and then washed with cold CHCl₃.



Scheme 4. Synthetic route to the new hybrid compound organic-inorganic [(H⁺DMAP-RDN). Br⁻].

II. 2. Single-crystal X-ray diffraction analysis.

A detailed description of the apparatus specifications and computational techniques for [(H⁺DMAP-RDN). Br⁻] single-crystal X-ray diffraction data collection and structural refinement processes was provided in the third chapter of part one. A summary of the key parameters for gathering and enhancing crystallographic data can be found in Table 16.

**Chapter II. Structural, spectroscopic, and electronic investigation of a new hybrid:
N,N-dimethyl-4-[(Z)-(4-oxo-2-sulfanylidene-1,3-thiazolidin-5-ylidene)methyl]
anilinium bromide**

Table 16. Structural data and recording conditions for [(H⁺DMAP-RDN) . Br⁻]

Crystal data	
Chemical formula	Br ⁻ ·C ₁₂ H ₁₃ N ₂ OS ₂ ⁺
<i>M_r</i>	345.27
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	200
<i>a</i> (Å), <i>b</i> (Å), <i>c</i> (Å)	9.8882 (3), 13.5763 (4), 10.3662 (3)
β (°)	94.114 (1)
<i>V</i> (Å ³)	1388.03 (7)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.25
Crystal size (mm)	0.4 × 0.3 × 0.2
<i>T_{min}</i> , <i>T_{max}</i>	0.651, 0.745
Reflections collected, Independent reflections, Observed reflections with [<i>I</i> > 2σ(<i>I</i>)]	21987, 2833, 2466
<i>R_{int}</i> , (sin θ/λ) _{max} (Å ⁻¹)	0.053, 0.625
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), Goodness-of-fit on <i>F</i> ²	0.027, 0.065, 1.04
No. of reflections, No. of parameters	2833, 169
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.33, -0.38

II. 3. FTIR Spectroscopic Characterization of [(H⁺DMAP-RDN) . Br⁻].

The FTIR spectrum (Figure 60) exhibits several characteristic absorption bands that confirm the presence of multiple functional groups and their interactions within the molecular framework. A broad and intense band observed in the high-wavenumber region around 3400–3200 cm⁻¹ is attributed to overlapping N–H stretching vibrations, indicating the presence of hydrogen-bonded donor groups. The bands appearing in the 3000–2850 cm⁻¹ region correspond to aliphatic C–H stretching vibrations of methyl and methylene groups. A strong absorption in the region 1700–1600 cm⁻¹ is assigned to C=O stretching vibrations, reflecting the presence of conjugated carbonyl or imine functionalities. Additional bands between 1550 and 1400 cm⁻¹ are associated with aromatic C=C stretching and N–H bending modes, while absorptions in the 1300–1000 cm⁻¹ region arise from C–N and C–S stretching

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anilinium bromide**

vibrations, characteristic of heterocyclic moieties. The fingerprint region below 1000 cm^{-1} displays multiple sharp bands attributed to out-of-plane bending vibrations and skeletal modes of the molecular backbone. Overall, the FTIR spectrum confirms the structural integrity of the compound and highlights the role of hydrogen bonding and heteroatom-containing functional groups in stabilizing the molecular structure.

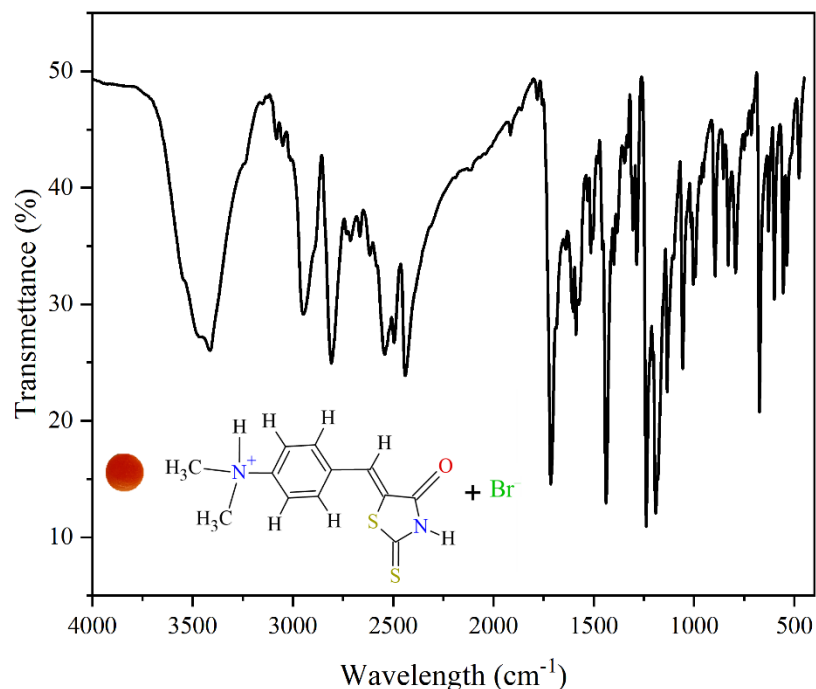


Figure 60. FTIR spectrum of $[(\text{H}^+\text{DMAP-RDN}) \cdot \text{Br}^-]$.

Table 17. FTIR wavenumber assignments of $[(\text{H}^+\text{DMAP-RDN}) \cdot \text{Br}^-]$.and corresponding vibrational modes.

Wavenumber (cm^{-1})	Assignment	Origin
3600–3200	Broad N–H stretching vibrations	Protonated amino groups; strong intermolecular hydrogen bonding
~3350–3200	N–H stretching	Protonated nitrogen atoms in the heterocyclic moiety
~3050–3000	Aromatic C–H stretching	Aromatic ring system
~2950–2850	Aliphatic C–H stretching	Methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2$) groups
~1710–1680	C=O stretching	Carbonyl group (conjugated system)
~1660–1620	C=O / C=N stretching	Heterocyclic carbonyl and imine functionalities
~1600–1550	C=C and C=N stretching	Aromatic and heterocyclic ring vibrations
~1500–1450	N–H bending / C–N stretching	Protonated heterocyclic moiety
~1450–1380	C–H bending	Methyl group deformation modes

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N,N-dimethyl-4-[(Z)-(4-oxo-2-sulfanylidene-1,3-thiazolidin-5-ylidene)methyl]
anilinium bromide**

~1380–1320	C–N stretching	Heterocyclic nitrogen-containing groups
~1300–1200	C–S stretching	Sulfur-containing heterocyclic ring
~1250–1000	C–N and C–C stretching	Backbone vibrations of aromatic and heterocyclic rings
~900–700	Aromatic C–H out-of-plane bending	Substituted aromatic ring system
~700–500	Ring deformation vibrations	Aromatic and heterocyclic skeletal modes

III. Description of the structure.

The first hybrid N, N-dimethyl-4-[(Z)-(4-oxo-2-sulfanylidene-1,3-thiazolidin-5 ylidene) methyl] anilinium Bromide, [(H⁺DMAP-RDN). Br⁻] (Figure 61 a) crystallizes in the monoclinic with *P*2₁/*c* space group. Its asymmetric unit is composed of two molecules, the N, N-dimethyl-4-[(Z)-(4-oxo-2-sulfanylidene-1,3-thiazolidin-5 ylidene) methyl] anilinium cation (H⁺DMAP-RDN) and the bromide anion Br⁻. Within the cation, the angle between the plane of the rhodanine ring and the phenyl ring is 17.40° (Figure 61 b), indicating a slight twist in the molecular conformation.

The protonation occurs at the nitrogen atom (N2) of the dimethylamino group attached to the phenyl ring, converting the tertiary amine into a quaternary ammonium center.

Perspective view of [(H⁺DMAP-RDN). Br⁻] clearly shows the spatial arrangement of all atoms, with the bromide counterion positioned near the protonated nitrogen center, indicating electrostatic attraction between the cationic and anionic species, the ionic components are held together by a strong N–H···Br hydrogen bonding interaction, A comparison with structurally related compounds retrieved from the CSD shows that the N–H···Br hydrogen-bond distance in the present structure (3.208 Å) falls within the typical range, being close to previously reported values of 3.172 Å⁹ and 3.217 Å¹⁰.

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N,N-dimethyl-4-[(*Z*)-(4-oxo-2-sulfanylidene-1,3-thiazolidin-5-ylidene)methyl]
anilinium bromide**

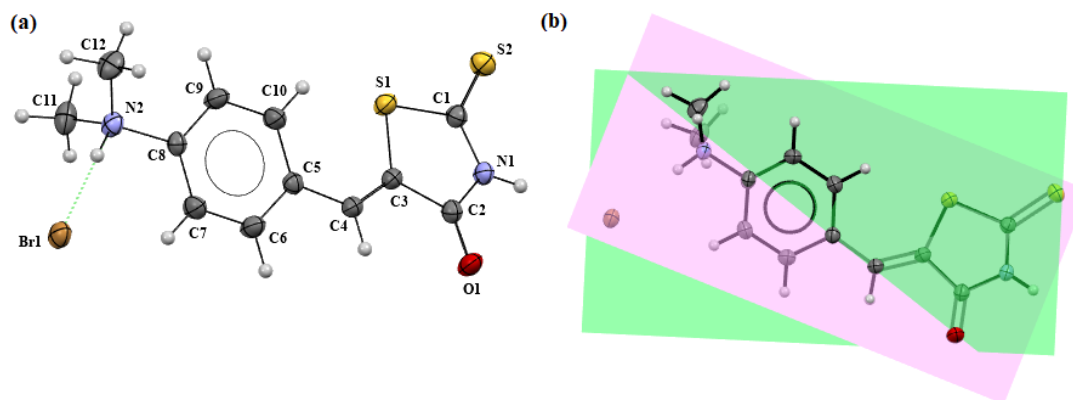


Figure 61. (a) Perspective view of $[(H^+DMAP-RDN) \cdot Br^-]$ with atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius, (b) angle between the plane of phenyl ring and rhodanine ring of asymmetric unit.

The supramolecular architecture of $[(H^+DMAP-RDN) \cdot Br^-]$ (Figure 62) exhibits highly ordered, anisotropic organization along the principal crystallographic axes.

Projections along *a* axis reveal the assembly of protonated ($H^+DMAP-RDN$) cations into columnar motifs, stabilized by extensive $\pi \cdots \pi$ stacking interactions between contiguous aromatic systems. The bromide counterions reside within interstitial voids, facilitating lattice stabilization through a network of electrostatic interactions and putative $N-H \cdots Br^-$ hydrogen bond.

When viewed along *b* axis, the molecular units adopt a slipped, quasi zig zag configuration, forming parallel arrays characterized by offset $\pi \cdots$ stacking rather than ideal face to face overlap. In this orientation, the bromide anions appear to function as bridging species, mediating interactions between adjacent cationic chains via ionic forces.

Furthermore, the structure manifests a layered packing motif along *c* axis, wherein discrete cationic sheets are intercalated by bromide counterions.

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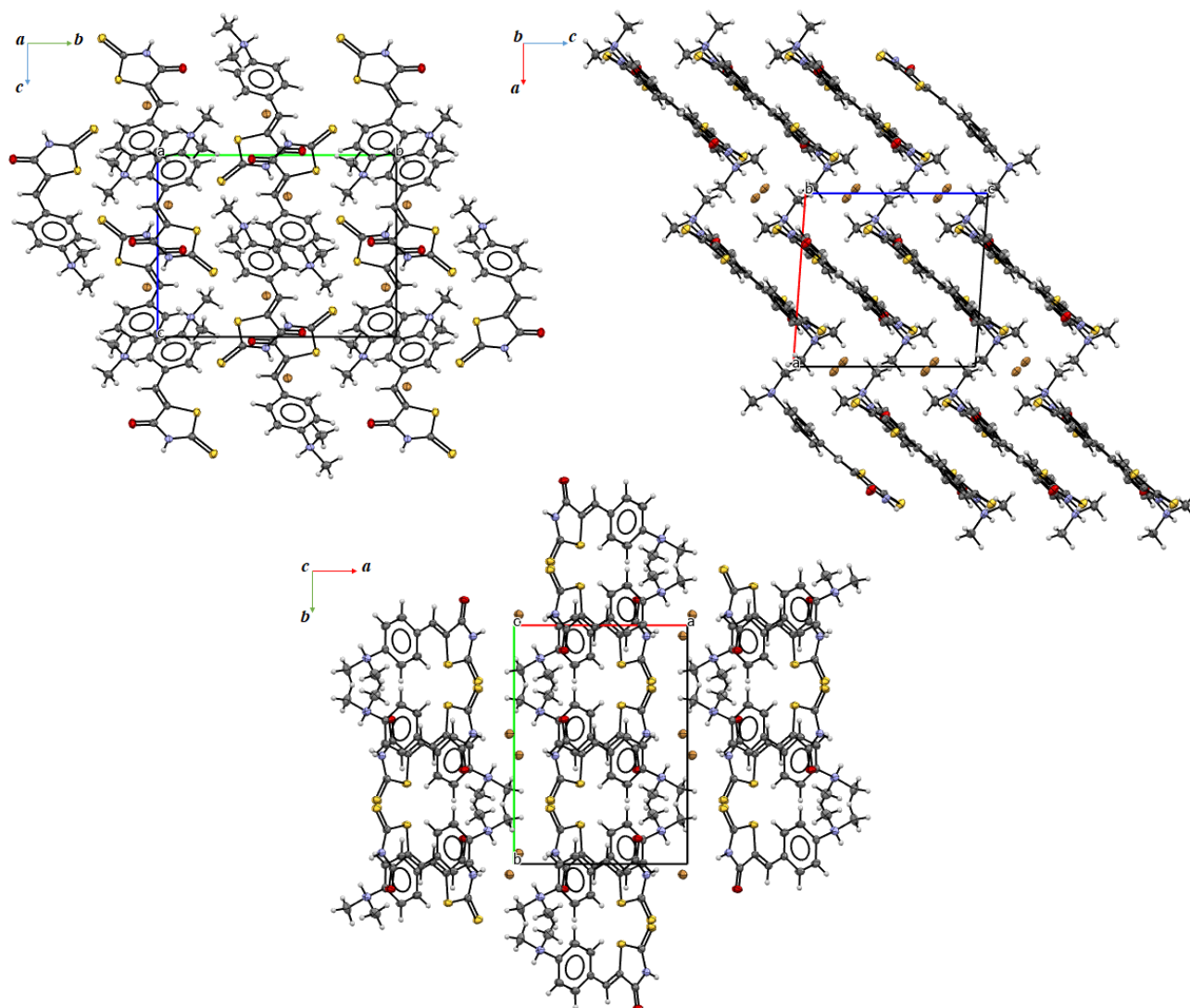


Figure 62. Crystal packing of $[(H^+DMAP-RDN) \cdot Br^-]$

The supramolecular architecture of the crystal is governed by a hierarchical network of classical and non-classical hydrogen-bonding interactions (Figure 63 a) that consolidate the three-dimensional framework. The structural assembly is primarily stabilized by a strong classical N2–H2···Br1 hydrogen bond ($D-A = 3.208 \text{ \AA}$) and a significant C9–H9···Br1 contact, which together form the core of the cooperative bonding network. The bromide counter-anion serves as a multi-coordinate acceptor, facilitating several auxiliary interactions including C7–H7···Br1 ($3.264 \text{ \AA}$) and N1–H1···Br1 ($3.703 \text{ \AA}$). These contacts, though weaker than the primary N2–H2···Br1 bond, are critical for connecting discrete molecular units into extended supramolecular motifs. Carbonyl oxygen O1 further contributes to the stabilization through C–H···O interactions, specifically C9–H9···O1 and C12–H12C···O1, with

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distances ranging between 3.164 and 3.556 Å. Additionally, the structure is refined by C—H···S interactions, including a localized intramolecular C10—H10···S1 contact (3.240 Å) and an intermolecular C11—H11B···S2 bond (3.983 Å) this hydrogen bonds leads to the establishment of well-defined graph-set patterns $R_7^5(28)$ (Figure 63 c)

The crystal packing shows $\pi\cdots\pi$ stacking interactions (Figure 63 b) between adjacent aromatic rings, with a centroid–centroid separation of about 3.957 Å, consistent with weak slipped stacking that contributes to lattice stabilization. In addition, the bromide anion exhibits an anion··· π interaction with the centroid of the rodanine ring (≈ 3.680 Å), providing further electrostatic stabilization to the supramolecular structure.

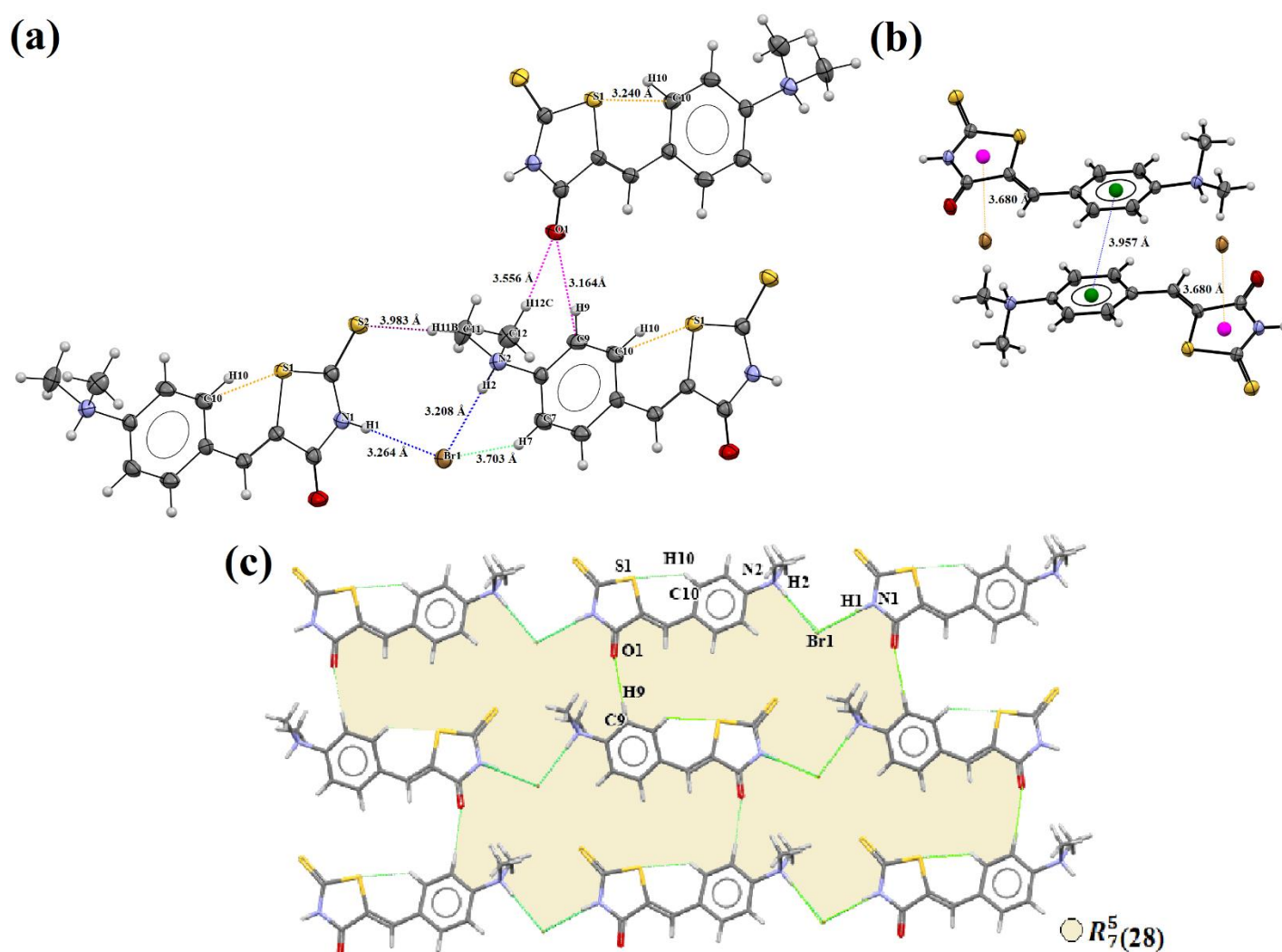


Figure 63. (a) Hydrogen-bonding interactions, (b) $\pi\cdots\pi$ stacking interactions and (c) supramolecular packing showing N—H···Br and C—H···O interactions forming ring motifs in $[(H^+DMAP-RDN) \cdot Br^-]$.

Table 18. Hydrogen-bond geometry (Å, °) of $[(H^+DMAP-RDN) \cdot Br^-]$.

$D-H\cdots A$	$D-H$ (Å)	$H\cdots A$ (Å)	$D\cdots A$ (Å)	$D-H\cdots A$ (°)
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N2—H2···Br1	0.89(3)	2.320	3.208	178.31
N1—H1···Br1	0.8800	2.426	3.264	159.32
C7—H7···Br1	0.9500	2.947	3.703	137.46
C10—H10···S1	0.9500	2.565	3.240	128.25
C11—H11B···S2	0.9800	3.044	3.983	160.95
C9—H9···O1	0.9500	2.258	3.164	159.11
C12—H12C···O1	0.9800	2.635	3.556	156.54

V. Hirshfeld surface analysis (HSA).

The Hirshfeld surface analysis of the hybrid organic–inorganic compound [(H⁺DMAP-RDN) Br[−]] provides detailed insight into the nature and spatial distribution of intermolecular interactions through the d_{norm} , d_e , and shape index mappings.

The Hirshfeld surface analysis of the [(H⁺DMAP-RDN) Br[−]] hybrid compound (Figure 64) reveals a crystal structure primarily stabilized by a complex network of supramolecular interactions. The d_{norm} surface highlights intense red spots corresponding to dominant N2–H2···Br1 and C9–H9···O1 hydrogen bonds, which play a crucial role in structural cohesion, supplemented by weaker N1–H1···Br1 and C–H···O/S contacts. Analysis of the d_e surface confirms the spatial accessibility of the bromide anion as a primary hydrogen-bond acceptor, consistent with the compound's ionic character. Furthermore, shape index mapping identifies characteristic red and blue triangular motifs on the aromatic and rhodamine rings, indicating significant $\pi \cdots \pi$ stacking interactions that contribute to the molecular packing efficiency. Collectively, these findings demonstrate that the interplay of strong hydrogen bonding, electrostatic forces, and aromatic stacking governs the supramolecular architecture, a behavior typical of Class I organic–inorganic hybrid materials.

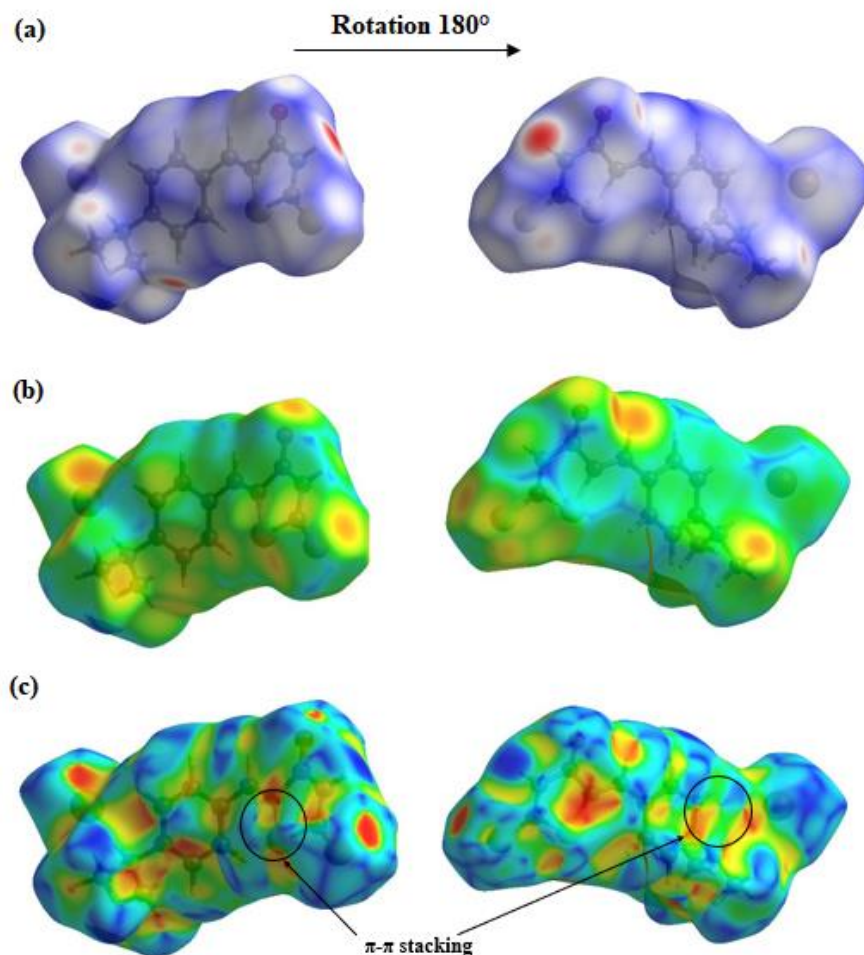


Figure 64. Hirshfeld surface analysis (a) d_{norm} , (b) d_e and (c) Shape Index of $[(H^+DMAP-RDN) Br^-]$

The fingerprint analysis of $[(H^+DMAP-RDN) Br^-]$ (Figure 65) reveals that the crystal packing is predominantly stabilized by hydrogen-mediated contacts, characteristic of Class I proton-transfer hybrid materials. Quantitative assessment indicates that $H\cdots H$ (25.6%) and $S\cdots H/H\cdots S$ (22.3%) interactions represent the largest contributions, reflecting dominant van der Waals forces and weak hydrogen bonding within the rhodanine moiety. The $Br\cdots H/H\cdots Br$ contacts (14.5%) underscore the central role of the bromide anion as a primary acceptor for directional $N-H\cdots Br^-$ and $C-H\cdots Br^-$ hydrogen bonds. Additionally, $H\cdots C/C\cdots H$ (12.2%) and $O\cdots H/H\cdots O$ (9.9%) contacts facilitate $C-H\cdots \pi$ interactions and supplementary carbonyl-mediated hydrogen bonding, while minor $C\cdots C$ contacts (4.7%) indicate secondary $\pi\cdots\pi$ stacking. Together, these multifaceted intermolecular interactions governed by $H\cdots H$, $S\cdots H$, and $Br\cdots H$ contacts collectively ensure the supramolecular organization and structural cohesion of the lattice.

