

Comprehensive study of a novel cobalt(II) complex: Synthesis, X-ray crystal structure, Hirshfeld surface analysis, computational quantum investigations, and molecular docking insights

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ARTICLE INFO

Keywords:

Cobalt complex
Hydrogen bonding
Supramolecular interactions
DFT calculations
X-ray diffraction
Antibacterial activity
Molecular docking

ABSTRACT

The design of metal complexes that combine structural sophistication with biological relevance has become a cornerstone of modern coordination chemistry. In this study, we present the synthesis and comprehensive characterization of a novel cobalt(II) complex, $[\text{Co}(\text{phen})_2(\eta^2\text{-bz})]\cdot 2\text{bzH}\cdot\text{NO}_3$ (1), featuring a distorted six-coordinate octahedral geometry, stabilized by two 1,10-phenanthroline and one benzoate ligands. The crystal structure was elucidated using single-crystal X-ray diffraction, revealing a robust supramolecular network strengthened by various non-covalent interactions, including C—H $\cdots$ O, O—H $\cdots$ O hydrogen bonds, and π – π stacking between aromatic rings. Density functional theory (DFT) calculations, employing the B3LYP/3-21G basis set, provided further insight into the optimized geometry and electronic properties, with a close match to experimental observations. Hirshfeld surface analysis quantified the intermolecular interactions, and molecular electrostatic potential (MEP) maps highlighted the reactive sites of the complex. Additionally, molecular docking studies demonstrated a strong binding affinity between the cobalt complex and *Klebsiella pneumoniae* receptors (PDB ID: 6RD3), suggesting potential antibacterial properties. This cobalt complex offers new insights into the structure–activity relationships of transition metal complexes and presents promising avenues for the development of novel therapeutic agents targeting multidrug-resistant bacteria. The findings from this study also pave the way for further exploration of cobalt complexes in catalytic and biomedical applications.

1. Introduction

Transition metal ions are indispensable in the chemistry of life [1], playing a pivotal role in numerous biochemical processes and acting as crucial cofactors in various enzymatic reactions. Their unique ability to adopt different oxidation states and coordination geometries makes them ideal for interacting with a wide range of biological molecules, thus influencing many of the vital processes in living organisms. Among these, cobalt is of particular importance due to its essential function in metalloproteins and enzymes, notably in the structure of Vitamin B12 (cobalamin), which is critical for DNA synthesis and cellular metabolism [2].

In coordination chemistry, the design of complexes involving transition metals like cobalt has opened new frontiers in the development of compounds with significant biological and therapeutic potential. Coordination complexes formed between metal ions and organic ligands are known for their structural diversity and capacity to exhibit a wide array of chemical and biological properties. In particular, mixed-ligand complexes, where a metal ion coordinates with two or more types of ligands, have gained increasing attention due to their ability to exhibit unique structural features and biological activities [3]. These complexes are not only fundamental to understanding metallo-enzyme function in vivo but also hold immense promise as catalysts, antimicrobial, pharmaceuticals, and anticancer agents [4–8].

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<https://doi.org/10.1016/j.poly.2025.117445>

Received 15 October 2024; Accepted 8 February 2025

Available online 13 February 2025

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Cobalt-based mixed-ligand complexes are especially intriguing due to the versatility of cobalt in adopting various coordination environments and oxidation states. The ability of cobalt to form stable complexes with both nitrogen-donor and oxygen-donor ligands makes it an ideal candidate for constructing supramolecular architectures with intricate bonding patterns [9]. Furthermore, the coordination environment around the cobalt center often leads to interesting geometric and electronic properties, which can be fine-tuned by careful selection of ligands. Such properties are highly desirable for applications ranging from catalysis to therapeutic interventions.

This study explores the synthesis and characterization of a novel cobalt(II) complex coordinated by 1,10-phenanthroline and benzoate ligands. This ligand combination stabilizes the metal center in a six-coordinate octahedral geometry and forms a supramolecular network of hydrogen bonding and π - π stacking, enhancing structural stability and functionality. These interactions contribute to the development of advanced supramolecular systems.

The development of such cobalt complexes with mixed ligands is of particular relevance in the context of biological systems, where metal ions frequently interact with multiple ligands to regulate enzymatic activity, molecular transport, and signal transduction [10]. Understanding the coordination behavior and electronic properties of these complexes can provide new insights into their potential biological activity and therapeutic applications. Cobalt complexes, in particular, have shown promise in areas such as antimicrobial activity, oxidative stress regulation, and as models for metallo-enzyme mimics. These characteristics highlight the significance of investigating new cobalt-based systems and their interactions with biological targets [10].

We report herein the synthesis and characterization of a novel cobalt (II) complex, $[\text{Co}(\text{phen})_2(\eta^2\text{-bz})]\cdot 2\text{bzH}\cdot\text{NO}_3$ (**1**), featuring a six-coordinate octahedral geometry stabilized by 1,10-phenanthroline and benzoate ligands. The structural features of this complex, including its intermolecular interactions and electronic properties, were thoroughly investigated using a combination of single-crystal X-ray diffraction, density functional theory (DFT) calculations, and Hirshfeld surface analysis. Moreover, molecular docking studies revealed promising interactions between the cobalt complex and *Klebsiella pneumoniae* receptors, suggesting potential antibacterial applications. This complex is similar to a previously published Cu(II) complex containing the same ligand (1,10-phenanthroline and benzoic acid) [11]. This work offers new insights into the structure-activity relationships of cobalt complexes and paves the way for their future exploration in therapeutic and catalytic applications. This study enhances understanding of bonding and interactions in cobalt-based mixed-ligand systems, paving the way for applications in medicinal chemistry, catalysis, and materials science. Control over coordination and intermolecular forces enables fine-tuning of properties, positioning the complex for future biological and industrial use.

2. Experimental methods

2.1. Materials and methods

The chemicals required for the synthesis of our complex were procured from Sigma Aldrich Chemical. Thin Layer Chromatography (TLC) using aluminum-backed silica plates was used to track the reaction's progress, and a UV lamp set at $\lambda = 254$ nm was used to find the spots. The FTIR was recorded on JASCO FT/IR-4100 with 4000–400 nm range KBr pellets. Spectrophotometer Perkin Elmer Lambda with 800–200 nm range was used for electronic spectra measurements. Multiwfn 3.8 is used to generate electron localized function (ELF) and local orbital locator (LOL) maps for topological studies. Autodock tools 1.5.6 software is used to model the ligand and protein mode of interactions. Discovery Studio Visualizer was designed to see the docked poses.