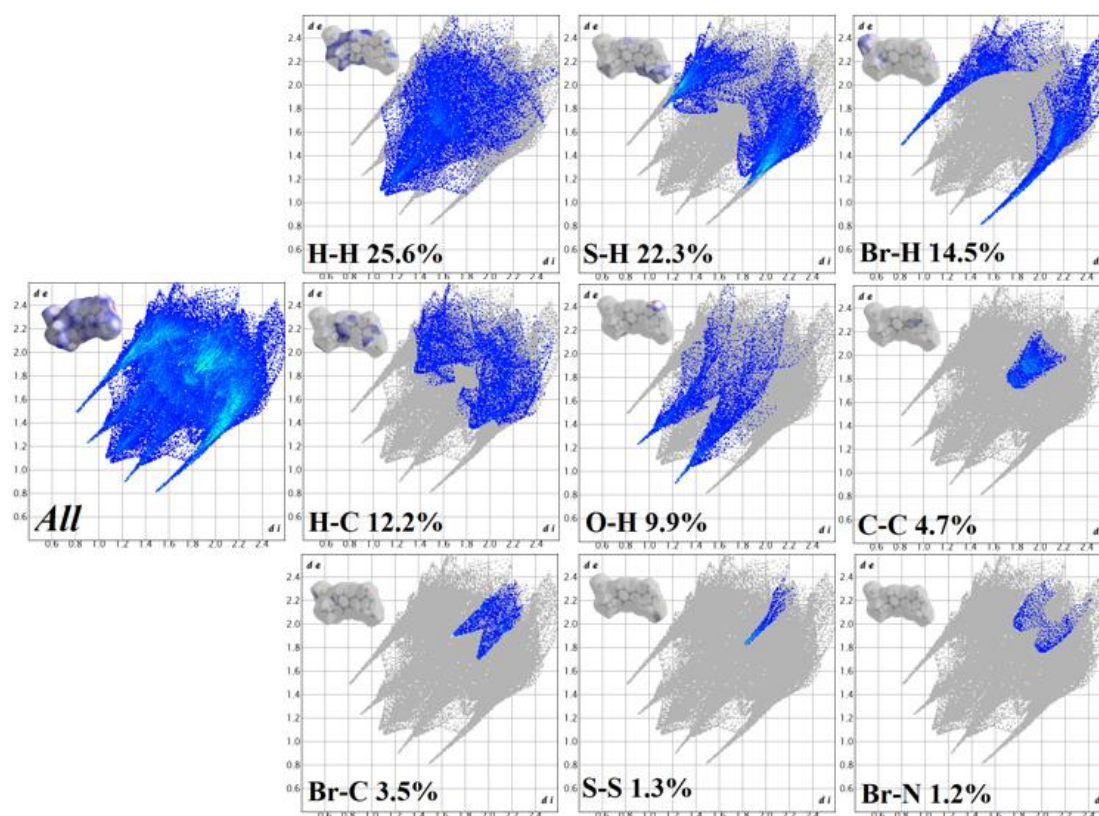


Figure 65. 2D Fingerprint plot illustrating contact contributions in [(H⁺DMAP-RDN) Br⁻].

VI. Density functional theory (DFT).

Density functional theory (DFT) calculations were carried out using the B3LYP functional in conjunction with the 6-311+G(d,p) basis set to optimize the molecular geometries in the gas phase.

VI. 1. Optimized geometric parameters.

Following the optimization of new hybrid compound molecular geometry [(H⁺DMAP-RDN) Br⁻] (Figure 66), We contrasted the experimental data with the different bond lengths and bond angles that were calculated theoretically. Table 19 contains a compilation of the results.

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anilinium bromide**

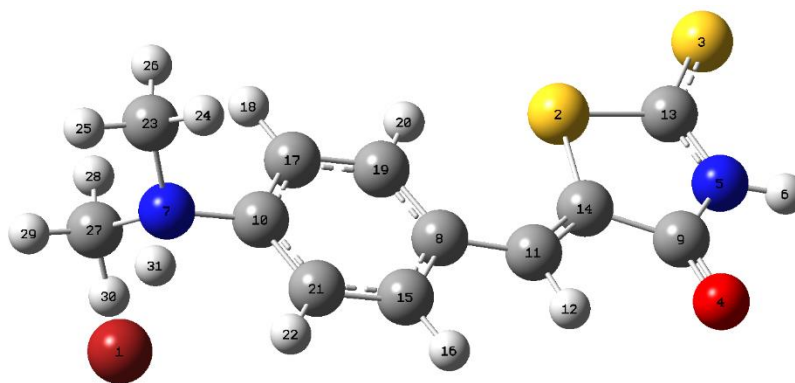


Figure 66. Optimized structure of the new hybrid organic inorganic compound of $[(H^+DMAP-RDN) Br^-]$ calculated using the B3LYP functional.

The experimental bond lengths range from 1.214 to 1.752 Å, with an average of 1.453 Å, while the optimized bond lengths range from 1.2069 to 1.7813 Å, with an average of 1.4605 Å. Experimental bond angles range from 92.83 ° to 130.01 °, with an average of 118.301 °, whereas theoretical bond angles range from 92.7295° to 131.591°, with an average of 119.61°. With correlation coefficients of $R^2 = 1$ and 0.9999 for bond lengths and angles, respectively, the distribution and correlation graphs in Figure 51 indicate good agreement between calculated and experimental values (Figure 67).

Table 19. Optimized bond lengths and bond angles for $[(H^+DMAP-RDN) Br^-]$ calculated by DFT in comparison with SC-XRD data.

Bond length	EXP (Å)	B3LYP (Å)	Bond length	EXP (Å)	B3LYP (Å)
S1—C1	1.752 (2)	1.7813	C5—C4	1.455 (3)	1.4542
S1—C3	1.748 (2)	1.7704	C5—C6	1.399 (3)	1.4072
S2—C1	1.636 (2)	1.6386	C5—C10	1.396 (3)	1.408
O1—C2	1.214 (3)	1.2069	C2—C3	1.491 (3)	1.4931
N1—C2	1.379 (3)	1.3987	C8—C9	1.384 (3)	1.3939
N1—C1	1.358 (3)	1.3661	C8—C7	1.377 (3)	1.3918
N2—C8	1.476 (3)	1.4697	C4—C3	1.339 (3)	1.3483
N2—C12	1.489 (3)	1.4925	C6—C7	1.381 (3)	1.3886
N2—C11	1.503 (3)	1.4925	C9—C10	1.382 (3)	1.3873
Bond angles	Exp (°)	B3LYP (°)	Bond angles	Exp (°)	B3LYP (°)
C3—S1—C1	92.83 (10)	92.7295	C7—C8—C9	121.12 (19)	120.7984
C1—N1—C2	117.81 (18)	119.7493	C3—C4—C5	130.01 (19)	131.591
C8—N2—C12	115.05 (17)	113.3183	S2—C1—S1	122.39 (12)	124.1466
C8—N2—C11	111.30 (16)	113.3184	N1—C1—S1	110.19 (15)	108.7736
C12—N2—C11	109.85 (17)	112.3669	N1—C1—S2	127.42 (17)	127.0799

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anilinium bromide**

C6—C5—C4	118.78 (18)	117.6778	C2—C3—S1	108.93 (15)	109.8347
C10—C5—C4	123.38 (19)	124.497	C4—C3—S1	129.84 (16)	130.5284
C10—C5—C6	117.8 (2)	117.8252	C4—C3—C2	121.21 (18)	119.6369
O1—C2—N1	123.99 (19)	123.9304	C7—C6—C5	121.28 (19)	121.742
O1—C2—C3	125.77 (19)	127.1566	C10—C9—C8	119.16 (19)	119.787
N1—C2—C3	110.22 (17)	108.913	C9—C10—C5	121.2 (2)	120.8952
C9—C8—N2	120.02 (18)	120.6094	C8—C7—C6	119.2 (2)	118.9521
C7—C8—N2	118.79 (18)	118.5922			

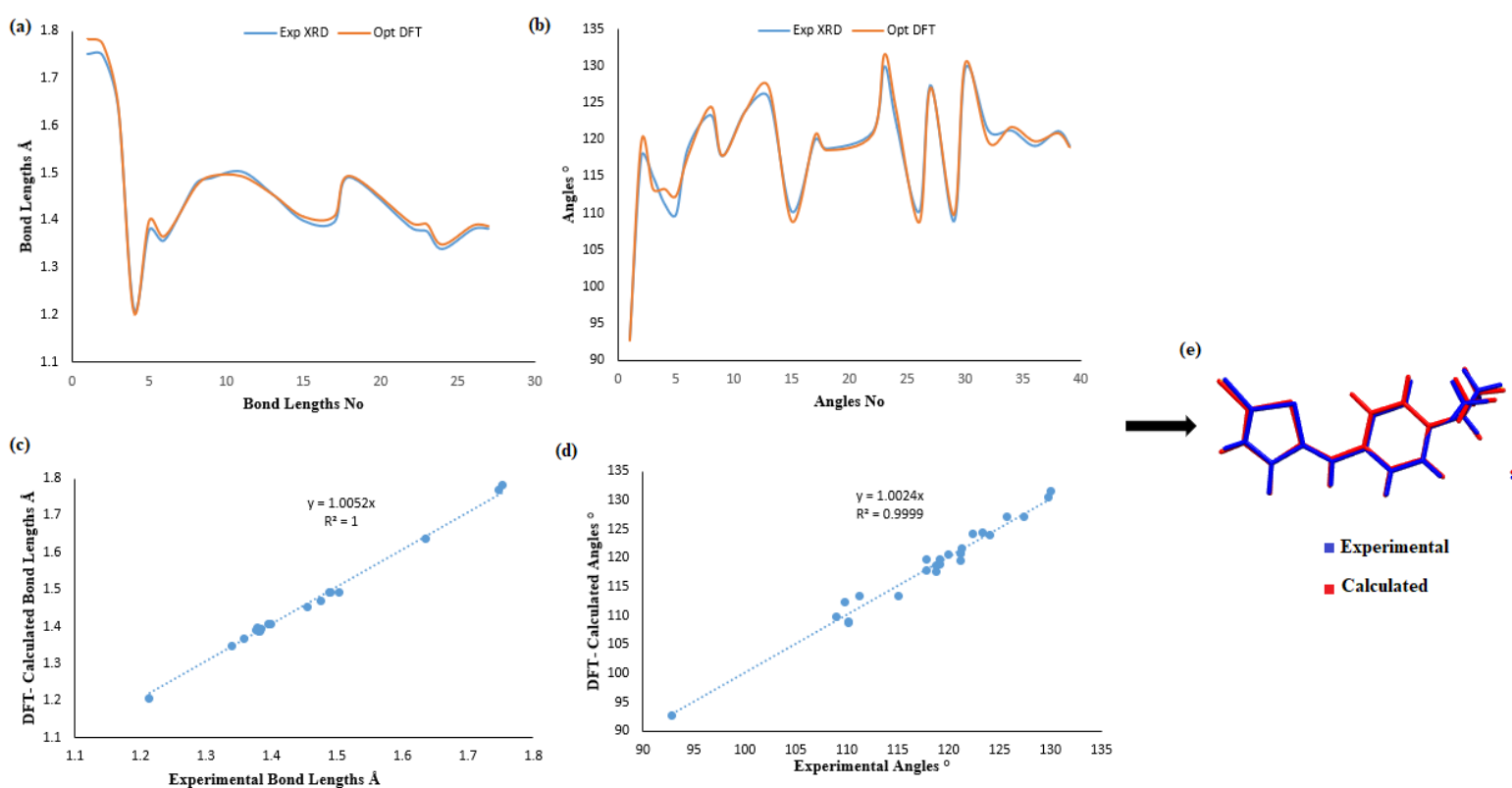


Figure 67. Comparison between experimental (SC-XRD) and DFT-optimized geometrical parameters for [(H⁺DMAP-RDN) Br⁻] (a) bond lengths, (b) bond angles, (c–d) regression plots showing near-unity correlation), and (e) superposition of experimental (blue) and calculated (red) molecular structures.

VI. 2. Frontier molecular orbitals (FMOs) and energy gap.

Frontier molecular orbital (FMO) analysis of [(H⁺DMAP-RDN) Br⁻] (Figure 68) reveals a distinct donor-acceptor electronic configuration characterized by a HOMO localized on the bromide anion (−5.855 eV) and a LUMO delocalized over the conjugated framework of the organic cation (−3.325 eV). This spatial separation between the electron-rich inorganic donor (Br⁻) and the heterocyclic organic acceptor

(H⁺DMAP-RDN) results in a moderate energy gap of 2.53 eV, signifying a pronounced charge-transfer character upon electronic excitation. These electronic features confirm that [(H⁺DMAP-RDN) Br⁻] behaves as an ionic hybrid system with significant potential for applications in optoelectronics and optical sensing, driven by efficient anion-to-cation charge-transfer processes.

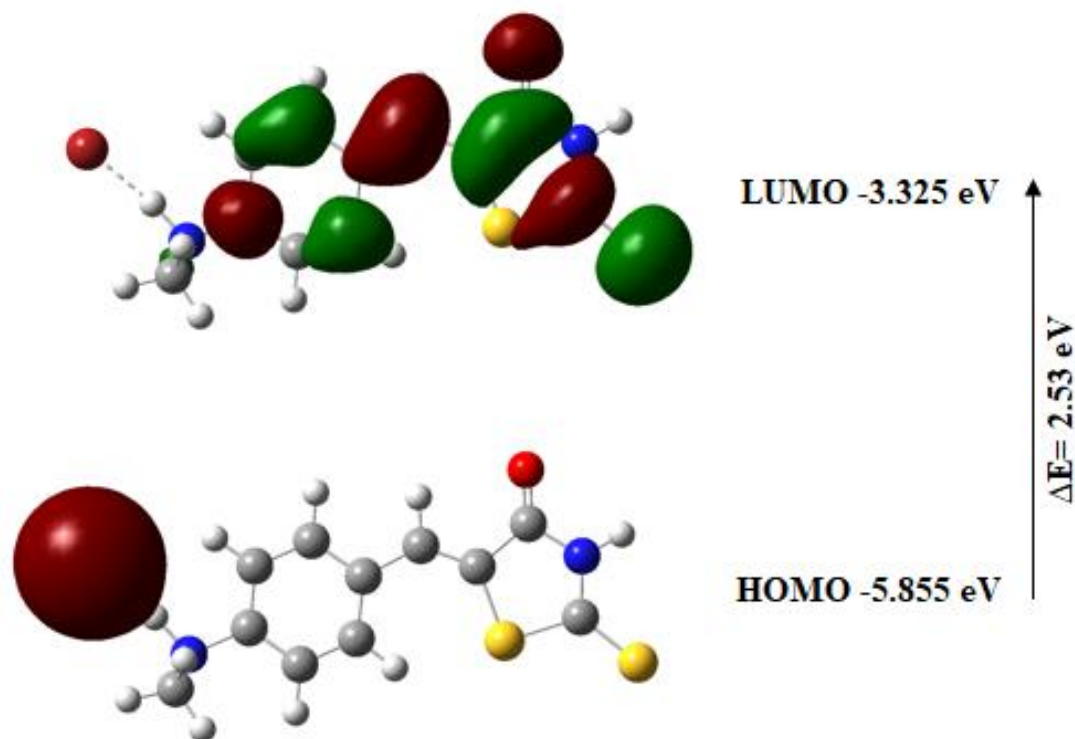


Figure 68. Frontier molecular orbitals (HOMO and LUMO) of [(H⁺DMAP-RDN) Br⁻] with their corresponding energies and energy gaps, showing the electronic distribution.

VI. 3. Analysis of molecular electrostatic potential (MEP) and Mulliken atomic charges.

The molecular electrostatic potential (MEP) (Figure 69 a) and Mulliken charge analyses of [(H⁺DMAP-RDN) Br⁻] reveal a pronounced charge separated electronic environment governed by the ionic nature of the proton-transfer salt. MEP mapping identifies the bromide anion and carbonyl oxygen atoms as the primary nucleophilic centers (negative potential), while the protonated DMAP nitrogen and adjacent hydrogen atoms serve as electrophilic sites (positive potential). Mulliken charges (Figure 69 b) quantitatively validate these observations, showing significant negative charge on the Br⁻ anion and electronegative heteroatoms (O, S), contrasted by high positive density on the protonated nitrogen. This distribution confirms a strong donor-acceptor relationship between the inorganic anion and organic cation, which

facilitates the formation of robust $\text{N-H}\cdots\text{Br}^-$ hydrogen bonds and drives the supramolecular assembly critical for the compound's optoelectronic and conducting properties.

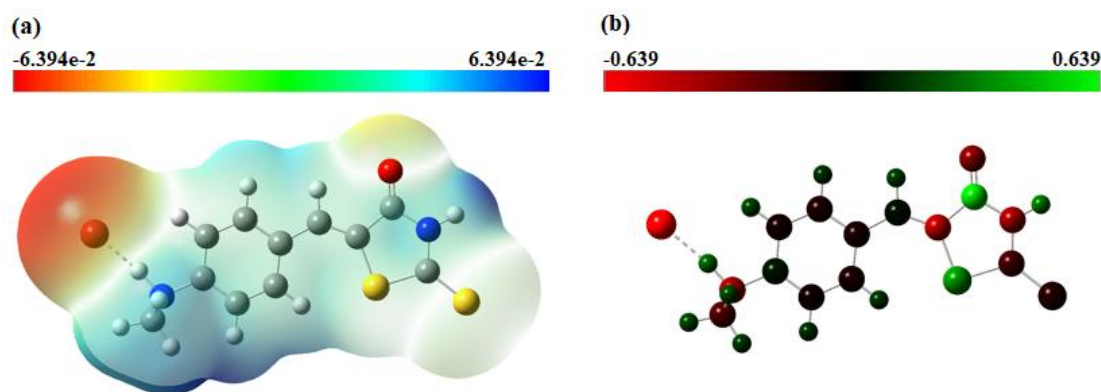


Figure 69. Molecular electrostatic potential (MEP) surface of $[(\text{H}^+\text{DMAP-RDN}) \text{Br}^-]$ showing the charge distribution and regions of electron density.

IV. 5. Reduced density gradient (RDG) analysis of noncovalent interactions (NCI).

The reduced density gradient (RDG) and noncovalent interaction (NCI) analysis of $[(\text{H}^+\text{DMAP-RDN}) \text{Br}^-]$ (Figure 70) demonstrates a stabilizing network of intermolecular forces characterized by both directional and dispersive contacts. The primary stabilization arises from a strong, attractive $\text{N-H}\cdots\text{Br}^-$ hydrogen bond, identified by blue-tinted isosurfaces between the protonated DMAP nitrogen and the bromide anion. This is complemented by significant van der Waals interactions and dispersion forces, evidenced by broad green isosurfaces, which facilitate the stacking of the aromatic pyridine and RDN moieties. While weaker $\text{C-H}\cdots\text{Br}$ and $\text{C-H}\cdots\pi$ contacts provide additional structural cohesion, localized steric repulsion indicated by red isosurfaces occurs near the methyl substituents. Ultimately, the solid-state stability of the hybrid salt is governed by the intricate balance between these specific, directional hydrogen bonds and diffuse non-covalent interactions.

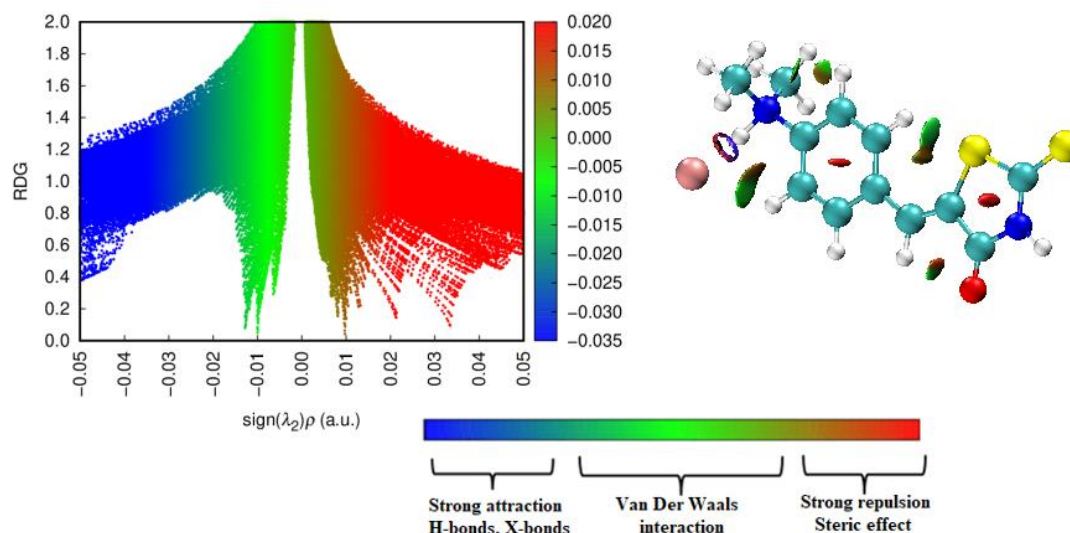


Figure 70. Reduced density gradient (RDG) and noncovalent interaction (NCI) analysis of $[(H^+DMAP-RDN) Br^-]$

V. Conclusion.

This chapter discusses the synthesis, structural elucidation, and electronic characterization of the proton-transfer hybrid organic-inorganic compound $[(H^+DMAP-RDN) Br^-]$. The compound, a stable crystalline material, was analyzed using single-crystal X-ray diffraction, revealing its monoclinic $P2_1/c$ structure. It features a protonated DMAP-RDN cation and bromide anion, with stability derived from a network of noncovalent interactions, including a primary $N-H \cdots Br$ hydrogen bond and various $C-H \cdots Br$ interactions. Hirshfeld surface analysis quantified these interactions, with dominant contributions from $H \cdots H$, $S \cdots H$, and $Br \cdots H$ contacts. DFT calculations confirmed the experimental geometry, showing a HOMO-LUMO gap of 2.53 eV and indicating donor-acceptor characteristics. MEP and Mulliken charge analyses mapped charge distributions in the compound. Furthermore, Reduced Density Gradient analysis visually confirmed the nature of intermolecular forces. Overall, this study elucidates the structure-property relationships in ionic hybrids, suggesting potential applications in optoelectronics and material development.

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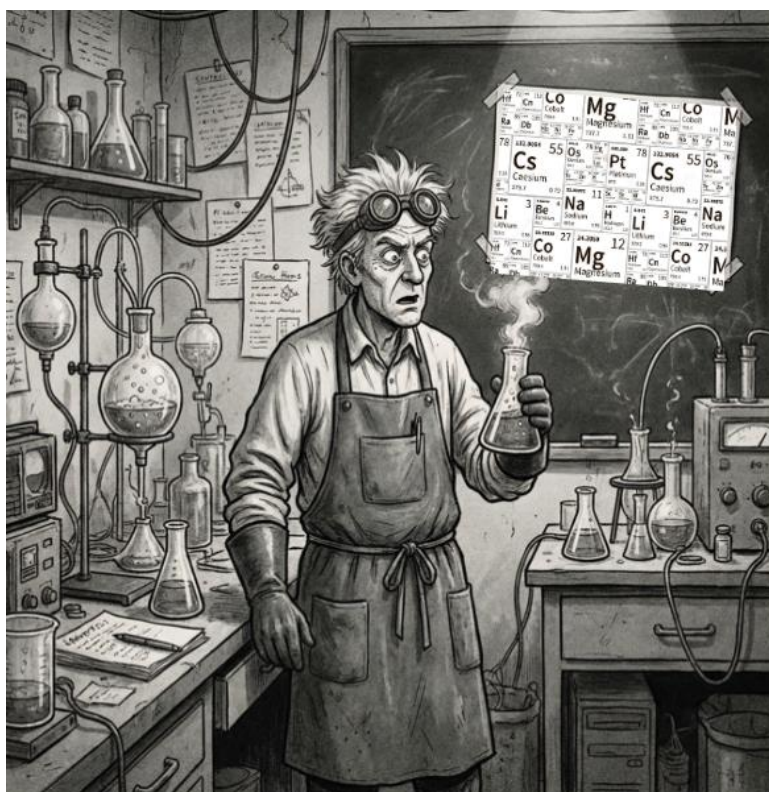
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PART THREE: COORDINATION

COMPOUND

“Synthesis: where your experiment’s motto is always ‘expect the unexpected.’”



Chapter I.

Coordination Chemistry and Organometallic Complexes: a Bibliographic Overview

I. Introduction

Coordination chemistry encompasses the study of compounds formed when metal atoms or ions bind to surrounding molecules or ions, termed ligands, through coordinate covalent bonds. This field represents one of the most vibrant and practically important areas of modern chemistry, bridging inorganic, organic, and physical chemistry while providing the theoretical foundation for understanding metal-based catalysis, bioinorganic processes, and materials design^{1,2}.

Organometallic chemistry, a specialized subdiscipline within coordination chemistry, focuses on compounds containing direct metal-carbon bonds. These organometallic complexes exhibit unique structural, electronic, and reactive properties that distinguish them from classical coordination compounds^{1, 3, 4}. The field has experienced remarkable growth since the mid-20th century, driven by discoveries such as ferrocene's sandwich structure and the development of transition metal-catalyzed reactions that have revolutionized organic synthesis^{3,5}.

The importance of coordination and organometallic chemistry extends far beyond academic interest. These compounds serve as catalysts in numerous industrial processes, including hydrogenation, hydroformylation, olefin polymerization, and cross-coupling reactions^{3, 6}. Recent advances have expanded applications into areas such as C-H activation, sustainable catalysis, and the development of molecular electronic devices⁶⁻⁸.

II. Historical development of coordination chemistry

The foundations of coordination chemistry were established in the late 19th and early 20th centuries through the pioneering work of Alfred Werner, who proposed the coordination theory to explain the structure and isomerism of metal complexes. Werner's insights, which earned him the Nobel Prize in Chemistry in 1913, established that metal ions could bind a definite number of ligands in specific geometric arrangements, introducing the concepts of coordination number and coordination sphere^{1,2}.

The field of organometallic chemistry emerged as a distinct discipline in the mid-20th century, catalyzed by several landmark discoveries. The synthesis and structural elucidation of ferrocene in the 1950s revealed the possibility of π -bonding between metals and organic ligands, fundamentally expanding the scope of metal-carbon interactions³. This discovery opened new avenues for understanding bonding in

transition metal complexes and stimulated intensive research into other organometallic systems.

The development of organometallic chemistry accelerated through the 1960s and 1970s with the discovery of numerous catalytic processes. The elucidation of mechanisms for hydrogenation, hydroformylation, and olefin metathesis demonstrated the practical utility of organometallic compounds and established the field's importance for industrial chemistry^{3, 5}. As Yamamoto noted, the mutual interaction between organometallic chemists and synthetic organic chemists eager to apply organometallic concepts to new types of organic synthesis accelerated development significantly⁵.

The evolution from classical coordination compounds to modern organometallic chemistry reflects a gradual recognition that metal-carbon bonds, once considered exotic, represent a continuum with other metal-ligand interactions. Advances in bonding theory have facilitated this unification, particularly the application of molecular orbital theory to transition metal complexes^{1, 9}.

III. Fundamental principles of coordination chemistry

III. 1. Coordination number and geometry

The coordination number of a metal center, defined as the number of ligand donor atoms directly bonded to the metal, represents a fundamental structural parameter in coordination chemistry. Common coordination numbers range from 2 to 9, with 4, 5, and 6 being most prevalent for transition metals^{1, 3}. The coordination number is influenced by multiple factors, including the metal's electronic configuration, oxidation state, size, and the steric and electronic properties of the ligands¹⁰.

Each coordination number is associated with characteristic geometric arrangements that minimize ligand-ligand repulsion while maximizing metal-ligand bonding. For example, four-coordinate complexes typically adopt tetrahedral or square-planar geometries, with the latter being particularly common for d^8 metal ions such as Pt(II), Pd(II), and Au(III)⁷. Six-coordinate complexes predominantly exhibit octahedral geometry, while five-coordinate species may adopt trigonal bipyramidal or square pyramidal structures^{1, 3}.

Gold (III) complexes exemplify the strong preference of certain metal ions for specific coordination geometries. As documented by Rocchigiani and colleagues, gold(III) adopts almost exclusively square-planar coordination geometry,

characteristic of heavy metal d^8 ions⁷. This geometric preference profoundly influences the reactivity and catalytic properties of gold(III) complexes.

Higher coordination numbers are observed particularly in lanthanide and actinide chemistry. The tris-{hydridotris(1-pyrazolyl)borato}actinide complexes studied by Apostolidis and coworkers exhibit nine-fold coordination in a tri-capped trigonal prismatic arrangement, reflecting the larger ionic radii and different bonding characteristics of f-block elements¹¹.

III. 2. Electron counting rules

Electron counting provides a systematic framework for understanding the stability and reactivity of coordination and organometallic complexes. The 18-electron rule, analogous to the octet rule in main group chemistry, states that stable transition metal complexes tend to have 18 valence electrons (corresponding to filled s, p, and d orbitals)^{3, 12}. This rule proves particularly useful for predicting the stability of organometallic compounds and understanding their reactivity patterns.

The 18-electron rule applies most reliably to low-valent transition metal complexes with strong-field ligands, particularly metal carbonyls and organometallic compounds of groups 6-10³. However, numerous stable complexes deviate from this rule. Square-planar d^8 complexes of Pt(II), Pd(II), and Au(III) are 16-electron species, while many catalytically active intermediates are coordinatively unsaturated with fewer than 18 electrons¹².

Recent work has emphasized the importance of "underligated" reactive complexes that deliberately violate the 18-electron rule paradigm. Danopoulos and colleagues described how coordinative and electronic unsaturation in 3d metal complexes stabilized by bulky N-heterocyclic carbenes (NHCs) leads to unusual reactivity and open-shell electronic structures¹². These complexes demonstrate that electronic unsaturation can be a design feature rather than a liability, enabling new reactivity patterns including C-H activation.

For organozinc compounds, the electron-deficient nature of zinc which supplies only two valence electrons despite having four low-lying orbitals available leads to strong electrophilic character and a pronounced tendency for complex formation¹³. This electron deficiency drives the formation of higher coordination numbers through intermolecular association and complex formation with donor ligands.

III. 3. Classification of ligands

Ligands are classified according to multiple criteria including their denticity (number of donor atoms), charge, and bonding mode. Monodentate ligands bind through a single donor atom, while polydentate or chelating ligands possess multiple donor sites that can simultaneously coordinate to a metal center^{1, 3, 14}. Chelating ligands generally form more stable complexes than monodentate ligands due to the chelate effect, an entropic advantage arising from the formation of ring structures.

The Covalent Bond Classification (CBC) system provides a systematic nomenclature for describing metal-ligand interactions based on the number of electrons contributed by the ligand and metal. Ligands are designated as L-type (two-electron donors), X-type (one-electron donors), or Z-type (electron acceptors)³. This classification proves particularly useful for electron counting and understanding reactivity patterns in organometallic chemistry.

Ligands can also be categorized by their electronic effects. σ -Donor ligands donate electron density to the metal through sigma bonds, while π -acceptor ligands (such as CO, alkenes, and alkynes) can accept electron density from filled metal d-orbitals into their empty π^* orbitals through back-bonding^{1, 3, 15}. This π -back-bonding stabilizes low oxidation state metal complexes and profoundly influences the reactivity of organometallic compounds.

The nature of substituent groups on ligands significantly affects their donor/acceptor ability and steric properties. Riihimäki's systematic study of aryl- and arylalkylphosphanes demonstrated how substituent effects influence coordination chemistry and catalytic properties, with correlations observed between ligand steric/electronic parameters (cone angles, NMR shifts) and catalytic behavior in hydroformylation reactions¹⁵.

IV. Structure and geometry of coordination complexes

The three-dimensional structure of coordination complexes is determined by the interplay of electronic factors (metal d-electron configuration, ligand field strength) and steric factors (ligand size, chelate ring constraints). Understanding these structural features is essential for predicting reactivity and designing functional complexes^{1, 3, 7}.

Square-planar geometry is characteristic of d^8 metal ions, particularly those of the second and third transition series such as Pt(II), Pd(II), and Au(III). The strong ligand field splitting in these heavy metals favors the low-spin configuration that leads to

square-planar geometry⁷. This geometry has profound implications for reactivity, as the open coordination sites perpendicular to the plane facilitate associative substitution mechanisms and enable catalytic cycles involving oxidative addition and reductive elimination.

Octahedral geometry represents the most common coordination geometry for transition metals, particularly for d^3 , d^6 , and d^0 configurations. The high symmetry of octahedral complexes simplifies their spectroscopic analysis and provides a useful reference point for understanding distortions caused by Jahn-Teller effects or chelate constraints^{1, 11}.

Tetrahedral geometry is common for d^0 and d^{10} configurations and for complexes with bulky ligands that prevent higher coordination numbers. The weaker ligand field splitting in tetrahedral complexes compared to octahedral geometry results in different electronic and magnetic properties¹.

Five-coordinate complexes occupy an intermediate position between four- and six-coordinate species and often exhibit fluxional behavior, interconverting between trigonal bipyramidal and square pyramidal geometries³. This fluxionality has important implications for catalytic mechanisms, as five-coordinate intermediates frequently appear in catalytic cycles.

Higher coordination numbers (7-9) are particularly common in lanthanide and actinide chemistry due to the larger ionic radii of f-block elements. The nine-coordinate actinide complexes studied by Apostolidis and colleagues adopt a tri-capped trigonal prismatic geometry, reflecting the geometric preferences of these large metal ions¹¹. The factors influencing coordination number in rare earth complexes include ionic radius, ligand size, and the balance between maximizing coordination number and minimizing ligand-ligand repulsion^{10, 16}.

Structural trans-effects and trans-influences represent important phenomena in square-planar and octahedral complexes. A strong trans-effect ligand weakens and labilizes the bond to the ligand in the trans position, influencing both thermodynamic stability and kinetic reactivity⁷. Rocchigiani and colleagues noted that in gold complexes, strong electron-donating ligands weaken gold-trans-ligand bonds through this mechanism, with important consequences for catalytic reactivity⁷.

V. Types of ligands and metal-ligand bonding

V. 1. σ -Donor ligands

σ -Donor ligands form coordinate covalent bonds by donating a lone pair of electrons into empty or partially filled metal orbitals. Common σ -donors include ammonia, amines, water, alcohols, ethers, halides, and phosphines^{1, 3, 15}. The strength of σ -donation depends on the ligand's basicity and the availability of the lone pair for bonding.

Phosphine ligands (PR_3) represent particularly important σ -donors in organometallic chemistry and catalysis. These ligands bind through the lone pair on phosphorus while their steric and electronic properties can be systematically varied through substituent modification¹⁵. Riihimäki's comprehensive study demonstrated how *o*-alkyl-substituted arylphosphanes exhibit modified steric and electronic properties that influence catalytic selectivity in hydroformylation reactions¹⁵.

N-Heterocyclic carbenes (NHCs) have emerged as powerful σ -donor ligands in modern coordination chemistry. These neutral two-electron donors form exceptionally strong metal-carbon bonds and can stabilize unusual oxidation states and coordination geometries⁶. Danopoulos and colleagues showed how bulky NHCs stabilize underligated 3d metal complexes with open-shell electronic structures, enabling new reactivity patterns⁶.

V. 2. π -Acceptor ligands

π -Acceptor ligands possess empty π^* orbitals that can accept electron density from filled metal d-orbitals through back-bonding. This π -back-donation is crucial for stabilizing low oxidation state metal complexes and profoundly influences the properties of organometallic compounds^{1, 3, 15}.

Carbon monoxide represents the archetypal π -acceptor ligand. Metal carbonyls exhibit strong M-CO bonds due to synergistic σ -donation (from the CO lone pair to the metal) and π -back-donation (from filled metal d-orbitals to the CO π^* orbital)^{3, 17}. This back-bonding weakens the C-O bond and strengthens the M-C bond, as evidenced by IR spectroscopy showing reduced C-O stretching frequencies in metal carbonyls compared to free CO.

Alkenes and alkynes also function as π -acceptor ligands, binding to metals through donation from their π bonding orbitals and accepting electron density into their π^* orbitals^{3, 7}. The synthesis and characterization of gold(III) alkene and alkyne

complexes by Rocchigiani and colleagues revealed that π -back-donation in these gold complexes is relatively small compared to other transition metals, reflecting gold's high electronegativity and the strong ligand field⁷.

The balance between σ -donation and π -acceptance can be quantified through various experimental and computational methods. Charge decomposition analysis applied to Au(III)-CO complexes revealed the relative contributions of these bonding components, providing insights into the unique reactivity of gold in catalysis⁷.

V. 3. π -Donor ligands

π -Donor ligands possess filled π -orbitals that can donate electron density to empty or partially filled metal d-orbitals. Common π -donors include halides, alkoxides, and other ligands with lone pairs in p-orbitals¹. π -Donation typically weakens the metal-ligand σ -bond while providing additional stabilization through the π -interaction.

The interplay between σ -donation and π -donation/acceptance determines the position of ligands in the spectrochemical series. Strong π -acceptors like CO and CN^- produce large ligand field splittings, while π -donors like halides produce smaller splittings¹.

V. 4. Chelating and multidentate ligands

Chelating ligands that bind through multiple donor atoms form particularly stable complexes due to the chelate effect. This enhanced stability arises primarily from favorable entropy changes when a single polydentate ligand replaces multiple monodentate ligands^{1,3}.

Functional chelating ligands have become increasingly important for controlling metal coordination sphere geometry and reactivity. Danopoulos and colleagues described how P,O-, P,N-, and N,O-type chelating ligands enable stereodifferentiation within the metal coordination sphere and fine-tuning of catalytic properties⁶. These ligands have found particular application in ethylene oligomerization catalysis, including the industrial Shell Higher Olefin Process (SHOP).

The design of chelating ligands allows control over bite angle (the angle subtended by the donor atoms at the metal center), which influences both the stability and reactivity of complexes. Ligands with constrained bite angles can enforce specific coordination geometries and influence the selectivity of catalytic reactions^{6,15}.

VI. Organometallic complexes: characteristics and bonding

VI. 1. Definition and scope

Organometallic compounds are defined as compounds containing at least one direct metal-carbon bond^{1, 3, 18, 19}. This definition encompasses a vast array of

structures ranging from simple alkyl and aryl complexes to sophisticated π -bonded systems involving alkenes, alkynes, and aromatic ligands. The field bridges inorganic and organic chemistry, with organometallic compounds exhibiting properties characteristic of both domains.

The scope of organometallic chemistry extends across the periodic table, though transition metal organometallics have received the most attention due to their catalytic applications^{1, 3, 5}. Main group organometallics, such as the organozinc compounds studied by van der Kerk, also play important roles in synthesis and catalysis¹³.

VI. 2. The 18-electron rule

The 18-electron rule provides a useful framework for understanding the stability and reactivity of organometallic complexes. Complexes with 18 valence electrons (corresponding to filled s, p, and d orbitals) are generally stable and relatively unreactive, while coordinatively unsaturated complexes with fewer than 18 electrons tend to be more reactive^{3, 6}.

However, the 18-electron rule is not absolute. Many stable and catalytically important organometallic complexes violate this rule. Square-planar d^8 complexes are inherently 16-electron species, and many catalytic cycles proceed through coordinatively unsaturated intermediates^{6, 7}. The recent emphasis on "underligated" complexes deliberately exploits electronic unsaturation to achieve unusual reactivity⁶.

VI. 3. Metal-carbon bonding

Metal-carbon bonds in organometallic compounds exhibit a range of bonding modes and strengths. Simple σ -bonded alkyl and aryl ligands form localized two-electron bonds analogous to C-C bonds in organic compounds, though M-C bonds are generally more polar and reactive^{1, 3}.

π -Bonded organometallic ligands, including alkenes, alkynes, allyl, and aromatic systems, exhibit more complex bonding involving both σ -donation and π -back-bonding^{2, 3, 7}. The Dewar-Chatt-Duncanson model describes alkene coordination as involving donation from the alkene π -orbital to the metal and back-donation from filled metal d-orbitals to the alkene π^* orbital^{1, 3}. This model has been extended to other unsaturated ligands and remains fundamental to understanding organometallic bonding.

Carbene and carbyne ligands represent extreme cases of metal-carbon multiple bonding. Fischer carbenes feature electrophilic carbene carbons and are stabilized by π -donor substituents, while Schrock carbenes exhibit nucleophilic character and

resemble metal-carbon double bonds³. These complexes play crucial roles in olefin metathesis and other catalytic transformations.

VI. 4. Common organometallic ligands

Metal carbonyls represent the most extensively studied class of organometallic compounds. The strong π -acceptor character of CO stabilizes low oxidation states and enables the formation of polynuclear clusters with metal-metal bonds^{3, 17}. Carbonyl ligands can adopt various bonding modes including terminal, bridging, and semi-bridging coordination.

Cyclopentadienyl (Cp) ligands and their derivatives form stable complexes with most transition metals. The discovery of ferrocene's sandwich structure revolutionized organometallic chemistry and established the importance of π -bonding in metal complexes³. Cp ligands function as six-electron donors (in the η^5 bonding mode) and provide both electronic and steric stabilization.

Alkyl and aryl ligands form σ -bonds to metals and are fundamental to organometallic reactivity. These ligands participate in key reactions including migratory insertion, β -hydride elimination, and reductive elimination^{3, 7}. The stability of metal-alkyl bonds varies widely depending on the metal, oxidation state, and ancillary ligands.

Alkene and alkyne ligands coordinate through their π -systems and are central to many catalytic processes. Recent advances in gold(III) chemistry have enabled the synthesis and characterization of previously elusive gold-alkene and gold-alkyne complexes, providing new insights into the bonding and reactivity of these fundamental organometallic species⁷.

VII. Applications of coordination and organometallic chemistry

VII. 1. Homogeneous catalysis

Homogeneous catalysis by coordination and organometallic complexes represents one of the most important applications of these compounds. Transition metal catalysts enable transformations that would be difficult or impossible using traditional organic chemistry methods, often with high selectivity and under mild conditions^{3, 6, 7, 20}.

Hydrogenation catalysis, pioneered by Wilkinson and others, uses rhodium and other transition metal complexes to reduce alkenes, alkynes, and other unsaturated substrates³. Asymmetric hydrogenation using chiral phosphine ligands has become a cornerstone of pharmaceutical synthesis, enabling the production of enantiomerically pure compounds.

Hydroformylation (the oxo process) converts alkenes to aldehydes through the addition of CO and H₂, catalyzed by rhodium or cobalt complexes^{3, 15}. This process represents one of the largest-scale applications of homogeneous catalysis, producing millions of tons of aldehydes annually for plasticizer and detergent production. Riihimäki's work demonstrated how ligand design influences selectivity in hydroformylation, with o-alkyl-substituted arylphosphanes increasing selectivity for branched aldehydes¹⁵.

Cross-coupling reactions catalyzed by palladium complexes have revolutionized organic synthesis, enabling the formation of C-C, C-N, and other bonds under mild conditions^{3, 8}. These reactions, including the Suzuki, Negishi, and Stille couplings, have become indispensable tools in pharmaceutical and materials synthesis. Yamamoto's pioneering work on nickel-catalyzed cross-coupling laid the foundation for these transformations⁵.

Olefin metathesis, catalyzed by ruthenium and molybdenum carbene complexes, enables the redistribution of alkylidene fragments between alkenes³. This powerful transformation has found applications ranging from polymer synthesis to pharmaceutical production and was recognized with the 2005 Nobel Prize in Chemistry.

Gold catalysis has emerged as a major area of research over the past two decades. Rocchigiani and colleagues reviewed recent advances in gold(III) chemistry, highlighting applications in C-C and C-E coupling reactions, Lewis acid catalysis for functionalization of unsaturated substrates, and photo-assisted catalysis⁷. The unique properties of gold including its high electronegativity and relativistic effects enable catalytic transformations that complement those of other transition metals.

VII. 2. Industrial processes

Coordination and organometallic chemistry underpin numerous large-scale industrial processes. The Monsanto and Cativa processes for methanol carbonylation to acetic acid use rhodium and iridium catalysts, respectively, producing millions of tons of acetic acid annually³. The Wacker process for ethylene oxidation to acetaldehyde employs palladium/copper catalysis and represents an early example of industrial homogeneous catalysis³.

Olefin polymerization using Ziegler-Natta catalysts and metallocene catalysts produces the majority of the world's polyethylene and polypropylene³. These titanium

and zirconium-based catalysts enable control over polymer molecular weight, tacticity, and other properties crucial for materials applications.

The Shell Higher Olefin Process (SHOP) uses nickel catalysts with functional chelating ligands to oligomerize ethylene to linear α -olefins⁶. These products serve as comonomers in polyethylene production and as feedstocks for detergents and other applications.

Organozinc coordination compounds catalyze cyclo-oligomerization and polymerization reactions, particularly for oxygen-containing monomers like aldehydes, lactones, and epoxides¹³. Van der Kerk's work established the coordination-insertion mechanism for these transformations and demonstrated the utility of organozinc reagents in stereoregular polymerization.

VII. 3. Organic synthesis

Organometallic reagents and catalysts have become indispensable tools in organic synthesis. Transition metal complexes enable selective C-H activation, allowing direct functionalization of C-H bonds without pre-activation [6, 21]. This capability has the potential to streamline synthetic routes and reduce waste in pharmaceutical and fine chemical production.

Palladacycles cyclic organometallic compounds containing palladium-carbon bonds serve as key intermediates in palladium-catalyzed reactions including coupling via C-H activation, intramolecular Stille reactions, and Heck-type cyclizations⁸. These species also function as active catalysts in Sonogashira cross-coupling and chemoselective hydrogenation reactions.

Organometallic compounds facilitate the synthesis of complex natural products and pharmaceuticals. Nudelman's work demonstrated how organolithium, organotin, and organochromium compounds enable selective bond formation, including the synthesis of carbamoyl compounds, β -alkyl substituted dihydrochalcones, and chiral products²¹.

VII. 4. Materials science

Coordination and organometallic compounds find diverse applications in materials science. Metal-organic frameworks (MOFs) and coordination polymers utilize metal-ligand coordination to create porous materials with applications in gas storage, separation, and catalysis²². Organometallic coordination networks based on π -bonded transition metal complexes represent an emerging class of functional materials²².

Organometallic compounds serve as precursors for materials deposition through chemical vapor deposition (CVD) and atomic layer deposition (ALD). Surface organometallic chemistry, which applies coordination chemistry principles to understand metal-surface interactions, guides the design of supported catalysts and surface modification strategies^{23, 24}.

Molecular electronic devices based on organometallic complexes exploit the unique electronic properties of metal centers for applications in sensing, switching, and energy conversion^{25, 26}. Ruthenium and other transition metal complexes with extended π -systems show promise for molecular electronics applications.

Bioorganometallic chemistry explores the interactions of organometallic compounds with biological systems, with applications in medicinal chemistry, biosensing, and biocatalysis³. Metal-based drugs, including platinum anticancer agents and gold antiarthritic compounds, demonstrate the therapeutic potential of coordination compounds.

VIII. Conclusion

Coordination and organometallic chemistry have become essential to modern chemistry, influencing catalysis, synthesis, and materials science. The field has progressed significantly from foundational theories to sophisticated understandings of metal-ligand interactions, aided by modern computational methods. This evolution highlights the continuum of coordination and organometallic chemistry, facilitating diverse applications in industrial and pharmaceutical contexts. Recent advancements in synthesizing complex organometallic species and developing innovative catalysts signal the field's vitality. Future prospects involve addressing sustainability and selectivity issues through enhanced ligand design and mechanistic insights, emphasizing the interplay between fundamental research and practical applications.

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Chapter II.

Planarity-Driven

Structure–Morphology

Correlations in a Co(II)

Benzoylacetate:

Comparative Insights

Across the $[M(bzac)_2]$

Family

I. Introduction.

Coordination compounds involving O-donor ligands are pivotal in modern inorganic and materials chemistry¹⁻³, extending beyond catalysis to applications in sensing and electronics⁴⁻⁶. The properties of these complexes are influenced by factors such as metal coordination geometry, ligand π -conjugation⁷, and supramolecular packing, which together affect charge delocalization and energy transfer⁸. Among O-donor ligands, β -diketonates are notable due to their consistent coordination chemistry across various metals, allowing for systematic studies of their effects on intermolecular behavior and crystal habit⁹. Benzoylacetate (bzac) is highlighted for its enhanced electronic and geometric properties, making it suitable for analyzing the relationship between metal configuration and crystal structures with direct implications for thin film emitters and related materials.¹⁰⁻¹²

However, existing research on β -diketonates is often fragmented, focusing on local geometries without establishing clear structural descriptors relating coordination to long-range packing. This gap limits the use of metal β -diketonates for understanding crystal morphology. Solid-state functions depend greatly on molecular packing influenced by weak interactions such as $\pi \cdots \pi$ overlaps¹³ and C–H $\cdots\pi$ contacts. Combining techniques like single-crystal X-ray diffraction and electronic structure analysis can enhance the understanding of the interplay between geometry and packing^{14,15}.