2.2. Synthesis and crystallization

The synthesis of (**1**) (Scheme 1) was achieved by mixing $\text{Co}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (0.5 g, 2.4 mmol) in 20 mL of water, benzoic acid (0.55 g, 4.5 mmol) and 0.2 g NaOH in 20 mL water and mechanically stirred at room temperature for one hour. To the resulting solution, 2.4 mmol phen (0.4 g) was added slowly and stirred at 60°C for 30 min. The brick red precipitate formed after few days and the crystals collected by filtration, washed with distilled water and dried in the air. Yield: 80 %. The complex exhibits a melting point of 220 °C and a brick-red color. UV-Vis spectroscopy reveals absorption maxima at 237, 294, and 656 nm. Elemental analysis for $\text{CoC}_{45}\text{H}_{33}\text{N}_5\text{O}_9$ ($M = 846.69$ g/mol) yielded the following results: C 63.97 % (calcd. 63.83 %), H 3.81 % (calcd. 3.93 %) and N 8.08 % (calcd. 8.27 %). These values confirm the expected composition and purity of the complex. IR spectral data (KBr disc, cm^{-1}): 3461(br), 3063(w), 2925(m), 2611(w), 1987(w), 1909(m), 1817(sh), 1713(s), 1594(w), 1519(s), 1427(s), 1384(sh), 1332(w), 1234(s), 1172(s), 1068(m), 1023(m), 848(s), 776(sh), 714(s), 649(s), 509(w), 425(m) [s, strong; m, medium; w, weak; br, broad; Sh, Shoulder].

2.3. Single crystal X-ray diffraction and structure refinement details

Crystal data, data collection and structure refinement details of (**1**) are summarized in Table 1. Single brown prism-shaped crystals of (**1**) were used as supplied. The single crystal diffraction measurements were performed on a 4-circles XCalibur, Eos diffractometer for (**1**) equipped with an Eos detector with a graphite monochromatized $\text{MoK}\alpha$ radiation, $\lambda = 0.71073$ Å. The structure has been solved in the space groups $I2/a$ by dual-space method using the program SHELXT [12], and successive Fourier difference syntheses, and were refined against F^2 by weighted full-matrix least squares methods including all reflections with SHELXL-2018 program [13]. All calculations were carried out using Olex2 1.3 software package [14]. Structural representations were drawn using Mercury [15]. All absorption corrections were performed with the multi-scan program [16]. All non-H atoms were refined anisotropically. All hydrogen atoms were located in difference density Fourier maps.

2.4. Hirshfeld surface (HS) calculations

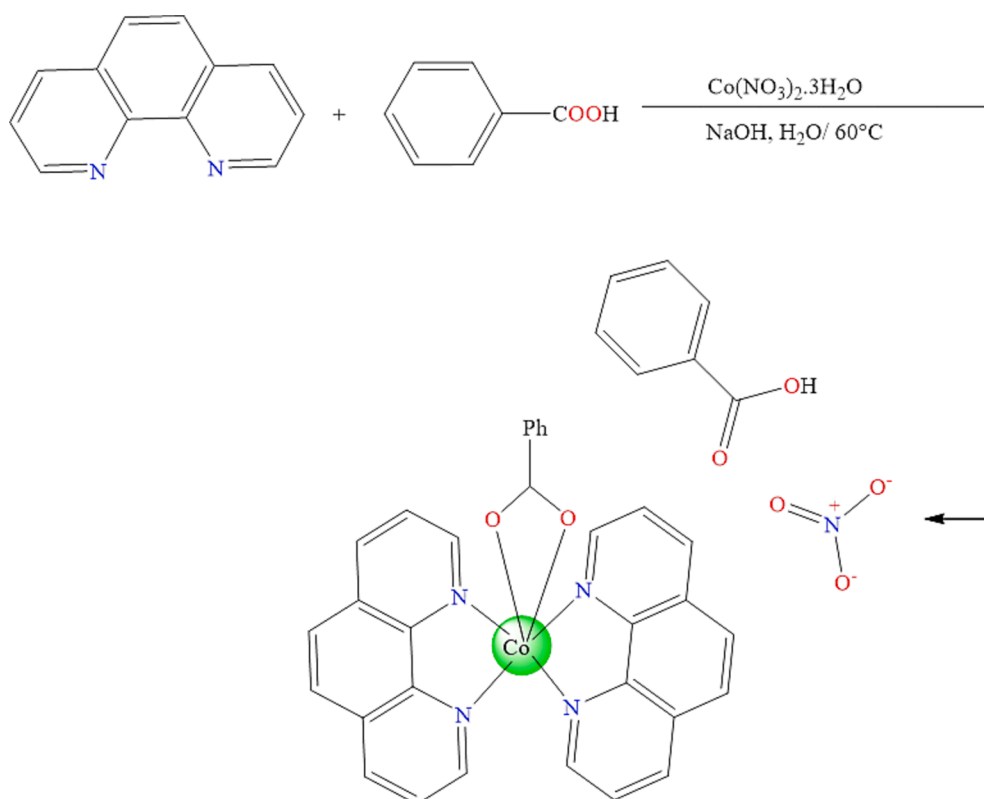
Hirshfeld surfaces (HS) were generated by using electron distributions derived from the sum of spherical electron densities attributed to individual atoms [17,18]. For a given crystal structure and a defined set of spherical atomic electron densities, the resulting HS is specific and unique to that structure [19]. This method has become increasingly popular for examining all interactions within a crystal structure. Using the *CrystalExplorer* software [20], we calculated both the three-dimensional HS and the two-dimensional fingerprint plots for complex (**1**), with visualizations based on the normalized contact distance (d_{norm}).

2.5. Computational details

The Gaussian 09 W program package was used to perform DFT calculations at the DFT/B3LYP and 3-21G basis sets to analyze the structural and electronic properties of our complex and the GausView 0.5 program [21,22]. Using the same technique, HOMO–LUMO plots and surface maps of molecular electrostatic potential were displayed. The Multiwfn program is used [23]. Additionally, Multiwfn software was used to create scatter plots of the reduced density gradients (RDGs) and noncovalent interactions (NCI), and VMD software was used to show the results [24]. Lastly, Multiwfn 3.8 was used to calculate LOL, and ELF functions.

2.6. Molecular docking

Molecular docking analysis was carried out to investigate the



Scheme 1. Reaction pathway for the synthesis of the cobalt(II) complex (1).

Table 1

Main crystallographic data and structure refinement details for (1).

Crystal data	Complex (1)
Chemical Formula	$C_{31}H_{21}CoN_4O_2 \cdot 2(C_7H_6O_2) \cdot NO_3$
Molecular weight (g/mol)	846.69
Elemental analysis found (calc)%	
C	63.97 (63.83)
H	3.81 (3.93)
N	8.08 (8.27)
Diffractionmeter,	Xcalibur, Eos
Radiation type	Mo K α ($\lambda = 0.71073$ Å)
T (K)	295(2)
Calculated density (Mg/m ³)	1.332
Crystal system	Monoclinic
Space group	$I2/a$
a (Å)	13.0418 (19)
b (Å)	19.9959 (16)
c (Å)	16.640 (2)
β (°)	112.231 (17)
V (Å ³)	4017.0 (10)
Z	4
μ (mm ⁻¹)	0.49
Crystal size (mm)	$0.52 \times 0.29 \times 0.22$
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12867, 3808 2842
$R(\text{int})^a$	0.032
Refinement	
$R[F^2 > 2\sigma(F^2)]^b$, $wR(F^2)^c$, S^d	0.047, 0.111, 1.04
No. of unique reflections	3808
No. of parameters	279
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.17, -0.32

^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.

biological activities of (1). To do that, the molecular docking evaluation of the synthesized Co(II) complex was done using Molegro virtual docker MVD 2019.7.0 software with the removal of all water molecules, against the active sites of the proteins of *klebsella pneumonia* (PDB ID: 6RD3) as the ligand 1,10-phenantroline had strong antibacterial activity *in vitro* [25,26]. The structure of the protein database and the three-dimensional structure of (1) was performed by ChemDraw 3D. PyMOL 1.9.0.0 software. The parameters calculated in the docking process are the energy values involved, in the form of MolDock Score, Hbond and Rerank Score as well as the RMSD value. To compute the strength of drug-receptor binding, the parameter that is often used is value Rerank Score.