The study details the synthesis of a new cobalt (II) benzoylacetate, [Co(bzac)₂], situated in a comparative framework with other metal analogues drawn from structural databases. By integrating experimental characterization with theoretical methods, this research aims to establish [Co(bzac)₂] as a benchmark for exploring structure-morphology correlations in the [M(bzac)₂] series, ultimately providing a model for designing coordination materials that optimize optical and morphological properties through controlled planarity and packing.

II. Experimental Methods

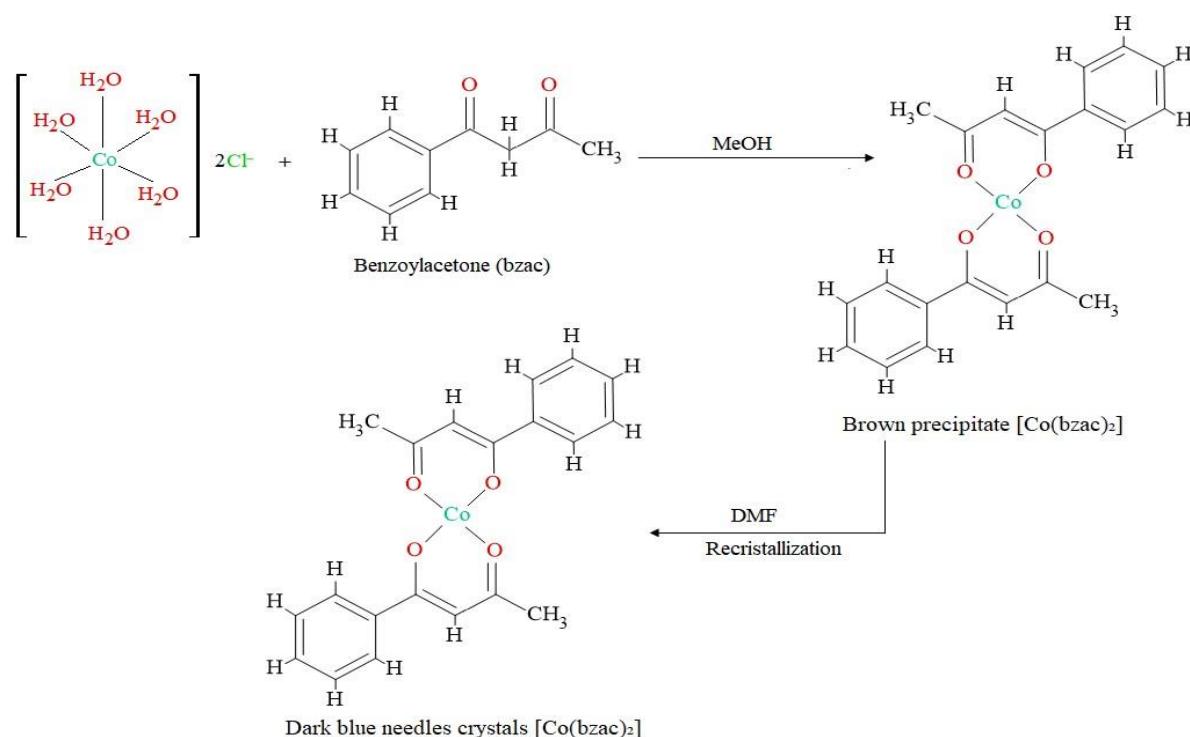
II. 1. Synthesis and crystallization.

All starting materials were purchased from Sigma-Aldrich and used without further purification : cobalt (II) chloride hexahydrate (CoCl₂·6H₂O, 99.99%), 1-phenyl-1,3-butanedione (bzac, 99%), and methanol (MeOH, $\geq 99\%$). The [Co(bzac)₂] complex was synthesized under ambient conditions.

Chapter II. Planarity-driven structure–morphology correlations in a Co(II) benzoylacetone: comparative insights across the $[M(\text{bzac})_2]$ family

Cobalt (II) chloride hexahydrate (1 mmol, 0.238 g) was dissolved in 10 mL of methanol with continuous stirring. Separately, 1-phenyl-1,3-butanedione (0.324 g, 2 mmol) was dissolved in 15 mL of methanol. The ligand solution was added dropwise to the cobalt solution under constant stirring at room temperature. The reaction mixture was stirred for 1 h, during which a brown precipitate gradually formed.

The solid product was collected by filtration, washed several times with cold methanol, and air-dried. The resulting powder was recrystallized from dimethylformamide (DMF) by slow solvent evaporation at room temperature. After several weeks, dark blue needle-shaped crystals suitable for X-ray diffraction were obtained in 45% yield (Scheme 5).



Scheme 5. Synthetic route to the $[\text{Co}(\text{bzac})_2]$ complex.

II. 2. Single crystal X-ray diffraction and structure refinement details.

Crystal data, experimental parameters, and structure refinement details for the title compound are summarized in Table 20. Dark-blue, needle-like single crystals were selected from the bulk material, mounted on a MiTiGen loop coated with perfluoroether oil, and measured on a Bruker D8 Venture diffractometer equipped with a PHOTON III CPAD detector. Data were collected at $T = 100(2)$ K using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) in ω -scan mode.

Chapter II. Planarity-driven structure–morphology correlations in a Co(II) benzoylacetonate: comparative insights across the $[M(\text{bzac})_2]$ family

The structure was solved by direct methods using *SHELXS*¹⁶ and refined by full-matrix least-squares on F^2 with *SHELXL*¹⁷. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated positions and refined using a riding model. A multi-scan absorption correction was applied using SADABS¹⁸, yielding an absorption coefficient of $\mu = 1.043 \text{ mm}^{-1}$ with $T_{\min} = 0.8610$ and $T_{\max} = 1.0000$.

The refinement converged smoothly to $R_1 = 0.0362$ and $wR_2 = 0.1103$ for all reflections, with a goodness of fit on F^2 of 1.128. The final difference Fourier map showed residual electron density peaks of $+1.081$ and $-0.677 \text{ e } \text{\AA}^{-3}$, indicating an accurate structural model with no significant disorder. All molecular graphics were generated using Mercury 2025.3¹⁹.

Table 20. Main crystallographic data and structure refinement details for complex $[\text{Co}(\text{bzac})_2]$

Crystal data	
Empirical Formula	$\text{C}_{20}\text{H}_{18}\text{CoO}_4$
Molecular weight (g/mol)	381.27
Diffractionmeter,	Bruker D8 Venture
Radiation type	Mo $K\alpha$ ($\lambda=0.71073 \text{ \AA}$)
T (K)	100(2)
Calculated density (Mg/m^3)	1.508
Crystal system	Monoclinic
Space group	$P2_1/n$
a ($\text{\AA}$)	4.3920 (17)
b ($\text{\AA}$)	10.3955 (6)
c ($\text{\AA}$)	18.497 (2)
β ($^\circ$)	96.233 (16)
V ($\text{\AA}^3$)	839.5(3)
Z	2
μ (mm^{-1})	1.044
Crystal size (mm)	$0.20 \times 0.08 \times 0.07$
$T_{\min}$, $T_{\max}$	0.861, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	82378, 4080, 3787

$R(\text{int})^{\text{a}}$	0.051
Refinement	
$R[F^2 > 2\sigma(F^2)]^{\text{b}}, wR(F^2)^{\text{c}}, S^{\text{d}}$	0.034, 0.113, 1.13
No. of parameters	115
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.75, -0.65

^a $R(\text{int}) = \Sigma(F_o^2 - \langle F_o^2 \rangle) / \Sigma(F_o^2)$

^b $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

^c $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2] / [\Sigma w(F_o^2)^2]\}^{1/2}$.

^d Goodness-of-fit $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

II. 3. Powder X-ray diffraction (PXRD).

Powder X-ray diffraction (PXRD) measurements were carried out at 296 K using a Rigaku SmartLab multipurpose diffractometer equipped with Cu $K\alpha$ radiation ($\lambda = 0.154056$ nm), operated at 40 kV and 30 mA. Data were collected in reflection geometry over a 2θ range of 5–50° with a step size of 0.02°.

A simulated PXRD pattern was generated from the refined single-crystal structure (CCDC 2498791) using Mercury (version 2025.3)¹⁹ to enable direct comparison between the experimental bulk microcrystalline sample and the single-crystal X-ray diffraction model.

The room-temperature PXRD pattern of $[\text{Co}(\text{bzac})_2]$ is shown in Figure 55, together with the pattern simulated from the single-crystal structure refined in space group $P2_1/n$. The experimental diffractogram is dominated by an intense reflection at $2\theta = 9.60^\circ$ ($I/I_{\text{max}} = 100\%$), accompanied by a weaker shoulder at 9.26° (2.9 % relative intensity) and additional reflections at 16.68° (14.5 %), 19.32° , 24.68° , 27.00° , and 35.18° . Within the experimental resolution, all observed peaks are fully consistent with those expected for the monoclinic unit cell determined by SC-XRD, and no extraneous reflections are detected over the 5–50° range. This confirms that the bulk microcrystalline material is a single phase corresponding to the $[\text{Co}(\text{bzac})_2]$ structure.

Using the lattice parameters obtained from SC-XRD (Table 20), the most intense reflection at $2\theta = 9.60^\circ$ can be indexed as the (002) plane ($d(002) \approx 9.19$ Å), corresponding to the repeat distance along the crystallographic c axis. This assignment is consistent with the layered packing of

nearly planar $[Co(bzac)_2]$ molecules: π -stacked benzoylacetate ligands and square-planar CoO_4 chromophores form corrugated sheets parallel to the (b,c) plane, whose periodic separation along c gives rise to the prominent low-angle (002) reflection. The higher-angle reflections at 16.68° , 19.32° , 24.68° , 27.00° , and 35.18° can be associated with higher-index planes such as (0 1 3), (0 2 2), (1 1 2), and (1 3 2), which probe increasingly complex combinations of in-plane and interlayer correlations within the same zigzag framework.

The excellent agreement between the experimental and simulated PXRD patterns, both in peak positions and overall profile, demonstrates that the structural features revealed by SC-XRD namely strictly square-planar CoO_4 coordination, nearly coplanar benzoylacetate ligands, and zigzag stacks of molecules along the [001] direction—are faithfully reproduced throughout the bulk material. Minor discrepancies in relative intensities are readily attributed to preferred orientation effects, as expected for samples composed of elongated, needle-like crystallites, where partial alignment enhances reflections associated with planes perpendicular to the growth direction (e.g., (002)).

From a structure property perspective, the PXRD results directly link local coordination geometry, supramolecular packing, and macroscopic crystal morphology. The intense low-angle (002) reflection reflects the long-range periodicity of the stacked molecular layers that also govern the BFDH-predicted crystal habit. Thus, the same planar CoO_4/β -diketonate architecture that enforces highly anisotropic packing is responsible for both (i) the dominant low-angle scattering in the PXRD pattern and (ii) the experimentally observed acicular growth along [001]. This coherent picture confirms that the pronounced morphological anisotropy of $[Co(bzac)_2]$ is an intrinsic consequence of its crystallographic structure rather than a kinetic artefact of the crystallization conditions.

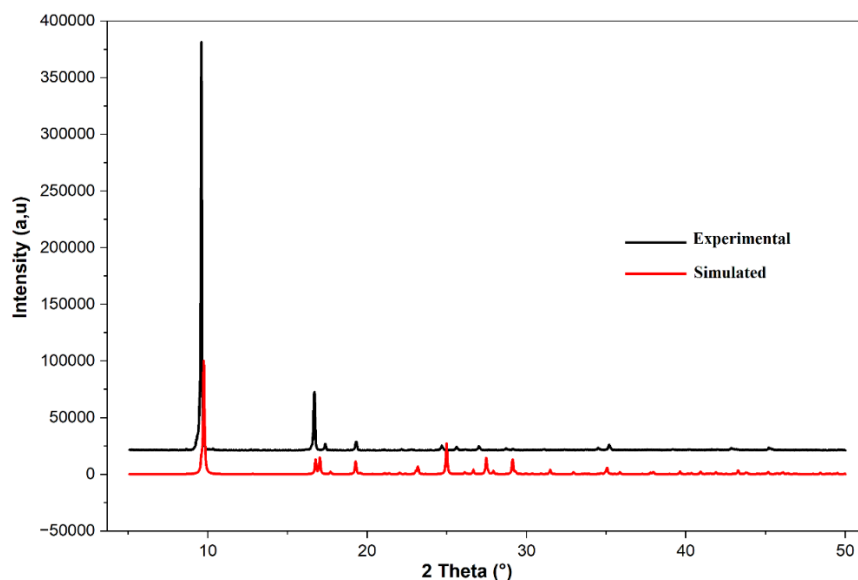


Figure 71. Experimental powder X-ray diffraction pattern of $[\text{Co}(\text{bzac})_2]$ (black), compared with the pattern simulated from the single-crystal structure (red). The excellent agreement in peak positions confirms the bulk phase purity and the correspondence between the microcrystalline sample and the SC-XRD model.

II. 4. FTIR spectroscopic characterization of $[\text{Co}(\text{bzac})_2]$.

Approximately 2 mg of the complex was finely ground and thoroughly mixed with 100 mg of dried, spectroscopic-grade KBr, then compressed into a pellet using a cold isostatic press at approximately 100 kPa. FT-IR spectra were recorded in transmission mode over the range $400\text{--}4000\text{ cm}^{-1}$ with a spectral resolution of 4 cm^{-1} , averaging 64 scans, using a PerkinElmer FT-IR spectrometer.

The infrared spectrum of $[\text{Co}(\text{bzac})_2]$ (Figure 72) displays the characteristic vibrational features associated with a coordinated β -diketonate environment²⁰. A strong absorption band observed at approximately $1610\text{--}1620\text{ cm}^{-1}$ is assigned to the $\nu(\text{C}=\text{O})$ stretching vibration of the enolized β -diketonate moiety, while the band near 1520 cm^{-1} corresponds to the $\nu(\text{C}=\text{C})$ stretching mode of the chelate ring²¹. The absence of the sharp carbonyl stretching band characteristic of the free ligand near 1700 cm^{-1} , together with the emergence of these two distinct absorptions, confirms enolization and O, O'-bidentate coordination of the bzac ligand to the Co(II) center⁹.

Additional bands in the $1250\text{--}1270\text{ cm}^{-1}$ and $\sim 1170\text{ cm}^{-1}$ regions are attributed to C–O stretching vibrations, further supporting metal–oxygen bond formation through the oxygen donor

atoms²². A medium-intensity band observed at 520–530 cm^{-1} is characteristic of the $\nu(\text{Co–O})$ stretching mode and is consistent with a square-planar CoO_4 coordination environment, as established by the X-ray diffraction data.

Overall, the IR spectroscopic results fully corroborate the crystallographic analysis, confirming chelation of the ligand through both oxygen atoms and the planar coordination geometry around the cobalt center.

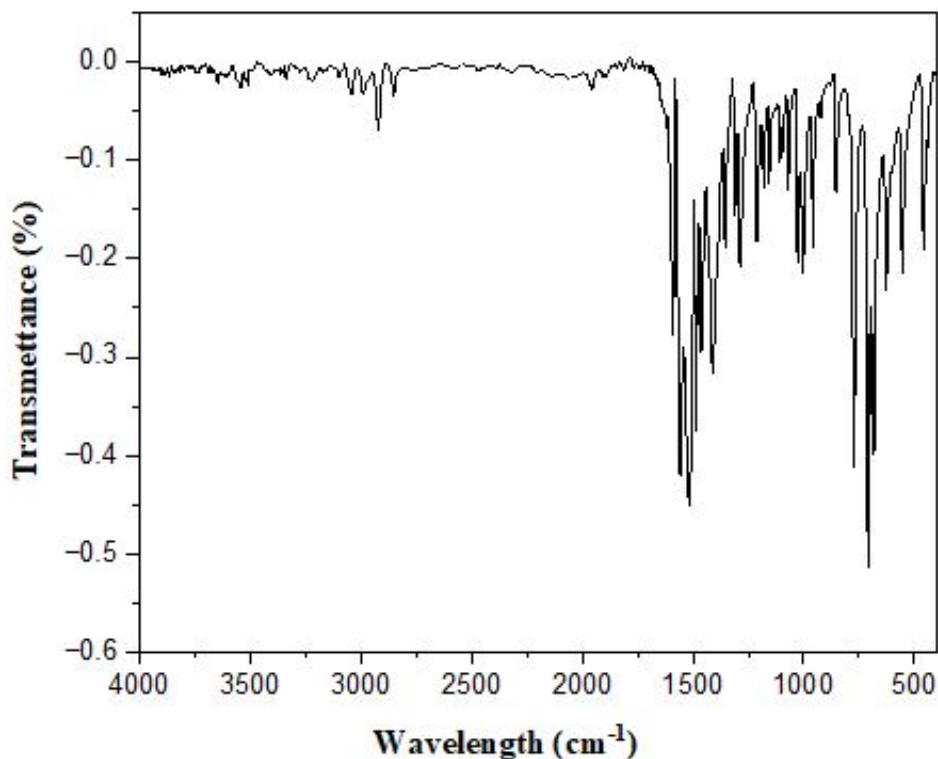


Figure 72. FTIR spectrum of complex $[\text{Co}(\text{bzac})_2]$

II. 4. UV-Vis spectroscopic characterization of $[\text{Co}(\text{bzac})_2]$.

UV–Vis absorption spectra of $[\text{Co}(\text{bzac})_2]$ were recorded in DMF using a Spectroscan 80D UV–Vis spectrophotometer over the wavelength range 190–500 nm. Measurements were performed at a scan rate of 100 nm min^{-1} with a spectral bandwidth of 2.0 nm.

The UV–Vis absorption spectrum of $[\text{Co}(\text{bzac})_2]$ (Figure 73) was recorded in methanol over the wavelength range 190–500 nm. The spectrum displays an intense absorption band in the ultraviolet region at approximately 280–290 nm, which is attributed to $\pi \rightarrow \pi^*$ transitions localized within the conjugated benzoylacetate (bzac) ligand framework²³. A shoulder of moderate intensity extending from approximately 340 to 380 nm can be assigned to $n \rightarrow \pi^*$ transitions involving non-bonding oxygen orbitals of the coordinated β -diketonate²⁴.

Within the visible region, only a very weak and broad absorption tail approaching 480–500 nm is observed. This feature is consistent with a Laporte-forbidden, metal-centered d–d transition expected for a square-planar Co(II) center in a D_{4h} -like ligand field²⁵. The overall spectral profile dominated by ligand-based $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions with only a faint low-energy contribution accords well with the electronic structure inferred from frontier molecular orbital analysis and the square-planar CoO_4 coordination geometry established by X-ray diffraction.

Taken together, the UV–Vis spectroscopic data, in excellent agreement with the crystallographic and comparative CSD analyses, confirm the coordination mode of the bzac ligands and validate the structural integrity of the $[\text{Co}(\text{bzac})_2]$ complex.

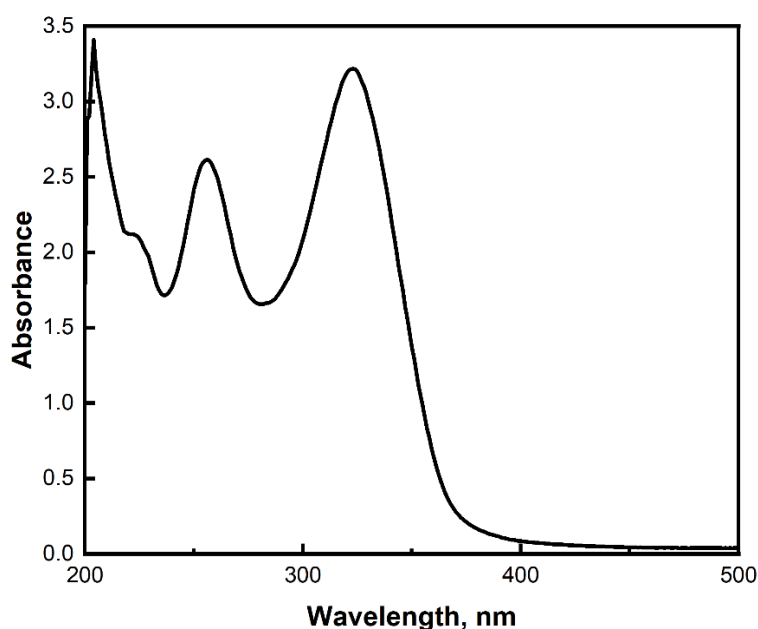


Figure 73. UV-Vis spectrum of complex $[\text{Co}(\text{bzac})_2]$

III. Crystal structure and supramolecular features.

The complex $[\text{Co}(\text{bzac})_2]$ crystallizes in the monoclinic crystal system, space group $P2_1/n$. The excellent refinement indicators attest to the high quality of the diffraction data. The absence of significant residual electron density ($\Delta\rho_{\text{max}} = 0.75 \text{ e } \text{\AA}^{-3}$; $\Delta\rho_{\text{min}} = -0.65 \text{ e } \text{\AA}^{-3}$) further confirms the accuracy of the refined structural model and the structural integrity of the complex.

The asymmetric unit comprises one half of a Co(II) ion, located on an inversion center at $(0, \frac{1}{2}, \frac{1}{2})$, together with one benzoylacetone (bzac) ligand coordinated in a bidentate chelating mode through the oxygen atoms O1 and O2 of the enolate and carbonyl groups. Each cobalt(II) center is thus coordinated by four oxygen donors, two from each of two symmetry-related bzac ligands,

forming a slightly distorted CoO_4 coordination environment. Through inversion symmetry, this arrangement results in a strictly square-planar geometry, as illustrated in Figure 74.

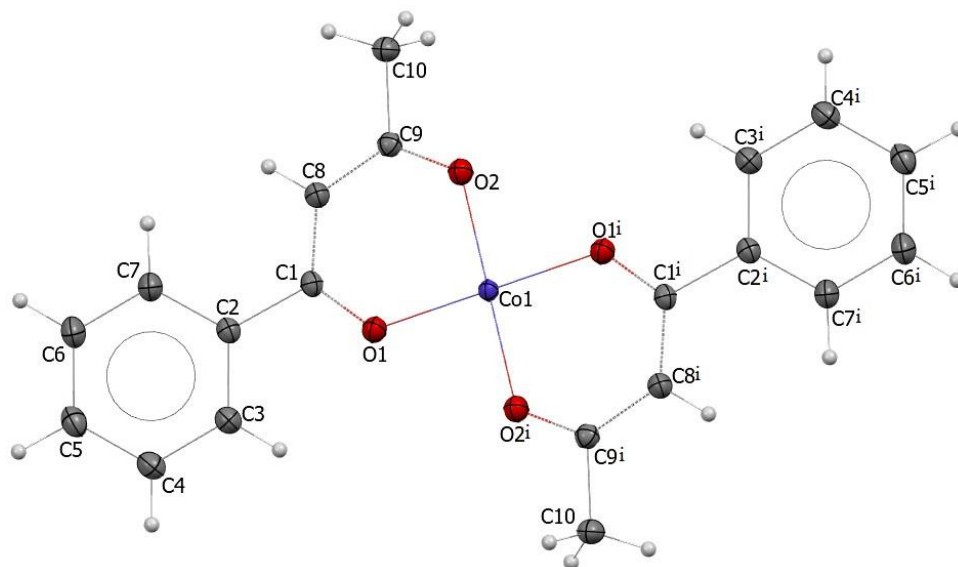


Figure 74. Perspective view of the $[\text{Co}(\text{bzac})_2]$ complex with atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius. Atoms labeled with the symbol “i” are generated by the crystallographic inversion centre (symmetry code: (i) $-x, -y, -z$.)

The Co–O bond lengths are nearly identical, with values of $\text{Co1–O1} = 1.9178(9) \text{ \AA}$ and $\text{Co1–O2} = 1.9209(8) \text{ \AA}$, while the O–Co–O bond angles span $86.52(4)^\circ$ to $93.48(4)^\circ$, consistent with a slightly distorted square-planar coordination geometry elongated along the trans O1–Co–O1 axis. The short and comparable Co–O distances reflect the strong donor ability of the enolate and carbonyl oxygen atoms, a characteristic feature of β -diketonate complexes²⁶. Similar geometrical parameters have been widely reported for $[\text{Co}(\beta\text{-diketonate})_2]$ systems, in which electronic delocalization within the O–C–C–O backbone stabilizes the metal center and enforces planarity of the chelate rings²⁷.

The coordinated bzac ligand adopts an almost planar conformation, with the cobalt atom lying close to the least-squares plane defined by O1–C1–C2–C3–O2. The aromatic phenyl substituent is nearly coplanar with the chelate ring, with a dihedral angle of approximately 12.15° , enabling effective π -conjugation across the ligand framework. This near coplanarity supports partial delocalization of electron density from the enolate moiety into the aromatic π system, a feature known to influence the photophysical properties of Co– β -diketonate complexes²⁸.

Analysis of the crystal packing reveals that $[\text{Co}(\text{bzac})_2]$ molecules assemble into zigzag layers parallel to the (b,c) plane. Each centrosymmetric molecule adopts an alternating orientation along the b axis, resulting in a corrugated stacking motif characteristic of the $P2_1/n$ space group. The nearly planar complexes are uniformly distributed within the unit cell, generating a well-organized three-dimensional framework with pronounced zigzag molecular alignment (Figure 75.a). Notably, a closely related zigzag packing arrangement has been reported for the tin(II) analogue $[\text{Sn}(\text{bzac})_2]$ by Ewings *et al.*²⁹, in which the molecules likewise adopt an alternating orientation along the monoclinic axes.

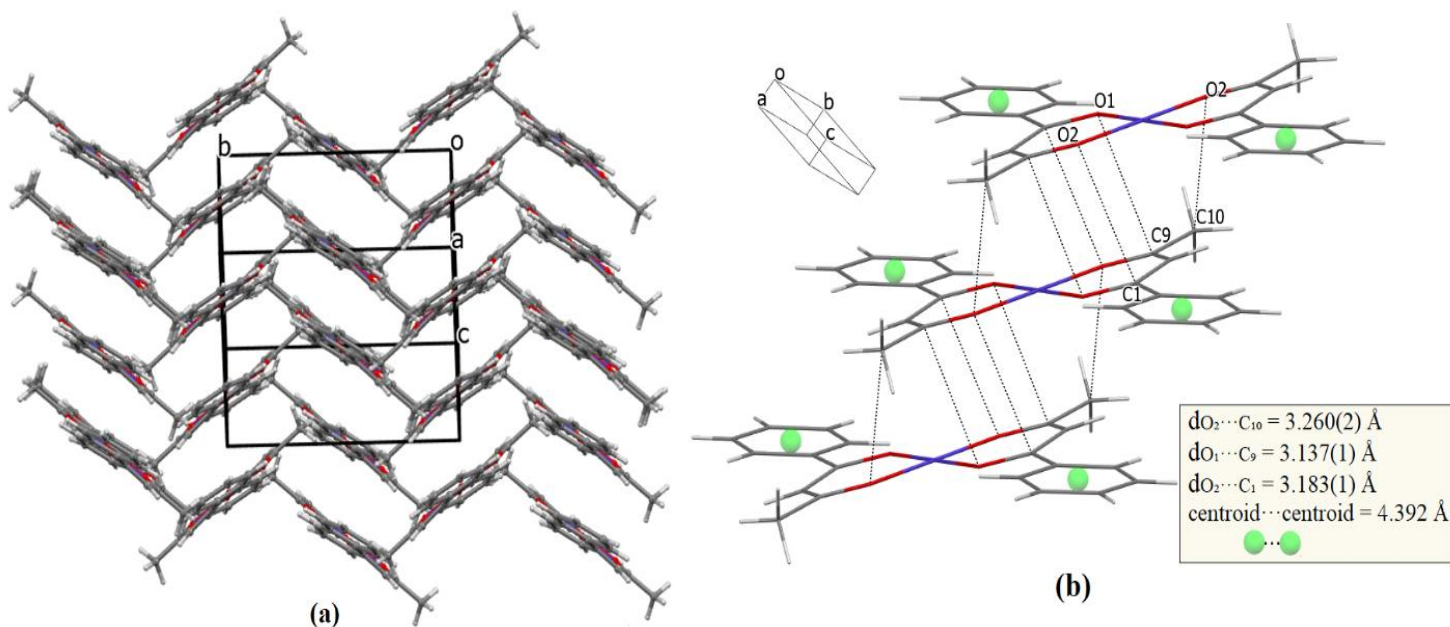


Figure 75. (a) Crystal packing of $[\text{Co}(\text{bzac})_2]$, showing zigzag molecular layers parallel to the (b,c) plane. (b) $\pi \cdots \pi$ stacking interactions between neighboring phenyl rings and illustration of $\text{O}_{\text{lp}} \cdots \text{C}\pi$ interactions between adjacent $[\text{Co}(\text{bzac})_2]$ molecules.

In the crystal packing, individual $[\text{Co}(\text{bzac})_2]$ molecules remain discrete rather than polymeric, yet they are interconnected through a network of weak $\text{C}-\text{H} \cdots \text{C}$ interactions and $\pi \cdots \pi$ stacking contacts. The $\pi-\pi$ interactions occur between adjacent phenyl rings, with a centroid–centroid separation of approximately $4.4 \text{ \AA}$ (Figure 75.b), which falls within the typical range reported for aromatic stacking in $\text{Co(II)}-\beta$ -diketonate systems ($3.8\text{--}4.4 \text{ \AA}$)³⁰. These supramolecular interactions contribute significantly to lattice stabilization and may facilitate intermolecular $\pi \cdots \pi$ coupling, thereby enhancing electronic communication across the crystal lattice³¹. Notably, such $\pi \cdots \pi$ contacts play a dual structural and electronic role: they reinforce lattice cohesion while enabling weak through-space charge delocalization and exciton migration,

phenomena that have been correlated with enhanced optical responses and low-dimensional conductivity in related Co– β -diketonate frameworks^{32,33}.

In addition, moderate C–H $\cdots$ C interactions constitute the primary supramolecular linkages between neighboring complexes. These contacts involve aromatic hydrogen atoms approaching the π clouds of adjacent phenyl rings, generating an extended three-dimensional framework stabilized by π -type interactions³⁴. The resulting molecular association gives rise to well-defined graph-set motifs $R_4^4(36)$ and $R_4^4(30)$ ³⁵ (Figure 76.a), which interconnect the complexes into corrugated supramolecular layers parallel to the (*b,c*) plane. The coexistence of these ring motifs with $\pi\cdots\pi$ stacking interactions (centroid–centroid distance = 4.392 Å) produces a highly ordered packing arrangement, in which each pseudo-square-planar Co(II) center is linked to its neighbors through a cooperative network of weak C–H $\cdots$ C contacts and aromatic overlaps³⁶.

A view of the crystal packing along the *a* axis (Figure 76.b) highlights the orderly arrangement of discrete complexes within the monoclinic unit cell. The Co(II) centers occupy inversion centers and are coordinated by two chelating bzac ligands. The molecules align along the *b* axis and alternate in orientation, resulting in a dense and regular packing motif.

Furthermore, the packing diagram (Figure 75.b) reveals short O $\cdots$ C intermolecular contacts between neighboring $[\text{Co}(\text{bzac})_2]$ units, with distances in the range 3.137–3.261 Å, slightly shorter than the sum of the corresponding van der Waals radii. These contacts involve the carbonyl and enolate oxygen atoms (O1, O2, O2') and β -diketonate carbon atoms (C9, C10) of adjacent molecules³⁷. The geometry of these contacts is indicative of lone-pair– π interactions, in which oxygen lone pairs interact with the delocalized π system of the O–C=C–C=O chelate ring^{38,39}. Such weak O $\cdots\pi$ interactions are frequently observed in β -diketonate frameworks and, while subtle, play an important stabilizing role in consolidating the zigzag supramolecular architecture of the crystal²⁴.

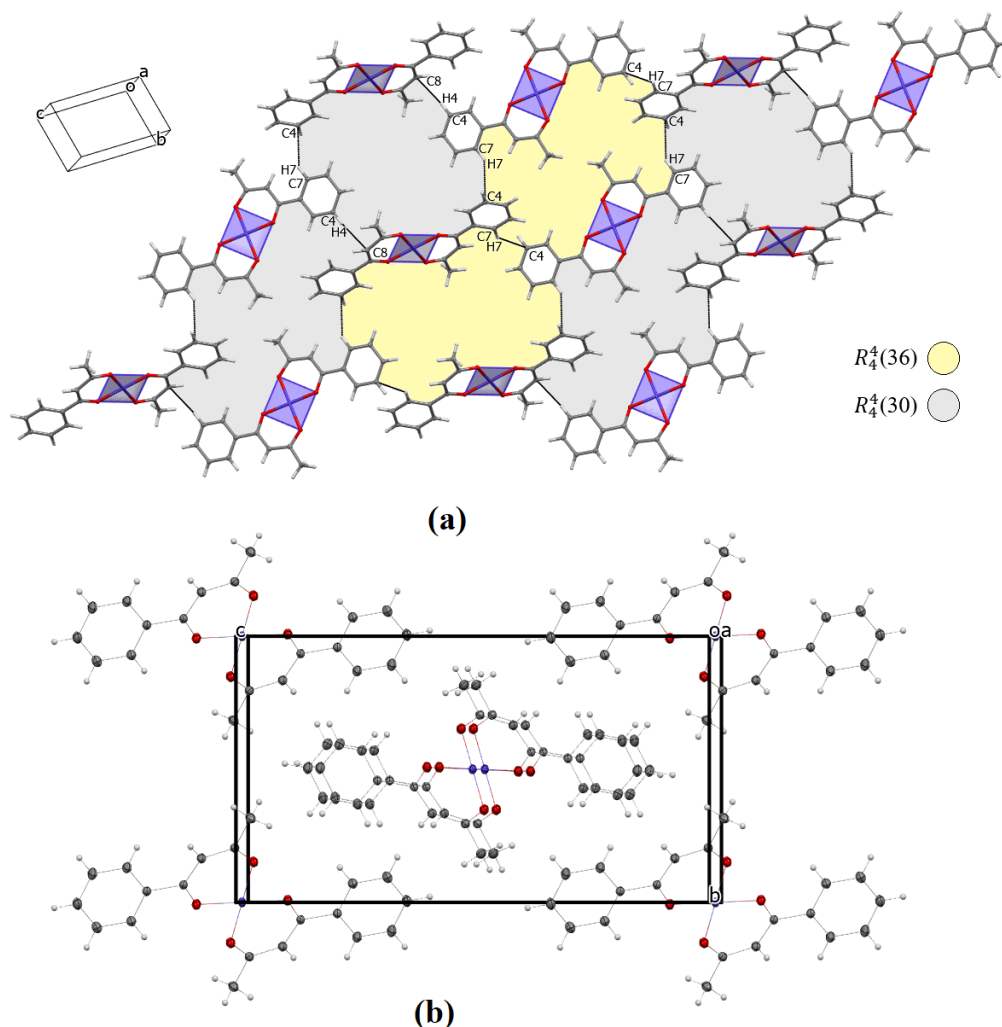


Figure 76. Supramolecular packing of $[\text{Co}(\text{bzac})_2]$ **(a)** showing $\text{C}-\text{H}\cdots\text{C}$ interactions forming $R_4^4(30)$ (grey) and $R_4^4(36)$ (yellow) ring motifs that link the complexes into layers parallel to the (b,c) plane, And **(b)** viewed along the a -axis, showing the centrosymmetric $\text{Co}(\text{II})$ complexes arranged in alternating rows along the b -axis within the monoclinic unit cell.

IV. Comparative crystallographic analysis based on the CSD.

A targeted Cambridge Structural Database (CSD) survey (v2025.3)⁴⁰ identified seven closely related structures of the $[\text{M}(\text{bzac})_2]$ type (where bzac = benzoylacetonate). This series is unique as only the metal center varies, while the bzac ligand and its bidentate O,O' -chelation motif remain constant. The identified compounds, with their corresponding refcodes, are: Pb (ZZZPQG⁴¹), Pd(*trans*) (PDPBTD⁴²), Pd(*cis*) (PBONSN²⁹), Sn (CBZACP⁴³), Cu (CUBEAC⁴⁴), Cu01 (CUBEAC01⁴⁵), and Cu02 (CUBEAC02⁴⁶). A visual summary is provided in Figure 77.

Chapter II. Planarity-driven structure–morphology correlations in a Co(II) benzoylacetonate: comparative insights across the $[M(bzac)_2]$ family

Crystallographically, all structures feature a mononuclear, non-polymeric $[M(bzac)_2]$ core stabilized by the bidentate O,O' chelation, forming the canonical six-membered β -diketonate ring. However, both the metal coordination geometry and the resulting supramolecular packing vary systematically with the identity of the metal center.

Lead (II) (ZZZPQG)⁴¹: Represents an early X-ray study. The reported space group ($P2_1an$, equivalent to the non-standard Pcn) and pseudo-halving of the cell are consistent with an approximately planar, holodirected PbO_4 environment. The original crystallographic coordinates were not deposited and remain unavailable in the CCDC.

Palladium (II) – *trans* Isomer (PDPBTD)⁴²: Adopts a classic square-planar PdO_4 geometry (d^8 configuration; $Pd-O \approx 1.97$ Å), with the metal and donor atoms coplanar by symmetry, forming layered packing parallel to the *b*-axis.

Palladium (II) – *cis* Isomer (PBONSN)²⁹: Reported later, this isomer retains the square-planar PdO_4 core but exhibits subtle torsional adjustments of the phenyl substituents, highlighting intramolecular steric effects within the *cis* configuration.

Tin (II) (CBZACP)⁴³: Adopts a distorted pseudo-trigonal bipyramidal geometry. The $Sn-O$ bond lengths differ between equatorial (2.135 Å) and axial (2.290 Å) positions, with the stereochemically active lone pair occupying an equatorial site. This geometry results in a monomeric, non-bridged molecular packing in space group $C2/c$.

Copper (II) Series (CUBEAC⁴⁴, CUBEAC01⁴⁵, CUBEAC02⁴⁶): Multiple structures confirm a consistent mononuclear, square-planar CuO_4 coordination, with subtle modulations from crystal packing and solvation.

The earliest (CUBEAC) shows discrete monomers ($P2_1/c$) with short intermolecular $Cu \cdots C$ contacts (~ 3.02 Å) supporting a pseudo-layered architecture. Later studies (CUBEAC01⁴⁵, CUBEAC02⁴⁶) confirmed the same O, O'-chelating mode. One variant (CUBEAC02⁴⁶) demonstrates the axial lability of Cu (II), exhibiting a slight distortion toward square-pyramidal geometry due to weak coordination from a methanol solvent molecule.

The present $[Co(bzac)_2]$ complex retains the invariant O, O'-chelating motif and features a centrosymmetric, four-coordinate CoO_4 core. Its molecular packing distinguishes it from the planar stacking of Pd (II)/Cu (II) analogues and the axially distorted Sn (II) structure. This confirms that the cobalt complex adopts a strict square-planar geometry, contrasting with the pseudo-trigonal bipyramidal geometry of Sn (II).

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The comparative analysis across the $[M(\text{bzac})_2]$ family, summarized in Table 21, reveals that while the bzac chelating topology is conserved, metal-dependent stereochemistry dictates the degree of planarity and supramolecular cohesion. This positions $[\text{Co}(\text{bzac})_2]$ as a crystallographically well-defined and significant member within this classical β -diketonate series.

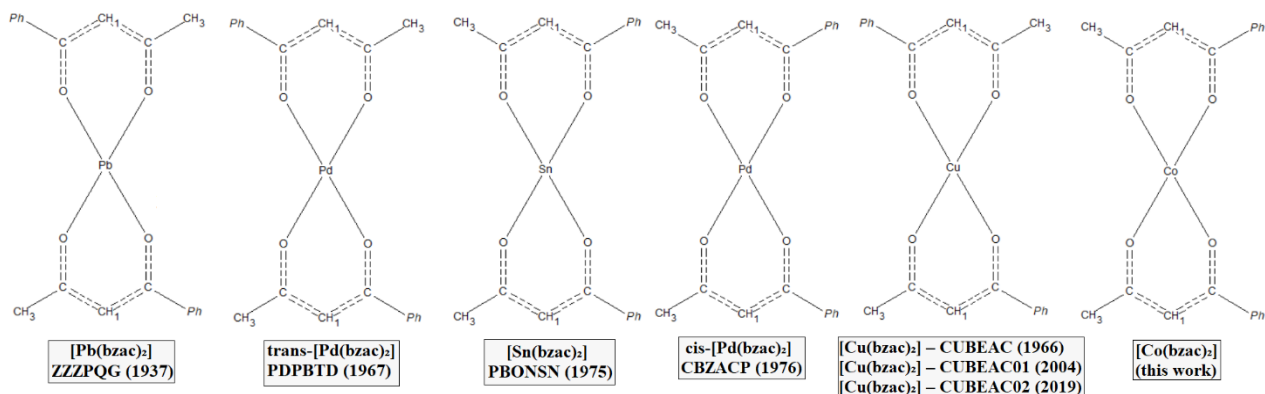


Figure 77. Chemical diagram of $[M(\text{bzac})_2]$ analogues ($M = \text{Pb}, \text{Pd}, \text{Sn}, \text{Cu}$ or Co) with corresponding CSD refcodes. $\text{Pt}(\text{bzac})_2$

Table 21. Crystallographic comparison of $[M(\text{bzac})_2]$ complexes reported in the CSD (v2025.3) and the present $[\text{Co}(\text{bzac})_2]$ compound.

Complex	Refcode	Space group	Geometry at M	M–O (Å)	Molecular arrangement	Year
$[\text{Pb}(\text{bzac})_2]$	ZZZPQG	$P2_1an$	Near-planar PbO_4 (holodirected)	nd*	nd*	1937 [50]
<i>trans</i> - $[\text{Pd}(\text{bzac})_2]$	PDPBTD	$P2_1/c$	Square-planar	1.965– 1.965	Layered packing along <i>b</i>	1967 [51]
$[\text{Sn}(\text{bzac})_2]$	PBONSN	$C2/c$	Hemidirected, pseudo- trigonal- bipyramidal	2.138– 2.294	Slightly twisted chelate planes	1975 [38]
<i>cis</i> -	CBZACP	$P2_1/c$	Square-planar	1.975– 1.978	Molecular stacking with	1976 [52]

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$[\text{Pd}(\text{bzac})_2]$					stereochemically active lone pair	
$[\text{Cu}(\text{bzac})_2]$	CUBEA C	$P2_1/c$	Square-planar	1.914– 1.931	Discrete monomers; pseudo-layered packing with $\text{Cu}\cdots\text{C}\approx 3.02\text{ \AA}$	1966 [53]
$[\text{Cu}(\text{bzac})_2]$	CUBEA C01	$P2_1/n$	Square-planar	1.918– 1.924	Planar molecular stacking	2004 [54]
$[\text{Cu}(\text{bzac})_2]$	CUBEA C02	$P2_1/c$	Distorted square-planar	1.914– 1.918	Weak axial elongation depending on solvation	2019 [55]
$[\text{Co}(\text{bzac})_2]$	/	$P2_1/n$	Strictly square-planar	1.919– 1.922	Zigzag layers parallel to (b,c)	This work

Note: (*) No atomic coordinates are available for the early $\text{Pb}(\text{bzac})_2$ report.

IV. 1. Comparative analysis of non-covalent interaction networks across the $[M(\text{bzac})_2]$ series.

To place the structural features of the new Co (II) derivative into a broader supramolecular context, we benchmarked its non-covalent interaction network against the full $[M(\text{bzac})_2]$ series ($M = \text{Co}, \text{Cu}, \text{Pd}, \text{Sn}$). This comparative analysis reveals a clear metal-dependence in π -stacking efficiency, metal-arene engagement, and the overall connectivity of secondary contacts.

The Co (II) and Cu (II) derivatives exhibit the shortest centroid-to-centroid ($\pi\cdots\pi$) separations and the most compact metal-to-arene approaches. This results in tightly packed, one-dimensional columnar stacks where the chelate planes and phenyl rings are efficiently π -locked.

$[\text{Co}(\text{bzac})_2]$: Strong $\pi\cdots\pi$ stacking, combined with relatively short $\text{Co}\cdots\text{C}(\text{arene})$ and $\text{C}-\text{H}\cdots\pi$ contacts, generates coherent aromatic columns aligned along the $\text{Co}\cdots\text{Co}$ vector.

Chapter II. *Planarity-driven structure–morphology correlations in a Co(II) benzoylacetate: comparative insights across the [M(bzac)₂] family*

[Cu(bzac)₂] variants: Preserve a similar packing motif, with even shorter Cu··· π interactions and additional C–H··· π links that rigidify the columns and provide lateral cross-linking.

Together, these features point to a more strongly interconnected, anisotropic lattice for the Co and Cu complexes, where the metal center not only defines the local coordination geometry but also amplifies long-range cohesion by mediating efficient π -stacking.

In contrast, the Sn (II) and Pd (II) congeners display weaker and more diffuse non-covalent networks.

[Sn(bzac)₂] (PBONSN): The framework is dominated by longer, more slipped π ··· π contacts and softer Sn···C(arene) approaches. Aromatic layers are maintained primarily by dispersive C···C contacts rather than directed metal-assisted stacking.

[Pd(bzac)₂] isomers: Illustrate the sensitivity of supramolecular assembly to both metal identity and ligand configuration. The *trans*-Pd complex features the longest and most offset π ··· π contacts of the series, with only modest Pd··· π engagement. The *cis*-Pd isomer supports a somewhat more compact Pd···arene approach but still lacks the dense, columnar connectivity observed for Co and Cu.

The evolution from Sn/Pd to Co/Cu corresponds to a progressive reinforcement and directionalization of the non-covalent interaction manifold. Co (II) and Cu (II) sit at the strongly stacked, structurally coherent end of the series.

This metal-dependent modulation of π ··· π , metal··· π , and C–H··· π contacts provides a clear structural rationale for the distinctive packing anisotropy and morphological behavior of [Co(bzac)₂]. It also underpins the structure–property correlations that can be drawn for this compound within the broader [M(bzac)₂] family.

Table 22. Key non-covalent interactions in the [M(bzac)₂] series (M = Co, Cu, Pd, Sn), highlighting the principal $\pi\cdots\pi$, metal– π , and C–H $\cdots\pi$ contacts extracted from the crystal structures.

Complex (CSD Refcode)	Key interaction type	Atoms / Rings involved	Distance (Å)	Structural significance
[Co(bzac)₂] (this work)	$\pi\cdots\pi$ stacking	Centroid $\cdots$ Centroid	4.39	Strong parallel stacking, generates columnar aromatic chains.
	Metal $\cdots$ Metal	Co1 $\cdots$ Co1	4.392	Linear Co $\cdots$ Co arrangement reinforcing the columns.
	Metal $\cdots$ Arene	Co1 $\cdots$ C3	3.27	Short Co $\cdots\pi$ contact stabilising the π -stack.
	C–H $\cdots\pi$ / C $\cdots$ H	C4 $\cdots$ H7 / H4 $\cdots$ C8	2.78–2.90	Tight side contacts locking adjacent columns/ stabilizing lateral packing.
[Sn(bzac)₂] (PBONSN)²⁹	$\pi\cdots\pi$ stacking	Centroid $\cdots$ Centroid	5.16	Moderately slipped rings, weaker π -stacking.
	Metal $\cdots$ Arene	Sn1 $\cdots$ C4 / Sn1 $\cdots$ C7	3.74–3.78	Weak Sn $\cdots$ C contacts contributing to layer cohesion.
	C $\cdots$ C	Several aromatic C $\cdots$ C	~3.30–3.40	Packing dominated by dispersive C $\cdots$ C interactions.
<i>trans</i>-[Pd(bzac)₂] (PDPBTD)⁴²	$\pi\cdots\pi$ stacking	Centroid $\cdots$ Centroid	5.74–5.88	Long, highly slipped π -contacts; only moderate stacking.
	Metal $\cdots$ Arene	Pd1 $\cdots$ C1	3.75	Weak Pd $\cdots\pi$ interaction.
	C $\cdots$ C	C8B $\cdots$ C8	3.37	Lateral aromatic contacts forming sheets.
<i>cis</i>-[Pd(bzac)₂]	$\pi\cdots\pi$ stacking	Centroid $\cdots$ Centroid	5.21	Shorter than <i>trans</i> , but still

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(CBZACP) ⁴³		roid		moderate and slipped.
	Metal⋯Arene	Pd1⋯C13	3.30	Strongest Pd⋯C(arene) interaction in the Pd series.
	C⋯C	C14⋯C20	3.41	Edge–edge aromatic contacts stabilizing ribbons.
[Cu(bzac)₂] (CUBEAC) ⁴⁴	$\pi\cdots\pi$ stacking	Centroid⋯Centroid	4.47	Strong, compact face-to-face stacking.
	Metal⋯Metal	Cu1⋯Cu1	4.475	Cu⋯Cu pathways parallel to aromatic columns.
	Metal⋯Arene	Cu1⋯C4	3.01	Very short Cu⋯ π contact, highly stabilising.
	C–H⋯ π	H5B⋯C4B / H5⋯C4	~2.95	Strong C–H⋯ π contacts tightening the lattice.
[Cu(bzac)₂] (CUBEAC01) ⁴⁵	$\pi\cdots\pi$ stacking	Centroid pairs	4.47	Twin strong π – π interactions, typical of Cu(bzac) ₂ .
	Metal⋯Arene	Cu1⋯C3 / Cu1⋯C3B	3.37–3.44	Cu⋯ π stabilisation on both faces.
	C–H⋯ π	H1B⋯C10 / H2⋯C...	~3.04	Locks aromatic layers in 3D.
[Cu(bzac)₂] (CUBEAC02) ⁴⁶	$\pi\cdots\pi$ stacking	Centroid pairs	4.47	Same strong face-to-face stacking as CUBEAC.
	Metal⋯Arene	Cu1⋯C10	3.02	Robust Cu⋯ π contact.
	C–H⋯ π	H17⋯C... / H19⋯C...	2.93–2.94	Shortest H⋯C contacts of all Cu complexes.