3. Results and discussion

3.1. Crystal structure analysis

Complex (1) crystallizes in the monoclinic system with space group $I2/a$. Structural analysis reveals that the Co(II) ion exhibits a distorted octahedral coordination environment (as shown in Table 2), formed by two bidentate phenanthroline (*phen*) ligands and one bidentate benzoate ligand (Fig. 1). However, the molecular structure reveals a significant disorder observed in the benzoate ligand. This disorder is attributed to the slight shift of the C5 atom from the special position. This resulted in the formation of a pseudo seven-membered ring. The Co(II) center in complex (1) lies on an inversion center. The basal plane is formed by two nitrogen atoms (N2 and the symmetry-related N2 through an inversion center) from the two phenanthroline (*phen*) ligands, along with two oxygen atoms (O1 and the symmetry-related O1 through the same inversion center) from the bidentate benzoate ligand [27]. The remaining axial positions are occupied by the other two nitrogen atoms (N2 and the symmetry-related N2) from the *phen* molecules. The positive charge on the cationic complex, $[Co(phen)_2(\eta^2-bz)]^+$, is balanced by the presence of one nitrate anion in the crystal lattice, while one neutral

Table 2
Selected bond lengths (Å) and bond angles (°) for (1).

Bond distances (Å)		DFT	Bond angles (°)		DFT
Co1—O1	2.1680 (17)	2.1678	O1 ⁱ —Co1—O1	60.15 (9)	59.92
Co1—O1 ⁱ	2.1679 (17)	2.1678	N1 ⁱ —Co1—O1	97.25 (7)	97.24
Co1—N1 ⁱ	2.096 (2)	2.096	N1—Co1—O1	154.20 (7)	154.20
Co1—N1	2.096 (2)	2.096	N1 ⁱ —Co1—O1 ⁱ	154.20 (7)	154.20
Co1—N2	2.113 (2)	2.113	N1—Co1—O1 ⁱ	97.25 (7)	97.24
Co1—N2 ⁱ	2.113 (2)	2.113	N1 ⁱ —Co1—N1	107.25 (11)	107.24
			N1 ⁱ —Co1—N2	100.49 (8)	100.49
			N1—Co1—N2 ⁱ	100.50 (8)	100.49
			N1 ⁱ —Co1—N2 ⁱ	78.54 (8)	78.54
			N1—Co1—N2	78.54 (8)	78.54
			N2—Co1—O1	89.34 (7)	89.33
			N2 ⁱ —Co1—O1 ⁱ	89.34 (7)	89.33
			N2 ⁱ —Co1—O1	92.04 (7)	92.04
			N2—Co1—O1 ⁱ	178.40 (11)	178.40

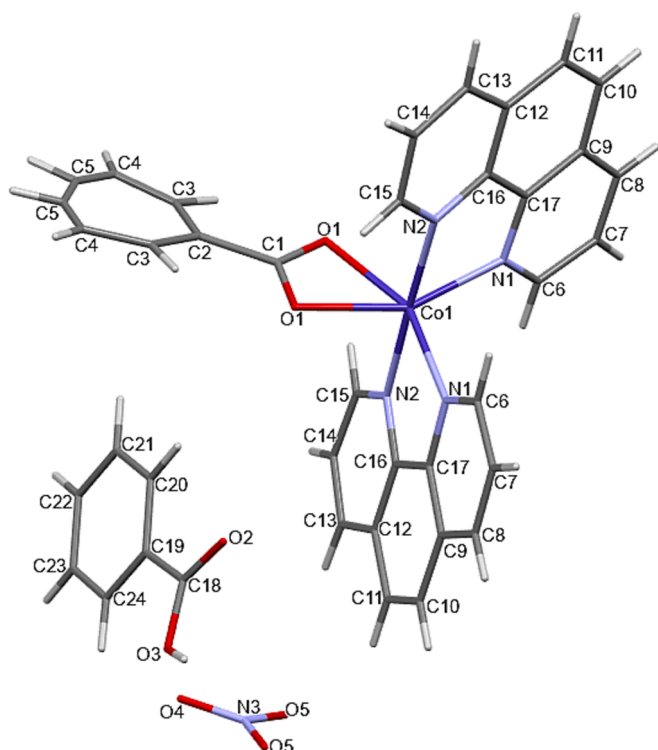


Fig. 1. Molecular structure of [Co(phen)₂(η²-bz)]·2bzH·NO₃ (1).

benzoic acid (bzH) molecule acts as a neutral ligand.

The X-ray crystal structure analysis of complex (1) shows significant aromatic π - π stacking and weak C—H...O interactions, leading to the formation of a 1D supramolecular chain (Fig. 2). There are two distinct types of aromatic π - π stacking interactions observed between the phen rings of adjacent cationic units. Both interactions result in a centroid-to-centroid distance of 3.730 Å within the 1D chains of complex (1), with the shortest distance between two carbon atoms being C6—C11 = 3.708 (5) Å (Fig. S1). Furthermore, each oxygen atom of the coordinated benzoate of one moiety functions as a bifurcated hydrogen bond acceptor, simultaneously accepting hydrogen bonds from two C—H groups of the same phen moiety thus forming a C—H...O type interaction with significant distances [O1...H10 = 2.492(1) Å, O1...H8 = 2.682(1) Å]. This configuration leads to the formation of $R_2^1(6)$ graph-set motifs [28].

Furthermore, the lattice benzoate (bzH) plays a key role in the crystal structure by engaging in two C—H...O hydrogen bonds with the two O5 oxygen atoms of the nitrate anion. This interaction creates a

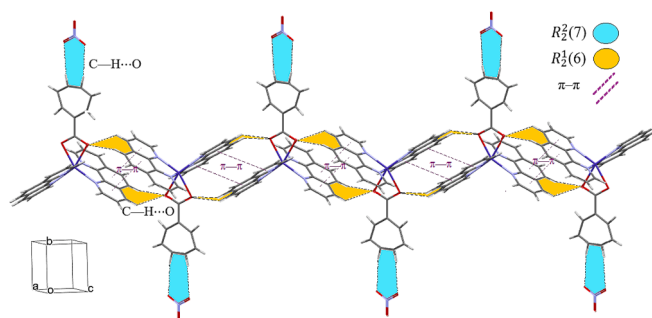


Fig. 2. Representation of the 1D supramolecular chain in complex (1), formed through C—H...O hydrogen bonds (black dashed lines) and π - π interactions (purple dashed lines) along with interactions involving NO₃⁻ anions and the monomeric complex.

characteristic $R_2^2(7)$ graph-set motif (Fig. 2), indicating a specific hydrogen-bonding pattern that contributes to the overall stability and organization of the crystal lattice. These interactions serve as a bridge between different structural units, reinforcing the supramolecular architecture of the crystal.

Each nitrate anion is participating in two O—H...O interactions, with an O3—H3A...O4 distance of 2.879(2) Å. Additionally, the O2 atom of benzoic acid (bzH) engages in moderate C—H...O hydrogen bonding interactions, with the C22—H22...O2 distance of 3.293 Å. The resulting supramolecular ring, consisting of twenty-six members, is described by Etter's graph-set notation as $R_6^4(26)$ (Fig. 3b). Upon closer examination, these [(bzH)₄(NO₃)₂]²⁻ cores interconnect to form an intriguing infinite supramolecular chair-like architecture, designated as {[(bzH)₄(NO₃)₂]²⁻}_n (Fig. 3a). A similar chair-like assembly has been observed in a related structure [29]. This type of hydrogen-bonding network plays a crucial role in stabilizing the crystal structure and highlights the intricate nature of supramolecular self-assembly in such systems.

The neighboring infinite supramolecular chair-like architectures contribute significantly to the stabilization of the compound's layered assembly (Fig. S1). These interactions enhance the overall structural integrity, ensuring the formation of a well-ordered, layered network. The intricate hydrogen bonding and intermolecular forces within this chair-like motif play a crucial role in maintaining the stability and rigidity of the layered structure.

The structural analysis of complex (1) reveals the presence of π - π electrostatic interactions along the crystallographic *b*-axis, involving both the lattice bzH molecules and coordinated phen moieties (Fig. S2). These π - π stacking interactions are distinctly observed between the aromatic rings of the coordinated phen and the bzH lattice components. The centroid-to-centroid distance between the two aromatic systems, specifically (C22, C19, C20, C21, C23, C24) and (C9, C11, C10, C16, C12, C17), measures 3.954 Å, with the closest C—C distance found to be 3.649 Å (C20—C11). These interactions further emphasize the significance of non-covalent forces in stabilizing the crystal lattice, suggesting that π - π stacking plays a crucial role not only in the overall packing of the structure but also in potentially influencing the physical properties of the material, such as its electronic and optical behavior [30,31]. Additionally, lone pair- π (l.p- π) interactions are observed between the O2 atom of the bzH moiety and the pyridyl ring of the phen (Fig. S2), with a separation distance of 3.614 Å. These interactions are crucial as they further contribute to the overall stability and organization of the crystal structure. Lone pair- π interactions play a significant role in molecular recognition and packing, enhancing the rigidity of the supramolecular framework by adding another layer of non-covalent stabilization. This type of interaction is especially important in fine-tuning the electronic environment and intermolecular forces within the crystal lattice [32,33].

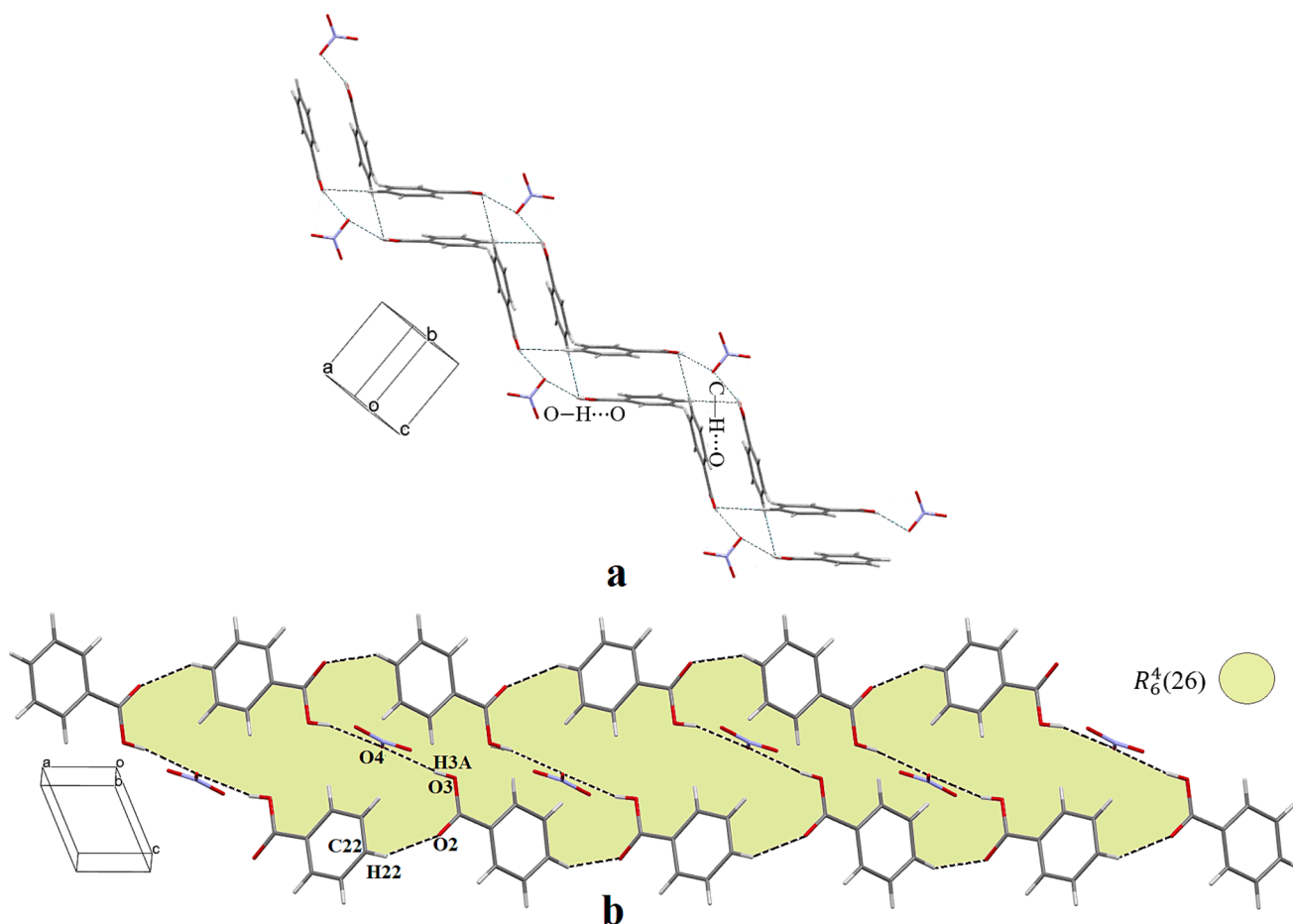


Fig. 3. A: Fascinating infinite supramolecular structure resembling a chair-like $[(bzH)_4(NO_3)_2]^{2-}$ arrangement in (1). b: A different view of –a– highlighting $R_6^4(26)$ Etter's graph-set notation and the interconnected $[(bzH)_4(NO_3)_2]^{2-}$ cores.