IV. 2. Comparative analysis of structural, electronic and supramolecular trends in the [M(bzac)₂] family.

The structural and electronic properties of the [M(bzac)₂] complexes evolve progressively with the metal center, moving from distortion by stereochemically active lone pairs to the rigid symmetry of ligand-field-stabilized square-planar geometries. A comparison across the Pb (II), Sn (II), Pd (II), Cu (II), and Co (II) analogues reveals this coherent structural continuum.

Lone-Pair vs. Planar Geometries: The series illustrates the classical contrast between main-group and transition-metal behavior. The Pb (II) and Sn (II) derivatives are defined by the inert-pair effect, with Sn (II) exhibiting explicit hemidirectional distortion. In contrast, the transition-metal centres (Pd, Cu, Co) adopt planar geometries stabilized by ligand-field effects.

Subtleties within Planar Geometries: Among the planar structures, fine variations exist. Pd (II) (d⁸) represents the ideal, strain-free square-planar limit. Cu (II) (d⁹) maintains this core geometry but reveals a latent Jahn-Teller instability through axial lability in the presence of donors. The Co (II) (d⁷) complex reported here adopts a rigid, centrosymmetric square-planar structure with no axial engagement.

Supramolecular and Electronic Consequences: This geometric evolution directly influences supramolecular organization and electronic communication. The distortion in Sn (II) disrupts continuous aromatic overlap. Conversely, the high planarity in Co(bzac)₂ and Cu(bzac)₂ facilitates efficient $\pi\cdots\pi$ stacking (centroid separations $\sim 3.9\text{--}4.4$ Å), with the Co analogue showing maximized overlap. This enhanced π -communication provides a structural basis for the charge-transfer and photophysical properties characteristic of such systems.

The [M(bzac)₂] family exemplifies a continuous transition from stereochemically active lone-pair distortion to ligand-field-enforced planarity. This progression mirrors the increasing role of metal d-orbitals in M–O π -bonding. Within this continuum, the Co (II) complex occupies a pivotal position: it combines the high planarity and rigidity of a d⁷ square-planar centre with a dense network of $\pi\cdots\pi$ interactions, making it a structurally definitive and electronically significant member of the series.

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Table 23. Comparative structural and electronic features of the [M(bzac)₂] series.

Metal center (Year) ⁴¹	Electronic configuration	Dominant stereochemical / ligand-field effect	Key supramolecular / intermolecular interactions	Electronic & optical implications
Pb(II) (1937)	6s ² 6p ⁰	Inert-pair effect → holodirected coordination (inactive lone pair)	Weak dispersion-driven contacts; no directional $\pi\cdots\pi$ stacking	Minimal covalency; electronic isolation of metal; weak optical activity
Sn(II) (1975) ²⁹	5s ² 5p ⁰	Active s ² lone pair → hemidirected geometry	Asymmetric packing; absence of $\pi\cdots\pi$ overlap	Strong stereochemical distortion; low conjugation; poor delocalization
Pd(II) (trans) (1967) ⁴²	4d ⁸	Ligand-field stabilization → perfect square-planar PdO ₄	Layered packing b; Pd and O coplanar by symmetry	High orbital overlap; strong M–O π back- bonding; intense LMCT absorption
Pd(II) (cis) (1976) ⁴³	4d ⁸	Same field as trans; steric torsion of phenyls	Weak interlayer $\pi\cdots\pi$; limited planarity	Reduced delocalization due to ligand torsion
Cu(II) (1966) ⁴⁴	3d ⁹	Jahn–Teller axial lability; dx ² –y ² ground state	Layer-like packing; short Cu $\cdots$ C contacts (~3.0 Å)	Partial electronic delocalization; moderate optical anisotropy
Cu(II) (2004) ⁴⁵	3d ⁹	Same field, minor axial strain; solvent- free form	Discrete monomers ; no polymerization	Stable planar field ; reproducible optical response
Cu(II) (2019) ⁴⁶	3d ⁹	Solvent coordination controls geometry (5- coord. ↔ 4-coord.)	$\pi\cdots\pi$ and H-bonding modulated by solvent inclusion	Solvent-dependent color, variable absorption edges

Co(II) (this work)	3d ⁷	Ligand-field stabilization under inversion symmetry	Zigzag $\pi\cdots\pi$ stacking (centroid–centroid = 4.39 Å); C–H $\cdots$ O & C– H $\cdots$ C motifs	Enhanced $\pi\cdots\pi$ coupling and charge delocalization; potential optical and semiconducting behavior
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IV. 3. Comparative morphological analysis of M(bzac)₂ complexes.

A comparative analysis of the calculated BFDH (Bravais-Friedel-Donnay-Harker) morphologies for the isostructural [M(bzac)₂] complexes (M = Pb, *trans*-Pd, *cis*-Pd, Sn, Cu, Co) reveals the significant influence of the metal center on crystal growth anisotropy and final habit. This qualitative comparison, based on the presence and prominence of dominant crystallographic planes from experimental data, provides a consistent framework for assessing how metal-dependent coordination and packing forces are expressed in external crystal morphology.

The [Cu(bzac)₂] series demonstrates a remarkable morphological evolution across different studies, progressing from a prismatic to a highly acicular habit. This trend highlights how subtle reinforcements in π -overlap and intermolecular interactions can dramatically amplify growth anisotropy along a specific crystallographic direction.

The newly synthesized [Co(bzac)₂] complex exhibits a distinctly acicular habit, elongated along [001]. This strong anisotropy is driven by $\pi\cdots\pi$ stacking and lone-pair $\cdots\pi$ (O $\cdots$ C) interactions, directly explaining the experimentally observed needle-like crystal morphology. The close similarity between the predicted morphology for [Co(bzac)₂] and the later [Cu(bzac)₂] structures underscore their shared structural motifs: square-planar coordination and stacking-driven, anisotropic growth.

In summary, the BFDH analysis successfully correlates metal identity and resulting coordination geometry with macroscopic crystal habit. The progression from isometric (Pb, *cis*-Pd) to acicular (Cu, Co) forms maps directly onto the increasing strength and directionality of π -stacking and other non-covalent interactions within the lattice.

IV. 3. 1. Morphology-structure correlation and comparative discussion.

The morphological sequence across the [M(bzac)₂] series follows a clear order of increasing anisotropy: Pb $\approx$ *cis*-Pd < *trans*-Pd < Sn < Cu < Co. This progression is a direct consequence of the interplay between the metal's coordination geometry, its electronic

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configuration, and the resulting supramolecular forces. Complexes with highly planar M–O cores (Pd, Cu, Co) promote layered or one-dimensional growth via directional interactions like π – π stacking, leading to acicular (needle-like) habits. In contrast, complexes where the metal has a stereochemically active lone pair (Pb, Sn) exhibit steric distortion and engage in more multidirectional secondary interactions, resulting in more isotropic, equant crystal shapes.

This comparative study confirms that the central metal ion is the primary determinant of crystal growth anisotropy. The newly synthesized $\text{Co}(\text{bzac})_2$ complex exhibits the most pronounced elongation. This is attributed to strong, cooperative $\pi \cdots \pi$ stacking and $\text{O} \cdots \text{C}(\text{lone-pair} \cdots \pi)$ contacts that preferentially guide growth along the $[001]$ direction, effectively bridging the structural and morphological behavior observed in the Cu (II) analogues.

This finding reinforces the intrinsic connection between a metal's electronic structure, the supramolecular architecture it enables, and the resulting external crystal morphology. It also validates the predictive accuracy of the BFDH model for analyzing metal– β -diketonate systems.

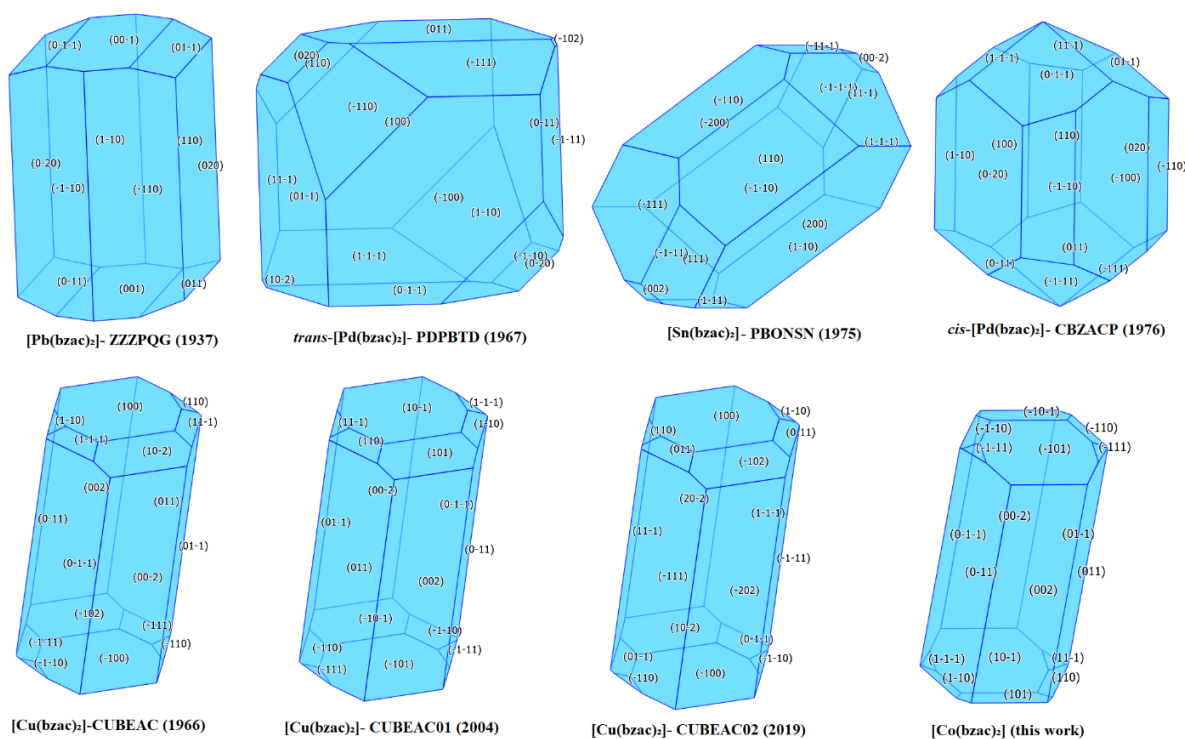


Figure 78. Predicted BFDH morphologies of the $[M(\text{bzac})_2]$ ($M = \text{Pb, Pd, Sn, Cu, Co}$) series generated from single-crystal data.

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Table 24. Morphology–structure correlation within the $[M(\text{bzac})_2]$ series

Complex Refcode Year	Dominant faces (BFDH)	Characteristic crystal habit	Main directional interactions	Growth anisotropy / elongation	Structural–morphological correlation
[Pb(bzac)₂] ZZZPQG (1937) ⁴¹	{110}, {001}, {011}	Prismatic, nearly isometric	Weak van der Waals and $\text{O}\cdots\text{C}(\text{lp}\cdots\pi)$	Very low	Isotropic growth due to lone- pair repulsion and absence of strong π -stacking
trans-[Pd(bzac)₂] PDPBTD (1967) ⁴²	{100}, {110}, {011}	Flattened polyhedron	$\pi\cdots\pi$ and C– $\text{H}\cdots\text{O}$ within layers	Moderate (2D)	Compact morphology governed by planar coordination and tight packing
[Sn(bzac)₂] PBONSN (1975) ²⁹	{110}, {200}, {002}	Elongated bipyramidal	$\text{O}\cdots\text{C}(\text{lp}\cdots\pi)$ and C–H $\cdots\text{O}$	Moderate	Slight elongation along [001] induced by asymmetric coordination and lone pair
cis-[Pd(bzac)₂] CBZACP (1976) ⁴³	{100}, {110}, {011}	Compact prismatic	Symmetric C– $\text{H}\cdots\text{O}$, weak $\pi\cdots\pi$	Low	Symmetric cis-configuration reduces anisotropy; denser 3D packing
[Cu(bzac)₂] CUBEAC (1966) ⁴⁴	{001}, {011}, {100}	Prismatic, slightly elongated	π – π stacking and $\text{O}\cdots\text{C}(\text{lp}\cdots\pi)$	High	Onset of 1D growth along [001] direction
[Cu(bzac)₂] CUBEAC01 (2004) ⁴⁵	{002}, {011}, {10–1}	Acicular	$\pi\cdots\pi$ stacking reinforced by axial elongation	Very high	Strong directional packing enhances anisotropy; needle- like habit
[Cu(bzac)₂] CUBEAC02 (2019) ⁴⁶	{100}, {10–1}, {011}	Needle-like (acicular)	Cooperative $\pi\cdots\pi$ and C– $\text{H}\cdots\text{O}$	Extreme	Solvation promotes 1D propagation and face- selective growth
[Co(bzac)₂] this work	{002}, {011}, {10–1}	Highly acicular, elongated along [001]	$\pi\cdots\pi$ stacking and $\text{O}\cdots\text{C}(\text{lp}\cdots\pi)$	Extreme	Maximum anisotropy driven by strong planar conjugation and directional stacking

IV. 4. Quantitative planarity metrics for the β -Diketonate chelate.

To quantitatively assess the "near-planarity" description of [M(bzac)₂] complexes, a consistent set of geometrical parameters was extracted from the Cambridge Structural Database (CSD) for a detailed comparison. These metrics, summarized in Table 6, probe different aspects of molecular planarity:

1. *RMSD_{chelate}*: Root-mean-square deviation of the O–C–C–O chelate backbone from its least-squares plane.
2. $\Delta(M-O_4)$: Displacement of the metal from the mean plane of the four coordinating oxygen atoms.
3. $\phi_{\text{chelate-phenyl}}$ *: Dihedral angle between the chelate ring and its appended phenyl ring.
4. ϕ_{inter} *: Dihedral angle between the two β -diketonate ligands, measuring their mutual twist.

Together, these parameters quantify the local distortion of the ligand skeleton and the overall co-planarity of the conjugated system around the metal center. Sn(bzac)₂ exhibits a flat chelate but a highly distorted, non-planar coordination sphere due to the stereochemically active lone pair (large $\Delta(\text{Sn}-O_4)$ and ϕ_{inter}). *cis*-Pd(bzac)₂ shows significant, molecule-dependent distortion in both the chelate backbone and phenyl ring orientation, induced by crystal packing. *trans*-Pd(bzac)₂ and the Cu(bzac)₂ series possess strictly planar M–O₄ cores and eclipsed ligands ($\phi_{\text{inter}} = 0^\circ$), with only minor ligand puckering and phenyl tilts. [Co(bzac)₂] resides at the high-planarity end of the series. It features a perfectly coplanar CoO₄ core, an eclipsed ligand arrangement ($\phi_{\text{inter}} = 0^\circ$), and a relatively small chelate-phenyl twist. The slightly higher *RMSD_{chelate}* value reflects a subtle, symmetric "breathing" of the chelate ring rather than a significant buckle. Special Case – Pb(bzac)₂: Quantitative metrics cannot be computed due to the unavailability of atomic coordinates. However, the original crystallographic description notes the molecule "very nearly has C_{2v} symmetry," supporting its qualitative classification as nearly planar.

This geometric analysis confirms that [Co(bzac)₂] is among the most planar members of the [M(bzac)₂] family. Its high degree of structural planarity is consistent with its plate-like predicted morphology and the minimal splitting of frontier π -orbitals observed in computational studies, underscoring the strong link between its precise molecular geometry and its broader physicochemical properties.

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Table 25. Quantitative descriptors of chelate planarity and coordination symmetry in M(bzac)₂ complexes

Complex	CSD refcode	RMSD _{chelate} (Å)	Δ(M– O ₄ plane) (Å)	Φ _{chelate– phenyl} (°)	Φ _{inter} (°)	Planarity
Pb(bzac) ₂	ZZZPQG ⁴¹	nd*	nd*	nd*	nd*	Nearly planar (C _{2v} -like pseudosymmetry)
Sn(bzac) ₂	PBONSN ²⁹	0.002	1.02	30.5	75.5	Hemidirected / distorted
trans-Pd(bzac) ₂	PDPBTD ⁴²	0.006	0.000	23.5	0.0	Highly planar
cis-Pd(bzac) ₂	CBZACP ⁴³	0.027 / 0.002 (A/B)	0.036	17 / 41 (A/B)	12.7	Planar
Cu(bzac) ₂	CUBEAC ⁴⁴	0.022	0.000	16.1	0.0	Planar
Cu(bzac) ₂	CUBEAC01 ⁴⁵	0.011	0.000	5.9	0.0	Planar
Cu(bzac) ₂	CUBEAC02 ⁴⁶	0.007	0.000	7.4	0.0	Slightly distorted
Co(bzac) ₂ (this work)	–	0.038	0.000	12.15	0.0	Highly planar

* No crystallographic atomic coordinates (x, y, z) were deposited for ZZZPQG (Pb(bzac)₂). The original X-ray report (Cox, Webster & Wardlaw, 1937)⁴⁷ states that the molecule “very nearly has C_{2v} symmetry”, which is only possible for a nearly planar configuration. Therefore, Pb(bzac)₂ is classified as *nearly planar*, although quantitative planarity metrics (RMSD, Δ(M–O₄), dihedral angles) cannot be compute.

V. Density functional theory (DFT).

The ground-state geometry of $[\text{Co}(\text{bzac})_2]$ was optimized using Density Functional Theory (DFT) with the B3LYP functional and the LanL2DZ basis set⁴⁸.

The DFT-optimized molecular structure of $[\text{Co}(\text{bzac})_2]$ retains the key experimental features: the planarity of the CoO_4 chromophore and the inversion symmetry at the cobalt center observed in the solid state (space group $P2_1/n$). Excellent agreement is observed between the calculated and experimental geometric parameters (see Table 26 for details). The calculated Co–O bond lengths (1.790–1.796 Å) are slightly shorter than the experimental values (1.918–1.921 Å). This discrepancy is consistent with the absence of intermolecular interactions in the gas-phase model⁴⁹. The mean C–C and C–O bond lengths (1.399 Å calc. vs. 1.395 Å exp.) and internal bond angles (range: 86.5–180°; mean deviation $\approx 1.7^\circ$) show near-perfect correlation with the experimental data. Strong linear correlations confirm the structural fidelity: bond lengths: $R^2 = 0.9996$ and bond angles: $R^2 = 0.9995$.

These relationships are illustrated in the regression plots (Figure 79.a–d), where the fitted equations yield a slope (γ) of approximately 1.002 and R^2 values near 0.999 for both parameters.

The superposition of the experimental (SC-XRD) and DFT-optimized geometries (Figure 79.e) demonstrates an almost perfect overlap of the molecular frameworks, visually confirming the remarkable consistency between the two structures and validating the accuracy of the computational model.

Table 26. Optimized bond lengths and bond angles for $[\text{Co}(\text{bzac})_2]$ complex calculated by DFT in comparison with SC-XRD data.

Bond length	EXP (Å)	B3LYP (Å)	Bond length	EXP (Å)	B3LYP (Å)
Co1—O1 ⁱ	1.9178 (9)	1.7897	C2—C3	1.3981 (15)	1.4056
Co1—O1	1.9178 (9)	1.7897	C2—C7	1.3990 (15)	1.4049
Co1—O2	1.9209 (8)	1.796	C7—C6	1.3921 (16)	1.3934
Co1—O2 ⁱ	1.9209 (8)	1.796	C5—C4	1.3903 (18)	1.3976
O1—C1	1.2770 (13)	1.311	C5—C6	1.3922 (17)	1.3976
O2—C9	1.2739 (13)	1.3114	C3—C4	1.3930 (16)	1.3916
C1—C8	1.4082 (14)	1.4004	C9—C8	1.4053 (14)	1.391
C1—C2	1.4932 (14)	1.483	C9—C10	1.5071 (15)	1.5102
Bond angles	Exp (°)	B3LYP (°)	Bond angles	Exp(°)	B3LYP (°)
O1 ⁱ —Co1—O1	180.0	180	C3—C2—C1	118.77 (9)	117.9136
O1 ⁱ —Co1—O2	93.48 (4)	94.1613	C7—C2—C1	122.30 (9)	123.2889
O1—Co1—O2	86.52 (4)	94.1613	C6—C7—C2	120.85 (10)	120.4628

O1 ⁱ —Co1—O2 ⁱ	86.52 (4)	85.8387	C4—C5—C6	119.93 (11)	119.6751
O1—Co1—O2 ⁱ	93.48 (4)	94.1613	C4—C3—C2	120.27 (10)	120.6445
O2—Co1—O2 ⁱ	180.0	180	C7—C6—C5	119.74 (11)	120.2658
C1—O1—Co1	126.68 (7)	129.6572	C5—C4—C3	120.33 (11)	120.1544
C9—O2—Co1	125.40 (7)	127.9538	O2—C9—C8	125.74 (9)	124.1837
O1—C1—C8	124.27 (9)	122.3517	O2—C9—C10	115.44 (9)	115.3839
O1—C1—C2	115.60 (9)	115.4125	C8—C9—C10	118.82 (9)	120.4324
C8—C1—C2	120.13 (9)	122.2358	C9—C8—C1	123.88 (9)	121.6924
C3—C2—C7	118.89 (9)	118.7974			

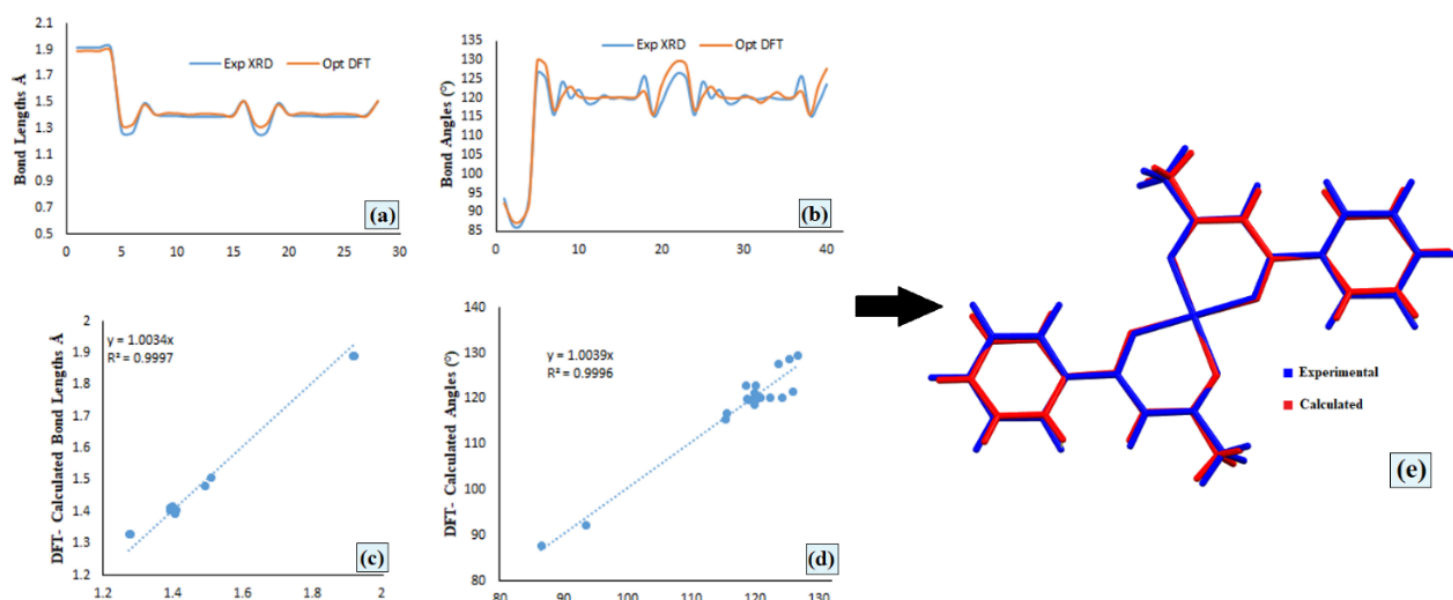


Figure 79. Comparison between experimental (SC-XRD) and DFT-optimized geometrical parameters for $[\text{Co}(\text{bzac})_2]$: **(a)** bond lengths, **(b)** bond angles, **(c–d)** regression plots showing near-unity correlation ($\gamma \approx 1.003$, $R^2 > 0.999$), and **(e)** superposition of experimental (blue) and calculated (red) molecular structures illustrating their excellent geometrical agreement.

V. 1. Frontier molecular orbitals (FMOs) and energy gap.

DFT (*B3LYP/LanL2DZ*) calculations reveal that $[\text{Co}(\text{bzac})_2]$ possesses ligand-dominated frontier orbitals with energies of HOMO = -5.80 eV, SOMO = -5.73 eV, and LUMO = -1.69 eV, corresponding to a HOMO–LUMO gap of $\Delta E \approx 4.11$ eV²⁷. The HOMO is a π -orbital localized on the β -diketone skeleton, the LUMO a π^* orbital delocalized over the phenyl-carbonyl system, and the SOMO a mixed $\sigma(\text{Co–O})/\pi$ state with minor metal character, consistent with a Co (II) d^7 configuration in a quasi-square-planar environment. This electronic structure accounts for the observed ligand-centered $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ UV absorptions, the weak d–d transition around 480–500 nm⁵⁰, and the $\nu(\text{Co–O})$ stretch at 520–530 cm^{-1} ⁵¹, while rationalizing

the $\pi\cdots\pi$ stacking, C–H $\cdots\pi$, and n(O) $\rightarrow\pi$ interactions that stabilize the zigzag layers and direct the anisotropic crystal growth along [001], in full agreement with BFDH predictions. The narrow HOMO–SOMO separation places [Co(bzac)₂] on the planar, highly directional end of the [M(bzac)₂] series, contrasting with the hemidirected distortions of p-block analogues, which is fully consistent with structural comparisons and the observed π -stacking–driven morphology.