3.2. Full interaction maps of (1)

The interaction map analysis for this study was performed using the MERCURY software [12] to visualize the structural features of the novel cobalt(II) complex, $[Co(phen)_2(\eta^2-bz)] \cdot 2bzH \cdot NO_3$ (1). As shown in Fig. 4, distinct interaction hotspots are clearly identified by the presence of intense, opaque red and blue regions, which correspond to areas of

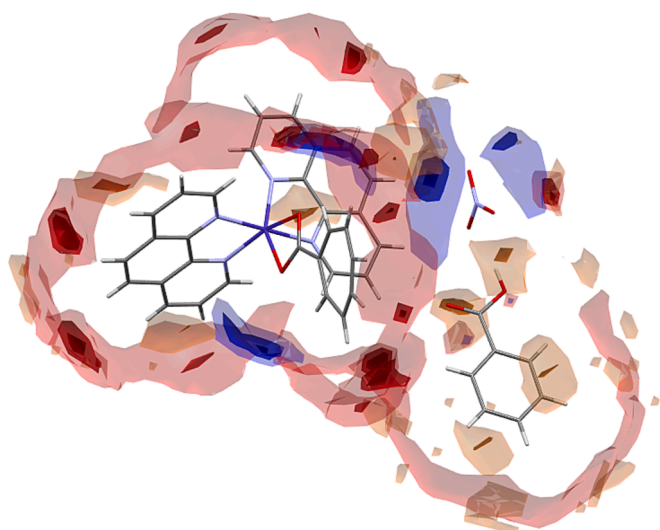


Fig. 4. Interaction maps surrounding the crystal structure of (1).

high interaction density. These regions indicate significant supramolecular interactions that play a crucial role in stabilizing the complex's crystalline architecture. The more pronounced blue hotspots are indicative of donor interactions, suggesting a strong propensity for interactions involving nitrogen atoms from the phenanthroline ligands. Nitrogen atoms serve as hydrogen bond acceptors, forming strong bonding networks. Red hotspots highlight oxygen atoms in the benzoate and nitrate, key to $O-H \cdots O$ and $C-H \cdots O$ interactions that stabilize the supramolecular framework. The contoured interaction map highlights strong and weak interactions, with translucent red and blue zones indicating lower intensities. Subtle $\pi-\pi$ stacking and van der Waals forces between 1,10-phenanthroline ligands contribute to structural stability, forming a robust supramolecular assembly that reinforces the crystal lattice. This analysis reveals the balance of conventional and non-conventional interactions shaping the complex's structural properties. Mapping interaction hotspots enhances understanding of ligand coordination and its impact on the complex's physical and chemical behavior, informing potential applications in catalysis and medicinal chemistry.

3.3. Hirshfeld surface analysis

Hirshfeld surface (HS) analysis effectively quantifies intermolecular interactions and aids in understanding three-dimensional crystal packing. The HS of (1) is illustrated in Figs. 5 and S3, displaying the d_{norm} , shape-index, and curvedness surfaces. The surface captures intermolecular distance information, which can be condensed into a two-dimensional scatter plot representing the external (d_e) and internal (d_i)

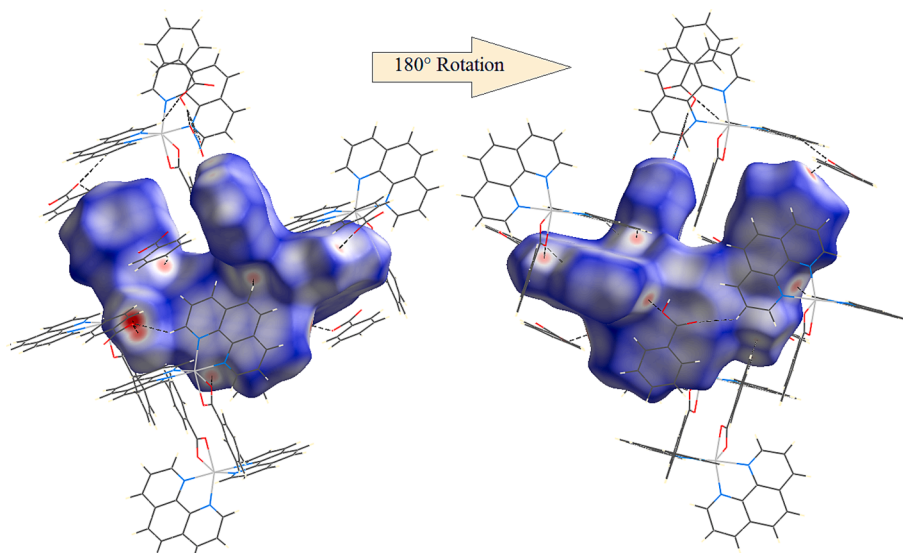


Fig. 5. 3D HSs mapped with d_{norm} in the range of 0.5–1.5 Å: front and back views. The red circles highlight short O—H...O hydrogen bonds, while the less intense spots indicate moderate C—H...O hydrogen bonds.

distances of atoms relative to the surface [34]. The d_{norm} surfaces highlight key hydrogen bonds, with dark-red regions indicating strong O—H...O interactions crucial for structural stability. Lighter red spots reflect weaker C—H...O interactions, suggesting a less significant role in the intermolecular framework.

Hirshfeld surface (HS) analysis offers a comprehensive view of intermolecular interactions within the crystal [35], extending beyond just hydrogen bonding to include weaker interactions such as those involving phenyl rings. The presence of red and blue triangular pairs, particularly when mapped over the shape index around the phenyl rings, provides clear evidence of $\pi\cdots\pi$ stacking interactions (Fig. S3). These $\pi\cdots\pi$ interactions, which were also identified in the detailed structural analysis, play a crucial role in the crystal packing. They contribute not only to the stabilization of the crystal structure but also influence its physical properties. By identifying these $\pi\cdots\pi$ interactions through both HS and structural analysis [36], we can unravel the complex network of forces at play, showcasing how even subtle interactions can significantly impact the overall supramolecular architecture [37]. This detailed understanding is essential for predicting material properties and for the rational design of new compounds with targeted functionalities [38]. Furthermore, the presence of $\pi\cdots\pi$ stacking interactions is further highlighted by the appearance of a flat region distinctly visible on the curvedness surface (Fig. S3), indicating the planar nature of the interacting aromatic rings. Flat regions on the curvedness surfaces highlight $\pi\cdots\pi$ interactions, confirming the parallel alignment of aromatic rings. These stacking interactions enhance crystal stability and packing efficiency, shaping its three-dimensional architecture.

3.4. Elemental analysis

The elemental composition of complex (1) (Table 1) was confirmed by CHN microanalysis, with the following percentages: Carbon (C) 63.97 %, Hydrogen (H) 3.81 % and Nitrogen (N) 8.08 %. This confirms the bulk composition in agreement with the X-ray crystal structure determination.

3.5. IR spectroscopy

FT-IR spectra of (1) has been recorded in the region 400–4000 cm^{-1} (Fig. 6). The band 3473 cm^{-1} can be assigned to the O—H stretching of benzoic acid. The aromatic stretching vibrations of (1) are observed at lower frequencies at 3064 cm^{-1} and 2922 cm^{-1} . The ν_{as} (COO^-) and ν_{s}

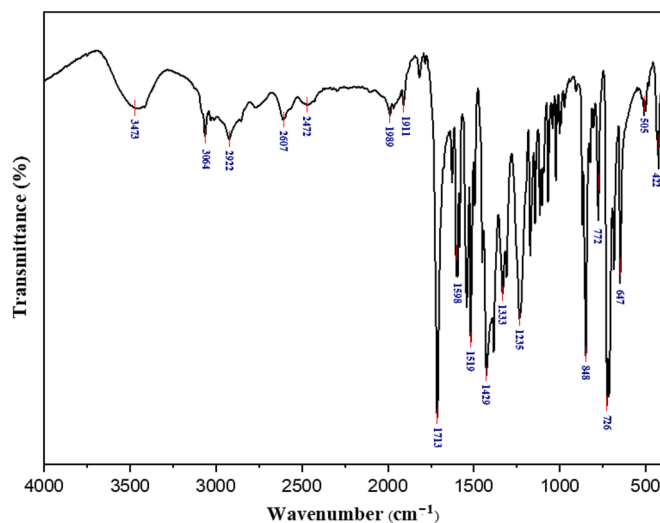


Fig. 6. FTIR spectra of complex (1).

(COO^-) at 1597 and 1333 cm^{-1} are attributed to the carboxylate group of benzoate, the differences between ν_{as} and ν_{s} (COO^-) are approximately 264 cm^{-1} shows that benzoate has bidentate coordination in complex (1) [39]. Above 1712 cm^{-1} stronger bands are seen, which suggests that the lattice of (1) contains uncoordinated carbonyl groups of bzH [40] and at 1519 cm^{-1} suggest the presence of bzH in the lattice of (1). The complex appear to contain free nitrate, as indicated by the strong absorption bands at 1428 cm^{-1} [41]. The coordination of the N, N'-donor ligand to the metal may be confirmed by the presence of the $\nu(\text{M}-\text{N})$ vibration bands at 422 cm^{-1} while the weak bands observed at 647 and 505 cm^{-1} have been assigned to $\nu(\text{M}-\text{O})$ [42].

3.6. Uv-vis spectroscopy

The UV-Visible spectrum of (1) was recorded in methanol between 200 and 800 nm (Fig. S4). The significant electronic absorption bands in the spectra of the complex displays a broad peak in the UV region at $\lambda = 237$ nm assigned to $\pi \rightarrow \pi^*$ transitions of the aromatic ligand [43]. However, $n \rightarrow \pi^*$ transition peak is found at 294 nm. The spectrum shows broad absorptions at 656 nm resulting from the usual ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$

for Co(II) coordination in the complex distorted octahedral environment [44].

3.7. Theoretical analysis

3.7.1. Structural optimization of (1)

Theoretical calculations for (1) were conducted using density functional theory (DFT) with the Gaussian 09 W software package. The molecular geometry (Fig. S5) was optimized using the B3LYP functional and the 3-21G basis set, providing an energy-minimized structure. Table 2 presents a detailed comparison between the calculated and experimental bond lengths and bond angles. Specifically, the theoretical Co—N and Co—O bond lengths were calculated to be in the ranges of 2.09–2.11 Å and 2.16 Å, respectively, which align closely with the experimentally observed values from the X-ray structure determination. These findings confirm the preservation of the distorted octahedral coordination geometry around the cobalt center in both the theoretical and experimental models.

The theoretical analysis indicates that the cobalt ion is coordinated by four nitrogen atoms from the two chelating 1,10-phenanthroline ligands and two oxygen atoms from the benzoate anion, forming a stable six-coordinate geometry. The Co—N bonds, associated with the phenanthroline ligands, exhibit a slight variation in length compared to the Co—O bonds, reflecting the differing electronic environments and coordination strengths of these two ligand types.

In conclusion, the DFT-calculated geometric parameters for the cobalt(II) complex align well with the experimentally derived values from single-crystal X-ray diffraction, affirming the validity of the computational approach and further supporting the experimental findings.

Molecular orbital analysis

Molecular orbital theory predicts and explains the chemical behavior of molecular systems. The HOMO-LUMO energy gap is a key descriptor, essential for determining electrical, optical, and chemical reactivity properties [45,46].

Table 3 shows computed electronic parameters, including chemical hardness (η), chemical potential (μ), and electrophilicity index (ω), derived from HOMO-LUMO energies [47–49]. Chemical potential (μ) reflects stability, hardness (η) indicates resistance to electronic deformation, and electrophilicity (ω) predicts the complex's electron-accepting reactivity. Both electronegativity (χ) and chemical potential (μ) are dependent on the chemical composition of (1). For the cobalt(II) complex studied here, a negative chemical potential of $\mu = -2.80$ eV and an electronegativity value of $\chi = 2.80$ eV were computed (Table 3). The low chemical potential and electronegativity suggest high reactivity, indicating a tendency to attract electrons. Combined with the 0.30 eV energy gap, complex (1) shows high reactivity and polarizability, favorable for catalytic and biological applications.

The distribution of HOMO and LUMO in (1) provides insights into its bonding. As shown in Fig. S6, HOMO electron density is localized on the nitrate group and cobalt center, indicating their role in electron donation. LUMO density spans the phenanthroline ligand, cobalt atom, and nitrate, highlighting potential nucleophilic and electronic interaction sites. The low HOMO-LUMO energy gap suggests high reactivity, making the complex a promising candidate for catalytic and biological applications. This narrow gap indicates significant polarizability, potentially contributing to biological activity. The calculated chemical potential (μ) confirms stability, while the global electrophilicity index (ω) highlights strong electrophilic reactivity, supporting its potential in diverse chemical environments [50].

Table 3
Chemical reactivity parameters.

Complex	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	χ (eV)	μ (eV)	η (eV)	ω (eV)
(1)	−2.95	−2.65	0.30	2.80	−2.80	0.15	26.13

3.7.2. Molecular electrostatic potential (MEP)

The molecular electrostatic potential (MEP) is a valuable tool for visualizing the distribution of electrostatic potential across a molecule, providing key insights into regions susceptible to electrophilic or nucleophilic attack. The MEP map of complex (1), illustrated in Fig. S7, is divided into three distinct color-coded regions, each corresponding to a different level of electrostatic potential. In contrast, the red regions, which signify areas of high electron density, are indicative of regions prone to electrophilic attack. These regions are primarily localized around the oxygen atoms of the benzoate ligand and the nitrate group, suggesting their role as electrophilic targets due to the high electron density accumulated at these sites. The blue regions, associated with areas of low electron density, correspond to zones where nucleophilic attack is more likely to occur. These regions are concentrated around the cobalt center and the nitrogen atoms of the 1,10-phenanthroline ligands, reflecting the nucleophilic character of these sites. This is particularly relevant in understanding the reactivity of the complex in biological environments, where such regions could interact with electrophilic species. Conversely, the positive electrostatic potential (blue areas), observed around the metal center and the nitrogen atoms of the ligands, highlights regions that can act as nucleophilic sites, which could participate in metal–ligand coordination and hydrogen bonding interactions.