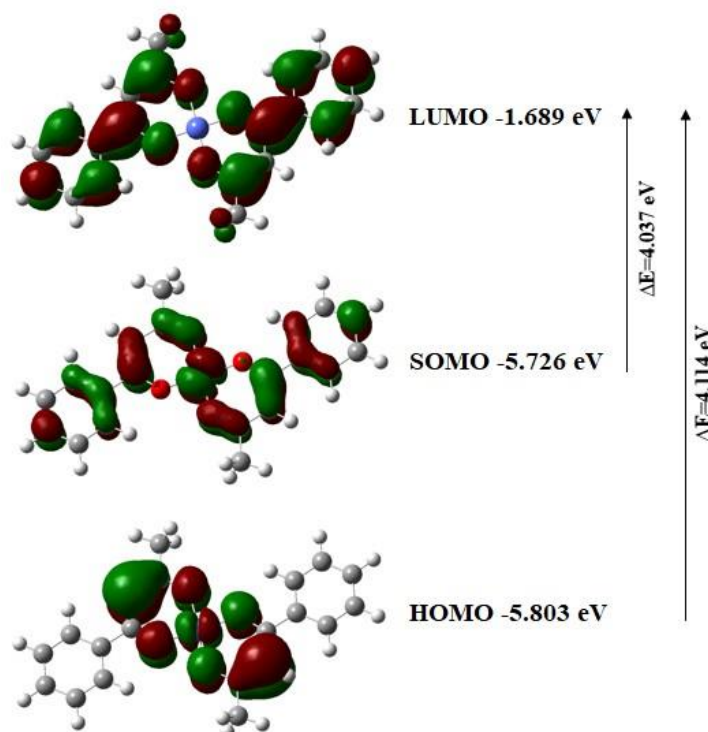


Figure 80. Frontier molecular orbitals (HOMO, SOMO, and LUMO) of [Co(bzac)₂] complex with their corresponding energies and energy gaps, showing the electronic distribution and transitions within the complex.

V. 2. Electrostatic profile: MEP and Mulliken charges.

The molecular electrostatic potential (MEP) surface of [Co(bzac)₂] ($\pm 5.60 \times 10^{-2}$ a.u.) (Figure 81.a) exhibits a ligand-polarized charge distribution, with highly negative regions (red) centered on the chelating oxygen atoms and O=C–C=C=O π -belts, and positive potential zones (blue–cyan) over the aromatic periphery and methylene hydrogens⁵². This pattern is quantitatively supported by Mulliken analysis (Figure 81.b), which shows a positively charged cobalt center (Co = +0.88 a.u.), negatively charged oxygens (O1/O2 $\approx$ -0.64/-0.61 a.u.), and an alternating charge sequence along the conjugated chain. The resulting electrostatic contrast drives key O $\cdots$ C intermolecular contacts (3.14–3.26 Å), identified as attractive lone-pair– π (n(O) $\rightarrow\pi$) interactions between electron-rich oxygens and the electron-poor aromatic systems of

neighboring molecules. This aligns perfectly with the frontier molecular orbital (FMO) topology, where the ligand-centered HOMO (π) and LUMO (π^*) facilitate these interactions, while the metal-ligand mixed SOMO remains confined to the Co–O core. Consequently, the electronic and electrostatic anisotropy governs the layered packing parallel to the (b,c) plane and the directional crystal growth along [001], in full agreement with BFDH morphology predictions⁵³. The non-covalent nature of these $n(\text{O}) \rightarrow \pi$ contacts is further corroborated by low-density green regions in the reduced density gradient (RDG) isosurface (Figure 82), typical of weak van der Waals interactions. Altogether, the integrated MEP, Mulliken, and FMO analyses confirm a highly polar Co–O core within a π -delocalized ligand framework, establishing a consistent link between the compound's electronic structure, its supramolecular recognition motifs, and its macroscopic morphological anisotropy.

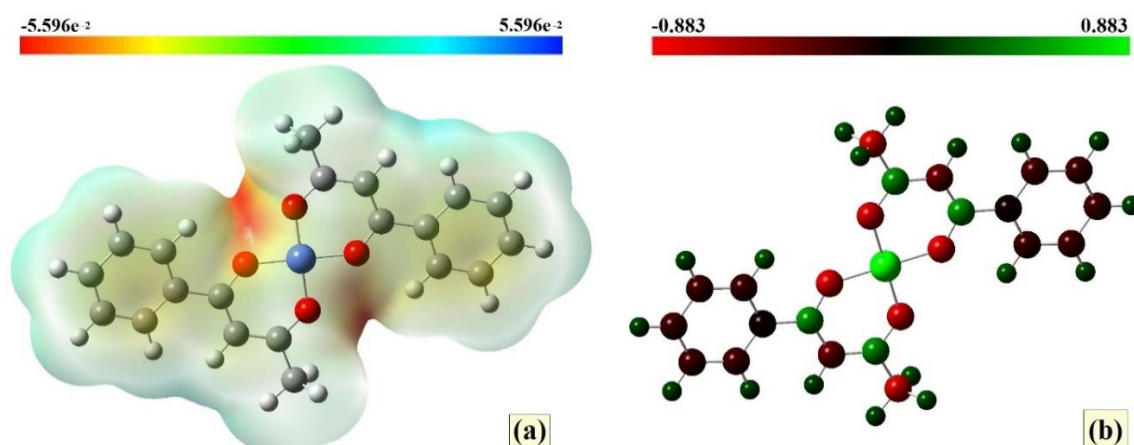


Figure 81. (a) Molecular electrostatic potential (MEP) surface of the $[\text{Co}(\text{bzac})_2]$ complex showing the spatial distribution of electrostatic potential mapped onto the electron density surface; (b) Mulliken atomic charge distribution illustrating the localized positive and negative charge regions within the molecular framework.

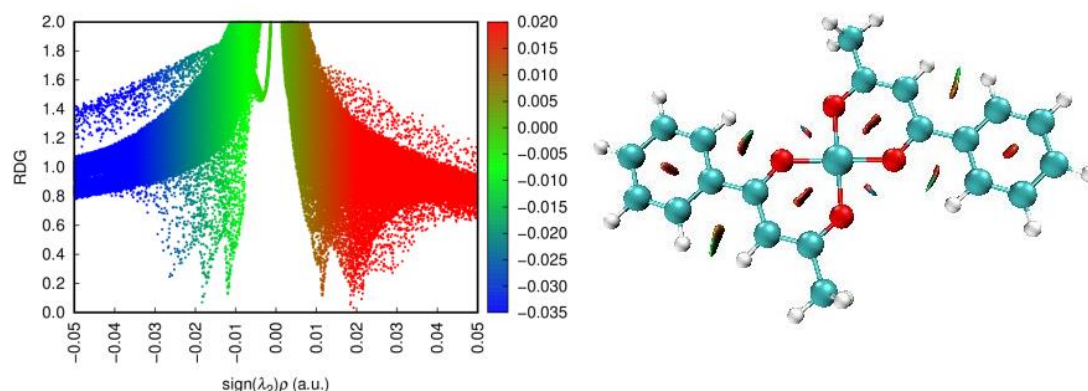


Figure 82. RDG isosurface and scatter plots of the $[\text{Co}(\text{bzac})_2]$ complex showing steric repulsion (red), van der Waals (green), and hydrogen-bonding (blue) interactions.

V. 3. TD-DFT electronic excitation analysis.

Time-dependent density functional theory (TD-DFT) calculations performed on the experimental geometry of [Co(bzac)₂] (Table 27) substantiate the UV–Vis spectral assignments and validate the electronic structure derived from crystallography and FMO analysis. The computations predict an intense, ligand-centered $\pi \rightarrow \pi^*$ excitation between 2.20–2.30 eV ($\approx$ 540–565 nm), in excellent agreement with the dominant experimental absorption band. A second, lower-intensity manifold of transitions in the range of ca. 2.00–2.10 eV ($\approx$ 590–620 nm) is assigned to $n \rightarrow \pi^*$ promotions involving oxygen lone pairs and the β -diketonate π^* system, matching the experimental shoulder observed at 600–630 nm and confirming its intraligand origin. Importantly, all metal-centered d–d excitations are calculated at substantially lower energies with near-zero oscillator strengths ($f \ll 10^{-3}$), consistent with the very weak, broad spectral tail extending into the near-infrared region. This behavior is characteristic of Laporte-forbidden Co (II) d–d transitions in a near-square-planar (D_{4h}-like) ligand field, aligning with the crystallographically observed planar CoO₄ chromophore. Collectively, the TD-DFT results corroborate the experimental spectrum and support a model where the low-energy optical response is metal-suppressed, while the visible region is dominated by ligand-centered π -activity—a structure–property relationship fully consistent with the planarity, conjugation, and electronic distribution established for [Co(bzac)₂].

Table 27. TD-DFT calculated vertical excitations for [Co(bzac)₂].

Transition	λ_{calc} (nm)	Dominant orbital contribution	Assignment
S ₀ → S ₁	636	HOMO–1 → LUMO	$n(\text{O}) \rightarrow \pi^*$
S ₀ → S ₂	590	HOMO–2 → LUMO	$n(\text{O}) \rightarrow \pi^*$
S ₀ → S ₃	551	HOMO → LUMO	$\pi \rightarrow \pi^*$ (ligand-centered)
S ₀ → S ₄	797	$d_{xy} \rightarrow d_{x^2-y^2}$	d–d (Laporte-forbidden)
S ₀ → S ₅	1333	$d_{xz} \rightarrow d_{z^2}$	d–d

VI. Conclusion.

This study establishes [Co(bzac)₂] as a key member of the [M(bzac)₂] series, illustrating how coordination symmetry and chelate planarity influence supramolecular organization and crystal morphology. Employing metrics of planarity,

CSD analysis, and morphology modeling reveals a structural evolution from p-block to d-block ions, enhancing chelate coplanarity and reinforcing several non-covalent interactions. $[\text{Co}(\text{bzac})_2]$ exhibits maximum planarity and stacking, leading to pronounced growth anisotropy aligned with its experimental habits and PXRD signatures. The ligand-rich electronic structure of $[\text{Co}(\text{bzac})_2]$, with its CoO_4 chromophore, generates geometric constraints that dictate optical responses, validated through various structural calculations. Consequently, this research presents a framework for understanding and predicting morphology in planar O-donor complexes, linking molecular planarity with macroscopic anisotropy while offering a methodology for designing anisotropic coordination materials.

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***GENERAL
CONCLUSION***

GENERAL CONCLUSION

This thesis has undertaken a comprehensive investigation of polymorphism in molecular solids and the structural chemistry of hybrid organic-inorganic compounds, addressing fundamental questions about how molecular-level structure and interactions determine macroscopic material properties. Through an integrated approach combining state-of-the-art experimental characterization with advanced computational analysis, this work has generated new knowledge, discovered novel materials, and established structure-property relationships with implications for crystal engineering, pharmaceutical science, and materials design.

The investigation of polymorphism across three distinct chemical systems—copper(II) diacetate monohydrate, cytosinium gallate, and a rhodanine derivative—has yielded several significant discoveries and insights:

Copper (II) Diacetate Monohydrate emerged as a particularly instructive case study. The discovery of a new triclinic polymorph (space group $P\bar{1}$), distinct from the known monoclinic forms ($C2/c$ and $P2_1/c$), demonstrated that even well-studied coordination compounds can harbor undiscovered polymorphic forms. Comprehensive characterization revealed that this new polymorph exhibits the smallest HOMO-LUMO gap among the known forms, indicating lower kinetic stability and enhanced chemical reactivity due to increased LUMO delocalization. The new polymorph also displays stronger charge polarization and more negative electrostatic potential, features that could influence its catalytic activity and coordination chemistry. Hirshfeld surface analysis revealed distinct intermolecular interaction profiles, with more pronounced O-H...O hydrogen bonds and H...H contacts contributing to its unique crystal packing. This case demonstrates how subtle variations in crystallization conditions can access different regions of the energy landscape, producing polymorphs with measurably different electronic structures and potentially different functional properties.

Cytosinium Gallate provided insights into polymorphism in organic salts formed through proton transfer between biologically relevant molecules. The identification of a new monoclinic polymorph (space group $P2_1$) with distinct unit cell parameters and crystal packing extended the known structural diversity of this pharmaceutical salt. Comparative analysis revealed that the new polymorph exhibits a smaller HOMO-LUMO gap, indicating greater polarizability and enhanced charge transfer propensity properties relevant to its potential pharmaceutical applications. The new form is characterized by stronger and more numerous hydrogen bonds, along with well-

GENERAL CONCLUSION

developed π - π stacking interactions, resulting in more compact and cohesive crystal packing. These structural differences could translate to variations in solubility, dissolution rate, and bioavailability, underscoring the pharmaceutical relevance of polymorphic control.

The Rhodanine Derivative study revealed a third polymorphic form of (Z)-5-{[4-(dimethylamino) phenyl] methylidene}-2-sulfanylidene-1,3-thiazolidin-4-one, crystallizing in the monoclinic space group $P2_1/c$. Comparative analysis across all three polymorphs showed similar hydrogen-bonding networks but variations in π - π stacking strength and packing efficiency. Interestingly, polymorphism in this system had negligible impact on the intrinsic electronic structure, with observed differences arising mainly from subtle solid-state packing effects rather than fundamental changes in molecular electronic configuration. This finding highlights an important distinction: while some systems exhibit dramatic electronic structure variations across polymorphs, others show primarily structural and packing differences with minimal electronic perturbation.

Collectively, these polymorphism studies demonstrate that the phenomenon is ubiquitous across diverse chemical systems coordination compounds, organic salts, and organic molecules and that each polymorph represents a distinct point in a complex energy landscape shaped by competing intermolecular interactions. The work establishes that polymorphic differences, while sometimes subtle at the molecular level, can produce measurable variations in electronic structure, thermal stability, and crystal packing that are relevant to practical applications.

The investigation of hybrid organic-inorganic materials explored how combining organic and inorganic components through proton transfer and coordination bonding generates materials with emergent properties:

The Proton-Transfer Hybrid N, N-dimethyl-4-[(Z)-(4-oxo-2-sulfanylidene-1,3-thiazolidin-5-ylidene) methyl] anilinium bromide exemplifies Class I hybrid materials stabilized by ionic and hydrogen-bonding interactions. Successful synthesis and crystallization in the monoclinic space group $P2_1/c$ yielded a stable material featuring a protonated organic cation and bromide anion held together by N-H...Br hydrogen bonds. Electronic structure analysis revealed a significant HOMO-LUMO gap of 2.53 eV with clear charge separation: the HOMO is localized on the bromide anion while the LUMO resides on the organic cation. This spatial separation of frontier orbitals establishes distinct donor-acceptor characteristics, suggesting potential applications in

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charge-transfer materials, nonlinear optics, or organic electronics. Hirshfeld surface analysis confirmed that H-involving contacts dominate the intermolecular interaction landscape, with significant contributions from π - π stacking. This study demonstrates how proton transfer can be strategically employed to create hybrid architectures with tailored electronic properties by controlling the spatial distribution of charge and frontier orbitals.

The synthesis and characterization of the cobalt(II) benzoylacetate complex [Co(bzac)₂] provided insights into how molecular geometry and intermolecular interactions determine crystal morphology:

The new complex adopts a strictly square-planar CoO₄ coordination geometry in the monoclinic space group $P2_1/n$, consistent with the d⁷ electronic configuration of Co (II) in a strong ligand field. Powder X-ray diffraction analysis revealed stacked molecular layers and pronounced acicular (needle-like) crystal growth along the [001] crystallographic direction. Detailed structural analysis established that this complex is among the most planar and cohesively stacked members of the [M(bzac)₂] family, with strong π - π stacking and O...C(lp $\rightarrow$ π) interactions driving the growth anisotropy. DFT calculations showed excellent agreement with experimental geometries and revealed that frontier orbitals are predominantly ligand-based, indicating that the electronic properties are largely determined by the benzoylacetate ligands rather than the metal center. This work establishes clear structure-morphology correlations: molecular planarity facilitates efficient π -stacking, which in turn drives preferential growth along specific crystallographic directions, producing characteristic needle-shaped crystals. These insights are valuable for controlling crystal habit in coordination compounds, a critical consideration for materials processing, catalysis, and device fabrication.

Looking forward, the convergence of advanced experimental techniques, computational methods, and data-driven approaches promises to transform our ability to predict, control, and design molecular solid-state materials. The integration of crystal structure prediction, machine learning, high-throughput screening, and automated synthesis could enable discovery of novel polymorphs and materials with unprecedented efficiency. The development of in situ characterization methods will provide real-time insights into crystallization mechanisms, enabling rational control of polymorphic outcome.

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Ultimately, the goal is to achieve the same level of rational design capability for solid-state materials that synthetic chemists have achieved for molecular synthesis: the ability to design a material with specific desired properties, predict its structure and characteristics, and synthesize it reproducibly. While significant challenges remain, the work presented in this thesis represents a step toward that goal, contributing fundamental knowledge, novel materials, and practical methodologies to the fields of crystal engineering, solid-state chemistry, and materials science.

The journey from molecular structure to material properties is complex, traversing multiple length scales and involving intricate interplay of electronic, structural, and thermodynamic factors. This thesis has illuminated portions of that journey, revealing how polymorphism and hybrid materials chemistry provide rich opportunities for scientific discovery and technological innovation. As we continue to develop more sophisticated experimental tools, more powerful computational methods, and deeper theoretical understanding, our ability to navigate this journey and to design materials with precisely tailored properties will only grow stronger.

The molecular solid state, with its infinite variety of possible structures and properties arising from finite sets of molecular building blocks, remains a frontier of scientific exploration. This thesis contributes to mapping that frontier, and in doing so, opens new paths for future explorers to follow.

Annexe

***Annexe A: Structural, spectroscopic and electronic investigation of polymorphism in
copper (II) diacetate monohydrate***

Table 1. Selected geometric parameters (Å, °)

Cu1—Cu1 ⁱ	2.6128 (7)	Cu2—Cu2 ⁱⁱ	2.6122 (4)
Cu1—O2	1.9867 (12)	Cu2—O8	2.1438 (12)
Cu1—O3	2.1449 (13)	Cu2—O7	1.9869 (12)
Cu1—O5 ⁱ	1.9574 (12)	Cu2—O10 ⁱⁱ	1.9920 (12)
Cu1—O4 ⁱ	1.9918 (12)	Cu2—O6	1.9460 (12)
Cu1—O1	1.9440 (11)	Cu2—O9 ⁱⁱ	1.9572 (12)
O2—C3	1.262 (2)	O8—H8A	0.8503
O3—H3A	0.8505	O8—H8B	0.8501
O3—H3B	0.8502	O7—C7	1.265 (2)
O5—Cu1 ⁱ	1.9574 (11)	O10—Cu2 ⁱⁱ	1.9919 (12)
O5—C1	1.263 (2)	O10—C7	1.267 (2)
O4—Cu1 ⁱ	1.9918 (12)	O6—C5	1.266 (2)
O4—C3	1.269 (2)	O9—Cu2 ⁱⁱ	1.9572 (12)
O1—C1	1.264 (2)	O9—C5	1.263 (2)
C4—H4A	0.9600	C6—H6A	0.9600
C4—H4B	0.9600	C6—H6B	0.9600
C4—H4C	0.9600	C6—H6C	0.9600
C4—C3	1.505 (2)	C6—C5	1.507 (2)
C2—H2A	0.9600	C8—H8C	0.9600
C2—H2B	0.9600	C8—H8D	0.9600
C2—H2C	0.9600	C8—H8E	0.9600
C2—C1	1.506 (2)	C8—C7	1.505 (2)
O2—Cu1—Cu1 ⁱ	86.72 (4)	O8—Cu2—Cu2 ⁱⁱ	173.92 (3)
O2—Cu1—O3	98.28 (5)	O7—Cu2—Cu2 ⁱⁱ	86.77 (3)
O2—Cu1—O4 ⁱ	168.99 (5)	O7—Cu2—O8	98.27 (5)
O3—Cu1—Cu1 ⁱ	173.97 (3)	O7—Cu2—O10 ⁱⁱ	169.01 (5)
O5 ⁱ —Cu1—Cu1 ⁱ	83.05 (4)	O10 ⁱⁱ —Cu2—Cu2 ⁱⁱ	82.41 (4)
O5 ⁱ —Cu1—O2	91.09 (5)	O10 ⁱⁱ —Cu2—O8	92.65 (5)
O5 ⁱ —Cu1—O3	93.44 (5)	O6—Cu2—Cu2 ⁱⁱ	86.23 (4)
O5 ⁱ —Cu1—O4 ⁱ	89.52 (5)	O6—Cu2—O8	97.36 (5)
O4 ⁱ —Cu1—Cu1 ⁱ	82.44 (4)	O6—Cu2—O7	87.15 (5)
O4 ⁱ —Cu1—O3	92.65 (5)	O6—Cu2—O10 ⁱⁱ	90.18 (5)

O1—Cu1—Cu1 ⁱ	86.22 (4)	O6—Cu2—O9 ⁱⁱ	169.25 (5)
O1—Cu1—O2	87.16 (5)	O9 ⁱⁱ —Cu2—Cu2 ⁱⁱ	83.07 (4)
O1—Cu1—O3	97.35 (5)	O9 ⁱⁱ —Cu2—O8	93.38 (5)
O1—Cu1—O5 ⁱ	169.21 (5)	O9 ⁱⁱ —Cu2—O7	91.18 (5)
O1—Cu1—O4 ⁱ	90.18 (5)	O9 ⁱⁱ —Cu2—O10 ⁱⁱ	89.47 (5)
C3—O2—Cu1	120.94 (10)	Cu2—O8—H8A	120.0
Cu1—O3—H3A	121.3	Cu2—O8—H8B	129.2
Cu1—O3—H3B	129.3	H8A—O8—H8B	104.5
H3A—O3—H3B	104.4	C7—O7—Cu2	120.86 (10)
C1—O5—Cu1 ⁱ	124.03 (11)	C7—O10—Cu2 ⁱⁱ	125.55 (10)
C3—O4—Cu1 ⁱ	125.43 (10)	C5—O6—Cu2	120.94 (10)
C1—O1—Cu1	121.03 (11)	C5—O9—Cu2 ⁱⁱ	124.10 (11)
H4A—C4—H4B	109.5	H6A—C6—H6B	109.5
H4A—C4—H4C	109.5	H6A—C6—H6C	109.5
H4B—C4—H4C	109.5	H6B—C6—H6C	109.5
C3—C4—H4A	109.5	C5—C6—H6A	109.5
C3—C4—H4B	109.5	C5—C6—H6B	109.5
C3—C4—H4C	109.5	C5—C6—H6C	109.5
O2—C3—O4	124.29 (15)	H8C—C8—H8D	109.5
O2—C3—C4	118.79 (14)	H8C—C8—H8E	109.5
O4—C3—C4	116.92 (14)	H8D—C8—H8E	109.5
H2A—C2—H2B	109.5	C7—C8—H8C	109.5
H2A—C2—H2C	109.5	C7—C8—H8D	109.5
H2B—C2—H2C	109.5	C7—C8—H8E	109.5
C1—C2—H2A	109.5	O6—C5—C6	117.28 (15)
C1—C2—H2B	109.5	O9—C5—O6	125.58 (15)
C1—C2—H2C	109.5	O9—C5—C6	117.13 (15)
O5—C1—O1	125.60 (15)	O7—C7—O10	124.21 (14)
O5—C1—C2	117.06 (15)	O7—C7—C8	118.72 (14)
O1—C1—C2	117.34 (15)	O10—C7—C8	117.07 (14)
Cu1—O2—C3—O4	-2.5 (2)	Cu2—O7—C7—O10	-2.7 (2)
Cu1—O2—C3—C4	176.42 (11)	Cu2—O7—C7—C8	176.46 (11)
Cu1 ⁱ —O5—C1—O1	-3.2 (2)	Cu2 ⁱⁱ —O10—C7—O7	5.6 (2)
Cu1 ⁱ —O5—C1—C2	177.48 (10)	Cu2 ⁱⁱ —O10—C7—C8	-173.55 (11)
Cu1 ⁱ —O4—C3—O2	5.4 (2)	Cu2—O6—C5—O9	1.9 (2)

Cu1 ⁱ —O4—C3—C4	-173.56 (11)	Cu2—O6—C5—C6	-179.08 (10)
Cu1—O1—C1—O5	1.6 (2)	Cu2 ⁱⁱ —O9—C5—O6	-3.4 (2)
Cu1—O1—C1—C2	-179.10 (10)	Cu2 ⁱⁱ —O9—C5—C6	177.53 (10)