The MEP analysis offers a detailed view of the electrostatic landscape of the complex, identifying key reactive sites for both electrophilic and nucleophilic interactions. This insight is crucial for predicting the chemical behavior of the complex in various environments, including its potential biological activity and its reactivity in catalytic processes.

3.7.3. ELF and LOL analyses

The Electron Localization Function (ELF) and Localized Orbital Locator (LOL) visualize electron density distribution, enabling analysis of localized and delocalized bonding interactions [51]. ELF maps electron pair density, while LOL highlights orbital gradients using kinetic energy density. These mappings identify reactive sites in (1), as shown in Fig. 7. ELF values range from 26.55 to 3.79 Bohr³, with blue regions indicating high electron localization (covalent sigma bonds) and red regions representing delocalized electron density in π -systems.

Delocalized electrons are primarily found on hydrogen atoms, shown by the greenish-blue color, indicating electron delocalization in the phenanthroline ligands. Blue areas represent strong sigma bonding between hydrogen and carbon in the heterocyclic rings, reflecting high

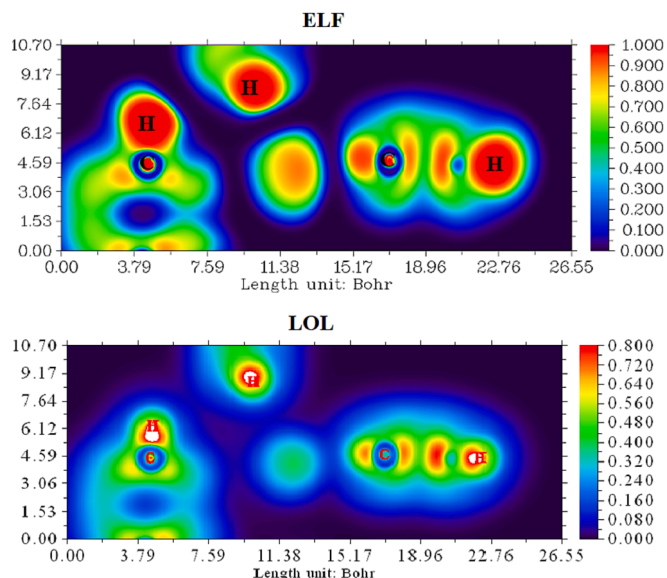


Fig. 7. ELF and LOL of (1).

electron density. Lower electron density on carbon atoms confirms their role in π -electron delocalization, while hydrogen atoms display higher density due to sigma bonding.

The color-coded maps emphasize the key bonding interactions: highly localized sigma bonds between the cobalt ion and its coordinating ligands, particularly nitrogen and oxygen atoms, are visible in the blue regions, while the more delocalized electrons in the π -systems of the phenanthroline ligands are observed in the green and red zones. This balance between localized and delocalized electrons is essential for the stability and reactivity of the complex.

3.7.4. Reduced density gradient (RDG)

The Reduced Density Gradient (RDG) is a powerful analytical tool used to visualize and quantify non-covalent interactions (NCI) within molecular systems. Computed using the Multiwfn software, RDG is a dimensionless quantity derived from the electron density and its first derivative [52]. This method provides a detailed representation of weak forces in real space, including attractive and repulsive interactions that do not involve electron sharing or transfer [53]. The RDG method is highly effective in distinguishing between various types of non-covalent interactions, such as hydrogen bonds (H-bonds), van der Waals forces, and steric repulsion, allowing for a comprehensive understanding of the molecular stability and reactivity of complex systems.

RDG analysis is useful for distinguishing bonding interactions ($\lambda_2 < 0$) from non-bonding ones ($\lambda_2 > 0$), with λ_2 serving as a key parameter for identifying attractive or repulsive forces [54]. The RDG plot for (1) (Fig. 8) highlights non-covalent forces contributing to structural stability. Three regions are visible: blue areas indicate strong attractive interactions, mainly hydrogen bonds, stabilizing the cobalt center through interactions with benzoate oxygen and phenanthroline nitrogen atoms. Red regions indicate steric repulsion within the aromatic rings of phenanthroline ligands, arising from electron cloud proximity. Despite this, steric interactions contribute to structural integrity and packing. Green regions highlight weaker van der Waals forces, particularly between benzoic acid and the nitrate anion, further stabilizing the crystal lattice. RDG analysis confirms that hydrogen bonding, van der Waals forces, and steric repulsion create a balanced interaction network, stabilizing the complex and supporting the cobalt ion's coordination. These findings align with X-ray data, underscoring the role of non-covalent interactions in maintaining structure and potential biological activity.

3.8. Molecular docking study

Molecular docking predicts ligand–protein interactions, offering insights into binding affinity and recognition. This study docked complex (1) with *Klebsiella pneumoniae* protein (PDB: 6RD3) to evaluate its interaction with a receptor linked to bacterial infections.

The molecular structure of the cobalt complex (1) was first optimized using the Gaussian software. Molecular docking simulations were performed using Molegro Virtual Docker (MVD 2019.7.0). The 3D structure of the protein was obtained from the Protein Data Bank (PDB). The docking results, summarized in Table 4 and visualized in Fig. 9, reveal that (1) exhibits a high affinity for the *Klebsiella pneumoniae* protein receptor. The docking poses show that the ligand forms hydrogen bond interactions with amino acid residues in the active site of the protein, including Met 36, Try 35, Asn 63, Gln 61, and Ala 62. These hydrogen bonds play a critical role in stabilizing the ligand–protein complex, ensuring a strong interaction between the cobalt complex and the receptor.

In addition to hydrogen bonds, significant steric interactions were observed with residues Gln 71, Asn 59, Val 60, Thr 34, Asp 18, and Gln 33. These steric interactions further enhance the binding affinity of the ligand, contributing to the overall stability of the docked complex. The combination of hydrogen bonding and steric interactions indicates that complex (1) is well-suited for targeting the active site of the protein. The complex has potential to inhibit the function of the protein.

The binding affinity of the complex was quantified by a Rerank score of -60.56 kcal/mol and a Moldock score of -120.50 kcal/mol, indicating strong and stable interactions with the bacterial protein. These results highlight the potential of complex (1) for therapeutic development, especially against drug-resistant bacterial strains. Hydrogen bonding between the ligand's heteroatoms (N and O) and the protein enhances interaction stability and specificity, reinforcing the complex's potential as a treatment for multidrug-resistant *Klebsiella pneumoniae*.

Molecular docking shows that complex (1) strongly binds to *Klebsiella pneumoniae* protein, making it a promising lead for antibacterial development. Its high affinity, stable hydrogen bonds, and steric interactions highlight potential efficacy against drug-resistant pathogens.

Given the labile nature of Co(II) ions, the stability of complex (1) in solution may vary, potentially leading to a mixture of coordination species. Such behavior is common for Co(II) complexes, where the observed solid-state structure might differ in solution. This aspect warrants further investigation, as it could influence the antibacterial activity.

Table 4

Binding interactions details of (1) docked at the binding pocket of the target proteins 6RD3.

Ligand	Enzyme	Type of interaction	Residue	Rerank Score
Complex (1)	6RD3	– Hydrogen bond – Steric interactions	Met 36, Try 35, Asn 63, Gln 61, Ala 62 Gln 71, Asn 59, Val 60, Thr 34, Asp 18, Gln 33	-60.56

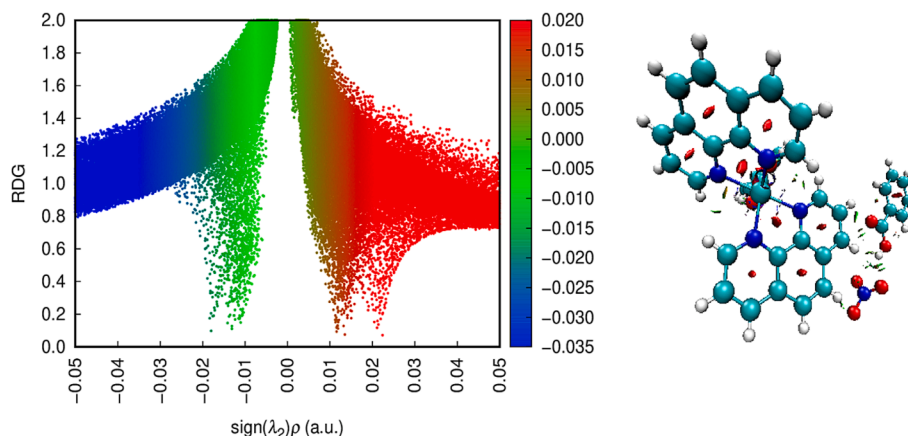


Fig. 8. RDG surface map of complex (1).

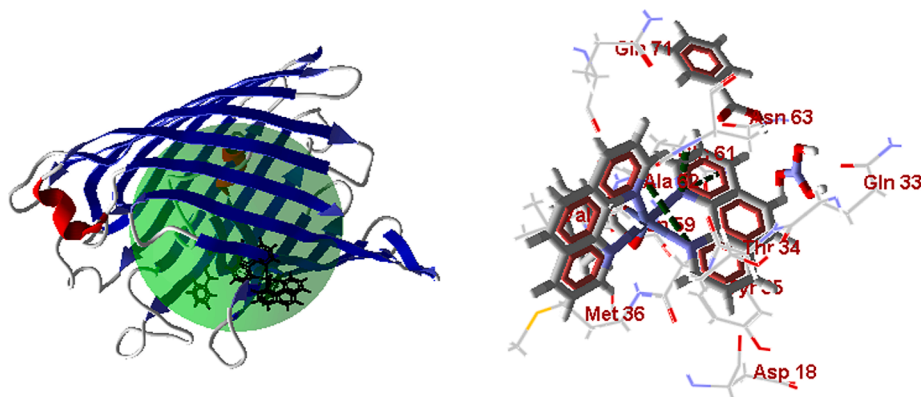


Fig. 9. The binding interactions of (1) against protein *K. pneumoniae* (PDB: 6rd3).

reported. Although our study does not include solution-state stability analysis, future work could focus on characterizing the behavior of complex (1) in solution to better understand its structure–activity relationship.

4. Conclusion

In this work, we synthesized and characterized a novel cobalt(II) complex, $[\text{Co}(\text{phen})_2(\eta^2\text{-bz})]\cdot 2\text{bzH}\cdot\text{NO}_3$ (1), with a six-coordinate octahedral geometry stabilized by 1,10-phenanthroline and benzoate ligands. Single-crystal X-ray diffraction revealed non-covalent interactions, including hydrogen bonding and π – π stacking, which enhance the stability and supramolecular framework of the complex. DFT calculations optimized the geometry and provided electronic insights, with strong agreement between experimental and theoretical data, confirming DFT's reliability. MEP and HOMO–LUMO analyses identified reactive sites, suggesting potential biological activity. Hirshfeld surface analysis highlighted the role of intermolecular interactions in crystal packing, reinforcing the structural stability and reactivity of the complex. Molecular docking revealed strong binding to *Klebsiella pneumoniae* receptors, suggesting potential antibacterial activity and positioning the complex as a candidate for developing new agents against multidrug-resistant bacteria. The similarities with copper(II) complexes containing the same ligands further emphasize the versatility and therapeutic potential of these systems in medicinal chemistry. However, it is important to note that the observed antibacterial activity of complex (1) is strongly linked to its structural integrity as determined in the solid state. Given the labile nature of Co(II) ions, it is possible that a mixture of coordination species forms in solution, potentially influencing biological activity. This raises the intriguing possibility that the active species interacting with bacterial receptors may differ from the isolated solid-state structure. While this study primarily focuses on the solid-state properties and their role in antibacterial interactions, future work should investigate the solution-state behavior of the complex. Techniques such as UV–Vis spectroscopy, potentiometric titrations, or NMR spectroscopy could provide valuable insights into its dynamic speciation in solution and its correlation with biological activity.

This study advances coordination chemistry by providing new insights into the structure–activity relationships of cobalt-based complexes. The integration of experimental and theoretical approaches enhanced our understanding of the complex's geometry and electronic properties, highlighting its potential for biomedical and catalytic applications. The findings pave the way for future investigations into the reactivity and biological activity of cobalt complexes, with prospects for developing novel materials of industrial and medicinal significance.

CRediT authorship contribution statement

Yasmina Sabeg: Project administration, Investigation. **Rim Benali-Cherif:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Methodology, Investigation, Conceptualization. **Wahiba Falek:** Methodology, Investigation. **Radhwane Takouachet:** Writing – original draft, Software, Methodology, Conceptualization. **Lynda Golea:** Writing – original draft, Validation, Supervision, Software, Methodology. **Muhittin Aygün:** Supervision, Software, Resources, Methodology. **Nourredine Benali-Cherif:** Visualization, Validation, Supervision, Software, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We thank the Algerian MESRS (Ministère de l'Enseignement Supérieur et de la Recherche Scientifique) and DGRSDT (Direction Générale de la Recherche Scientifique et du Développement Technologique) and Abbes Laghrour Khenchela University, for financial support.

Appendix A. Supplementary data

CCDC 2366740 contain the supplementary crystallographic data for (1). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2025.117445>.

Data availability

Data will be made available on request.

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