Symmetry code(s): (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+1, -z$

Annexe B: Structural, spectroscopic, and electronic investigation of polymorphism in cytosinium gallate

Table 2. Selected geometric parameters (Å, °)

O2—C1	1.270 (3)	N1—C11	1.368 (3)
O8—C8	1.230 (2)	N1—H1	0.92 (3)
O6—H6	0.8400	C2—C7	1.400 (3)
O6—C6	1.360 (2)	C2—C1	1.503 (3)
O5—H5	0.8400	C2—C3	1.403 (3)
O5—C5	1.368 (3)	C5—C6	1.398 (3)
O1—C1	1.266 (2)	C5—C4	1.388 (3)
O4—H4	0.8400	C6—C7	1.390 (3)
O4—C4	1.383 (2)	C7—H7	0.9500
N2—C9	1.363 (3)	C9—C10	1.425 (3)
N2—C8	1.384 (3)	C3—H3	0.9500
N2—H2	0.90 (3)	C3—C4	1.386 (3)
N3—H3A	0.8800	C11—H11	0.9500
N3—H3B	0.8800	C11—C10	1.343 (3)
N3—C9	1.313 (3)	C10—H10	0.9500
N1—C8	1.364 (3)		
C6—O6—H6	109.5	C6—C7—H7	120.2
C5—O5—H5	109.5	N2—C9—C10	118.21 (18)
C4—O4—H4	109.5	N3—C9—N2	119.1 (2)
C9—N2—C8	124.17 (19)	N3—C9—C10	122.64 (18)
C9—N2—H2	120.0 (16)	O8—C8—N2	122.1 (2)
C8—N2—H2	115.9 (16)	O8—C8—N1	122.84 (19)
H3A—N3—H3B	120.0	N1—C8—N2	115.03 (18)
C9—N3—H3A	120.0	O2—C1—C2	119.61 (17)
C9—N3—H3B	120.0	O1—C1—O2	122.71 (19)
C8—N1—C11	122.96 (18)	O1—C1—C2	117.67 (18)
C8—N1—H1	117.5 (19)	C2—C3—H3	120.0
C11—N1—H1	119.5 (19)	C4—C3—C2	119.98 (18)

C7—C2—C1	121.26 (18)	C4—C3—H3	120.0
C7—C2—C3	119.87 (18)	N1—C11—H11	119.1
C3—C2—C1	118.87 (17)	C10—C11—N1	121.8 (2)
O5—C5—C6	120.92 (18)	C10—C11—H11	119.1
O5—C5—C4	119.05 (18)	O4—C4—C5	121.14 (19)
C4—C5—C6	120.0 (2)	O4—C4—C3	118.58 (18)
O6—C6—C5	114.17 (19)	C3—C4—C5	120.22 (19)
O6—C6—C7	125.51 (18)	C9—C10—H10	121.1
C7—C6—C5	120.26 (18)	C11—C10—C9	117.78 (19)
C2—C7—H7	120.2	C11—C10—H10	121.1
C6—C7—C2	119.62 (18)		
O6—C6—C7—C2	175.36 (19)	C7—C2—C3—C4	1.9 (3)
O5—C5—C6—O6	2.8 (3)	C9—N2—C8—O8	176.66 (18)
O5—C5—C6—C7	179.97 (18)	C9—N2—C8—N1	-2.8 (3)
O5—C5—C4—O4	-1.3 (3)	C8—N2—C9—N3	-177.35 (18)
O5—C5—C4—C3	-178.64 (18)	C8—N2—C9—C10	2.9 (3)
N2—C9—C10—C11	-1.3 (3)	C8—N1—C11—C10	0.1 (3)
N3—C9—C10—C11	178.92 (19)	C1—C2—C7—C6	179.40 (17)
N1—C11—C10—C9	-0.1 (3)	C1—C2—C3—C4	-178.04 (18)
C2—C3—C4—O4	-178.65 (17)	C3—C2—C7—C6	-0.6 (3)
C2—C3—C4—C5	-1.2 (3)	C3—C2—C1—O2	172.36 (18)
C5—C6—C7—C2	-1.5 (3)	C3—C2—C1—O1	-7.3 (3)
C6—C5—C4—O4	176.51 (17)	C11—N1—C8—O8	-178.19 (19)
C6—C5—C4—C3	-0.8 (3)	C11—N1—C8—N2	1.2 (3)
C7—C2—C1—O2	-7.6 (3)	C4—C5—C6—O6	-174.98 (18)
C7—C2—C1—O1	172.71 (18)	C4—C5—C6—C7	2.2 (3)

Annexe C: Structural, spectroscopic, and electronic investigation of polymorphism in (Z)-5-{{4-(dimethylamino) phenyl} methylidene}-2-sulfanylidene-1,3-thiazolidin-4-one

Table 3. Selected geometric parameters (Å, °)

S1—C3	1.756 (3)	C8—C7	1.410 (4)
S1—C1	1.755 (3)	C9—H9	0.9500
S2—C1	1.626 (3)	C9—C10	1.370 (4)

O1—C2	1.223 (4)	C10—H10	0.9500
N1—H1	0.8800	C4—H4	0.9500
N1—C2	1.379 (4)	C4—C3	1.347 (4)
N1—C1	1.365 (4)	C7—H7	0.9500
N2—C8	1.366 (4)	C7—C6	1.367 (4)
N2—C11	1.450 (4)	C6—H6	0.9500
N2—C12	1.455 (4)	C11—H11A	0.9800
C2—C3	1.469 (4)	C11—H11B	0.9800
C5—C10	1.407 (4)	C11—H11C	0.9800
C5—C4	1.439 (4)	C12—H12A	0.9800
C5—C6	1.405 (4)	C12—H12B	0.9800
C8—C9	1.417 (4)	C12—H12C	0.9800
C1—S1—C3	92.96 (14)	C2—C3—S1	109.1 (2)
C2—N1—H1	120.8	C4—C3—S1	128.5 (2)
C1—N1—H1	120.8	C4—C3—C2	122.3 (3)
C1—N1—C2	118.4 (2)	C8—C7—H7	119.5
C8—N2—C11	121.0 (2)	C6—C7—C8	121.0 (3)
C8—N2—C12	120.4 (3)	C6—C7—H7	119.5
C11—N2—C12	118.1 (2)	C5—C6—H6	118.6
O1—C2—N1	123.2 (3)	C7—C6—C5	122.7 (3)
O1—C2—C3	126.4 (3)	C7—C6—H6	118.6
N1—C2—C3	110.3 (3)	S2—C1—S1	122.74 (18)
C10—C5—C4	124.9 (3)	N1—C1—S1	109.1 (2)
C6—C5—C10	115.9 (3)	N1—C1—S2	128.2 (2)
C6—C5—C4	119.2 (3)	N2—C11—H11A	109.5
N2—C8—C9	120.9 (3)	N2—C11—H11B	109.5
N2—C8—C7	122.2 (3)	N2—C11—H11C	109.5
C7—C8—C9	116.9 (3)	H11A—C11—H11B	109.5
C8—C9—H9	119.5	H11A—C11—H11C	109.5
C10—C9—C8	121.0 (3)	H11B—C11—H11C	109.5
C10—C9—H9	119.5	N2—C12—H12A	109.5
C5—C10—H10	118.8	N2—C12—H12B	109.5
C9—C10—C5	122.4 (3)	N2—C12—H12C	109.5
C9—C10—H10	118.8	H12A—C12—H12B	109.5
C5—C4—H4	114.4	H12A—C12—H12C	109.5

C3—C4—C5	131.2 (3)	H12B—C12—H12C	109.5
C3—C4—H4	114.4		
O1—C2—C3—S1	-178.7 (3)	C4—C5—C10—C9	176.3 (3)
O1—C2—C3—C4	-0.5 (5)	C4—C5—C6—C7	-176.2 (3)
N1—C2—C3—S1	0.8 (3)	C3—S1—C1—S2	180.0 (2)
N1—C2—C3—C4	179.1 (3)	C3—S1—C1—N1	-0.7 (2)
N2—C8—C9—C10	-178.1 (3)	C7—C8—C9—C10	2.0 (4)
N2—C8—C7—C6	178.4 (3)	C6—C5—C10—C9	-1.6 (4)
C2—N1—C1—S1	1.4 (3)	C6—C5—C4—C3	174.4 (3)
C2—N1—C1—S2	-179.3 (2)	C1—S1—C3—C2	-0.1 (2)
C5—C4—C3—S1	0.4 (5)	C1—S1—C3—C4	-178.2 (3)
C5—C4—C3—C2	-177.4 (3)	C1—N1—C2—O1	178.1 (3)
C8—C9—C10—C5	-0.4 (5)	C1—N1—C2—C3	-1.5 (4)
C8—C7—C6—C5	-0.2 (5)	C11—N2—C8—C9	2.8 (4)
C9—C8—C7—C6	-1.7 (4)	C11—N2—C8—C7	-177.3 (3)
C10—C5—C4—C3	-3.5 (5)	C12—N2—C8—C9	175.0 (3)
C10—C5—C6—C7	1.9 (4)	C12—N2—C8—C7	-5.2 (4)

***Annexe D. Structural, spectroscopic, and electronic investigation of a new hybrid:
N, N-dimethyl-4-[(Z)-(4-oxo-2-sulfanylidene-1,3-thiazolidin-5 ylidene) methyl]
anilinium Bromide***

Table 4. Selected geometric parameters (Å, °)

S1—C1	1.752 (2)	C8—C7	1.377 (3)
S1—C3	1.748 (2)	C4—H4	0.9500
S2—C1	1.636 (2)	C4—C3	1.339 (3)
O1—C2	1.214 (3)	C6—H6	0.9500
N1—H1	0.8800	C6—C7	1.381 (3)
N1—C2	1.379 (3)	C9—H9	0.9500
N1—C1	1.358 (3)	C9—C10	1.382 (3)
N2—C8	1.476 (3)	C10—H10	0.9500
N2—C12	1.489 (3)	C7—H7	0.9500
N2—C11	1.503 (3)	C12—H12A	0.9800
N2—H2	0.89 (3)	C12—H12B	0.9800
C5—C4	1.455 (3)	C12—H12C	0.9800
C5—C6	1.399 (3)	C11—H11A	0.9800
C5—C10	1.396 (3)	C11—H11B	0.9800

C2—C3	1.491 (3)	C11—H11C	0.9800
C8—C9	1.384 (3)		
C3—S1—C1	92.83 (10)	C4—C3—S1	129.84 (16)
C2—N1—H1	121.1	C4—C3—C2	121.21 (18)
C1—N1—H1	121.1	C5—C6—H6	119.4
C1—N1—C2	117.81 (18)	C7—C6—C5	121.28 (19)
C8—N2—C12	115.05 (17)	C7—C6—H6	119.4
C8—N2—C11	111.30 (16)	C8—C9—H9	120.4
C8—N2—H2	109.0 (17)	C10—C9—C8	119.16 (19)
C12—N2—C11	109.85 (17)	C10—C9—H9	120.4
C12—N2—H2	104.3 (17)	C5—C10—H10	119.4
C11—N2—H2	106.8 (16)	C9—C10—C5	121.2 (2)
C6—C5—C4	118.78 (18)	C9—C10—H10	119.4
C10—C5—C4	123.38 (19)	C8—C7—C6	119.2 (2)
C10—C5—C6	117.8 (2)	C8—C7—H7	120.4
O1—C2—N1	123.99 (19)	C6—C7—H7	120.4
O1—C2—C3	125.77 (19)	N2—C12—H12A	109.5
N1—C2—C3	110.22 (17)	N2—C12—H12B	109.5
C9—C8—N2	120.02 (18)	N2—C12—H12C	109.5
C7—C8—N2	118.79 (18)	H12A—C12—H12B	109.5
C7—C8—C9	121.12 (19)	H12A—C12—H12C	109.5
C5—C4—H4	115.0	H12B—C12—H12C	109.5
C3—C4—C5	130.01 (19)	N2—C11—H11A	109.5
C3—C4—H4	115.0	N2—C11—H11B	109.5
S2—C1—S1	122.39 (12)	N2—C11—H11C	109.5
N1—C1—S1	110.19 (15)	H11A—C11—H11B	109.5
N1—C1—S2	127.42 (17)	H11A—C11—H11C	109.5
C2—C3—S1	108.93 (15)	H11B—C11—H11C	109.5
O1—C2—C3—S1	-178.46 (18)	C1—S1—C3—C4	-177.8 (2)
O1—C2—C3—C4	0.1 (3)	C1—N1—C2—O1	177.5 (2)
N1—C2—C3—S1	0.1 (2)	C1—N1—C2—C3	-1.1 (3)
N1—C2—C3—C4	178.71 (19)	C3—S1—C1—S2	178.08 (14)
N2—C8—C9—C10	-174.9 (2)	C3—S1—C1—N1	-1.22 (16)
N2—C8—C7—C6	174.8 (2)	C6—C5—C4—C3	166.0 (2)
C5—C4—C3—S1	-3.3 (4)	C6—C5—C10—C9	-3.8 (3)

C5—C4—C3—C2	178.4 (2)	C9—C8—C7—C6	-2.1 (3)
C5—C6—C7—C8	-0.7 (3)	C10—C5—C4—C3	-15.4 (4)
C2—N1—C1—S1	1.6 (2)	C10—C5—C6—C7	3.6 (3)
C2—N1—C1—S2	-177.66 (16)	C7—C8—C9—C10	1.9 (3)
C8—C9—C10—C5	1.2 (3)	C12—N2—C8—C9	-48.8 (3)
C4—C5—C6—C7	-177.7 (2)	C12—N2—C8—C7	134.4 (2)
C4—C5—C10—C9	177.5 (2)	C11—N2—C8—C9	77.0 (2)
C1—S1—C3—C2	0.61 (16)	C11—N2—C8—C7	-99.9 (2)

***Annexe E: Planarity-driven structure–morphology correlations in a Co(II)
benzoylacetate: comparative insights across the [M(bzac)₂] family***

Table 5. Selected geometric parameters (Å, °)

Co1—O1 ⁱ	1.9178 (9)	C5—C6	1.3922 (17)
Co1—O1	1.9178 (9)	C5—H5	0.9855 (13)
Co1—O2	1.9209 (8)	C3—C4	1.3930 (16)
Co1—O2 ⁱ	1.9209 (8)	C3—H3	0.9341 (11)
O1—C1	1.2770 (13)	C6—H6	0.9633 (12)
O2—C9	1.2739 (13)	C4—H4	0.9212 (11)
C1—C8	1.4082 (14)	C9—C8 ⁱ	1.4053 (14)
C1—C2	1.4932 (14)	C9—C10	1.5071 (15)
C2—C3	1.3981 (15)	C8—H8	0.9310 (10)
C2—C7	1.3990 (15)	C10—H10B	0.9590 (11)
C7—C6	1.3921 (16)	C10—H10A	0.9765 (12)
C7—H7	0.9875 (11)	C10—H10C	0.9162 (12)
C5—C4	1.3903 (18)		
O1 ⁱ —Co1—O1	180.0	C4—C3—H3	119.86 (11)
O1 ⁱ —Co1—O2	93.48 (4)	C2—C3—H3	119.77 (10)
O1—Co1—O2	86.52 (4)	C7—C6—C5	119.74 (11)
O1 ⁱ —Co1—O2 ⁱ	86.52 (4)	C7—C6—H6	119.11 (12)
O1—Co1—O2 ⁱ	93.48 (4)	C5—C6—H6	121.04 (11)
O2—Co1—O2 ⁱ	180.0	C5—C4—C3	120.33 (11)
C1—O1—Co1	126.68 (7)	C5—C4—H4	119.86 (11)
C9—O2—Co1	125.40 (7)	C3—C4—H4	119.81 (12)
O1—C1—C8	124.27 (9)	O2—C9—C8 ⁱ	125.74 (9)
O1—C1—C2	115.60 (9)	O2—C9—C10	115.44 (9)
C8—C1—C2	120.13 (9)	C8 ⁱ —C9—C10	118.82 (9)

C3—C2—C7	118.89 (9)	C9 ⁱ —C8—C1	123.88 (9)
C3—C2—C1	118.77 (9)	C9 ⁱ —C8—H8	117.16 (10)
C7—C2—C1	122.30 (9)	C1—C8—H8	118.78 (10)
C6—C7—C2	120.85 (10)	C9—C10—H10B	110.89 (10)
C6—C7—H7	117.82 (11)	C9—C10—H10A	106.12 (10)
C2—C7—H7	121.26 (10)	H10B—C10—H10A	114.27 (12)
C4—C5—C6	119.93 (11)	C9—C10—H10C	110.70 (11)
C4—C5—H5	122.23 (12)	H10B—C10—H10C	109.66 (12)
C6—C5—H5	117.84 (12)	H10A—C10—H10C	105.01 (11)
C4—C3—C2	120.27 (10)		
Co1—O1—C1— C8	1.38 (15)	C1—C2—C3—C4	177.82 (10)
Co1—O1—C1— C2	-177.54 (7)	C2—C7—C6—C5	-0.27 (19)
O1—C1—C2—C3	-12.15 (14)	C4—C5—C6—C7	0.3 (2)
C8—C1—C2—C3	168.89 (10)	C6—C5—C4—C3	0.0 (2)
O1—C1—C2—C7	165.24 (10)	C2—C3—C4—C5	-0.35 (18)
C8—C1—C2—C7	-13.72 (15)	Co1—O2—C9—C8 ⁱ	-4.69 (15)
C3—C2—C7—C6	-0.04 (17)	Co1—O2—C9—C10	175.09 (7)
C1—C2—C7—C6	-177.42 (11)	O1—C1—C8—C9 ⁱ	-6.28 (17)
C7—C2—C3—C4	0.35 (17)	C2—C1—C8—C9 ⁱ	172.59 (10)

Symmetry code(s): (i) $-x, -y, -z$.

Abstract

This thesis investigates polymorphism in molecular solids and the structural chemistry of hybrid organic-inorganic compounds and organometallic complex through integrated experimental characterization (single-crystal X-ray diffraction, spectroscopy) and computational methods (density functional theory, Hirshfeld surface analysis).

The research comprises three parts. **Part One** explores polymorphism through three model systems. A new triclinic polymorph of copper (II) diacetate monohydrate (space group $P\bar{1}$) was discovered which is considered as a Metal-Organic Framework (MOF), exhibiting the smallest HOMO-LUMO gap among known forms and enhanced chemical reactivity. A new monoclinic polymorph of cytosinium gallate (space group $P2_1$) demonstrated stronger hydrogen bonding and π - π stacking with pharmaceutical relevance. A third polymorphic form of a rhodanine derivative (space group $P2_1/c$) revealed that polymorphism can arise primarily from packing variations with minimal electronic perturbation.

Part Two reports the synthesis of N,N-dimethyl-4-[(Z)-(4-oxo-2-sulfanylidene-1,3-thiazolidin-5-ylidene)methyl]anilinium bromide, a hybrid compound with a 2.53 eV HOMO-LUMO gap and spatial separation of frontier orbitals, establishing donor-acceptor characteristics for potential applications in charge-transfer materials.

Part Three characterizes a new cobalt(II) benzoylacetate complex $[\text{Co}(\text{bzac})_2]$ with square-planar CoO_4 geometry (space group $P2_1/n$) exhibiting acicular morphology driven by strong π - π stacking, establishing structure-morphology correlations.

This work demonstrates that polymorphism is ubiquitous across diverse chemical systems and that polymorphic differences produce measurable variations in electronic structure, stability, and packing relevant to pharmaceuticals, catalysis, and materials science. The integrated experimental-computational methodology provides a framework for rational materials design and crystal engineering.

Keywords: Polymorphism, Metal-Organic Framework, Hybrid Materials, Crystal Engineering, Structure-Property Relationships, DFT, X-ray Diffraction, Coordination Compounds

Résumé

Cette thèse porte sur l'étude du polymorphisme dans les solides moléculaires ainsi que sur la chimie structurale des composés hybrides organiques-inorganiques et des complexes organométalliques, à travers une approche intégrée combinant des techniques expérimentales (diffraction des rayons X sur monocristal, spectroscopies) et des méthodes computationnelles (théorie de la fonctionnelle de la densité, analyse des surfaces de Hirshfeld).

Le travail de recherche est structuré en trois parties. **La première partie** explore le polymorphisme à travers trois systèmes modèles. Un nouveau polymorphe triclinique de l'acétate de cuivre(II) monohydraté (groupe d'espace $P\bar{1}$) a été découvert ; il est considéré comme un Metal-Organic Framework (MOF) et présente le plus faible écart HOMO-LUMO parmi les formes connues, ainsi qu'une réactivité chimique accrue. Un nouveau polymorphe monoclinique du gallate de cytosinium (groupe d'espace $P2_1$) montre un renforcement des liaisons hydrogène et des interactions π - π , présentant un intérêt potentiel dans le domaine pharmaceutique. Un troisième polymorphe d'un dérivé de la rhodanine (groupe d'espace $P2_1/c$) a révélé que le polymorphisme peut résulter principalement de variations d'empilement cristallin, avec des perturbations électroniques minimales.

La deuxième partie décrit la synthèse du bromure de N,N-diméthyl-4-[(Z)-(4-oxo-2-sulfanylidène-1,3-thiazolidin-5-ylidène)méthyl]anilinium, un composé hybride présentant un

écart HOMO–LUMO de 2,53 eV et une séparation spatiale des orbitales frontières, établissant des caractéristiques donneur–accepteur prometteuses pour des applications potentielles dans les matériaux à transfert de charge.

La troisième partie concerne la caractérisation d'un nouveau complexe de benzoylettonate de cobalt(II), [Co(bzac)₂], présentant une géométrie CoO₄ plan carré (groupe d'espace P2₁/n) et une morphologie aciculaire induite par de fortes interactions π – π , permettant d'établir des corrélations structure–morphologie.

Ce travail démontre que le polymorphisme est omniprésent dans des systèmes chimiques variés et que les différences polymorphiques induisent des variations mesurables des structures électroniques, de la stabilité et de l'organisation cristalline, pertinentes pour les domaines pharmaceutique, catalytique et des matériaux. L'approche intégrée expérimentale–computationnelle proposée constitue un cadre pertinent pour la conception rationnelle de matériaux et l'ingénierie cristalline.

Mots-clés: Polymorphisme, Metal–Organic Framework, Matériaux hybrides, Ingénierie cristalline, Relations structure–propriété, DFT, Diffraction des rayons X, Composés de coordination.

المخلص

تتناول هذه الأطروحة دراسة التعدد الشكلي في المواد الصلبة الجزيئية والكيمياء البنيوية للمركبات الهجينة العضوية–اللاعضوية والمعقدات العضوية الفلزية، وذلك من خلال منهجية متكاملة تجمع بين التقنيات التجريبية (حيود الأشعة السينية على البلورات المفردة، التحاليل الطيفية (والأساليب الحسابية) نظرية دالة الكثافة، تحليل أسطح هيرشفلد).

يتكون هذا العمل البحثي من ثلاثة أجزاء.

يستعرض الجزء الأول ظاهرة التعدد الشكلي من خلال ثلاثة أنظمة نموذجية. تم اكتشاف شكل بلوري جديد ثلاثي الميل من أسيتات النحاس الثنائي أحادي الإماهة، ويُعد هذا الشكل إطارًا عضويًا فلزيًا، حيث يُظهر أصغر فجوة طاقية بين مداري مقارنة بالأشكال المعروفة، إضافة إلى نشاط كيميائي معزز. كما تم تحديد شكل بلوري أحادي الميل جديد لغالات السيتوسينيوم يتميز بروابط هيدروجينية أقوى وتراص أوضح، مما يمنحه أهمية محتملة في المجال الصيدلاني. أما الشكل الثالث، وهو مشتق من الروداتين، فقد أظهر أن التعدد الشكلي يمكن أن ينشأ أساسًا من اختلافات في التعبئة البلورية مع تأثيرات إلكترونية محدودة.

يعرض الجزء الثاني تحضير مركب هجين هو بروميد-ثنائي ميثيل-4-أوكزو-2-سلفانيلدين-1,3-ثيازوليدين-5-يليدين (ميثيل) أنيلينيوم، والذي يتميز بفجوة مقدارها 2.53 إلكترون فولت وبفصل مكاني بين المدارات الجبهية، مما يؤكد خصائص مانح–مستقبل تجعله مرشحًا لتطبيقات محتملة في مواد نقل الشحنة.

أما الجزء الثالث فيتناول توصيف معقد جديد من بنزويل أسيتونات الكوبالت الثنائي، يتميز بهندسة مربعة مستوية وبمورفولوجيا إبرية ناتجة عن تفاعلات قوية، مما يسمح بإقامة علاقات واضحة بين البنية والمورفولوجيا.

تُظهر هذه الدراسة أن التعدد الشكلي ظاهرة واسعة الانتشار في أنظمة كيميائية متنوعة، وأن الاختلافات بين الأشكال البلورية تؤدي إلى تغيرات قابلة للقياس في البنية الإلكترونية والاستقرار والتعبئة البلورية، ذات أهمية في مجالات الصيدلة والتحفيز وعلوم المواد. كما توفر المنهجية المتكاملة التجريبية–الحسابية إطارًا فعالًا للتصميم العقلاني للمواد وهندسة البلورات.

الكلمات المفتاحية:

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