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Synthesis, Characterization and properties studies of new magnetic materials

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Abstract. We are interested in molecular polymetallic species having high spin and nuclearities in relation to the field of so call single-molecule magnets (SMMs). The goal is to find a way to synthesis metal clusters which may have application in magnetism and nano-sciences. With this purpose, we decided to investigate the coordination chemistry of the Schiff base. Along this way we were able to create cubane-like complexes and elaborate new Single Molecule-Magnets. The idea was to use Schiff base ligands and different metals to generate high nuclear complexes. Complexation of Schiff base with copper has been investigated. Tetranuclear complex with a cubane like core have been synthesised with (Schiff base), with the same base and cobalt we obtains an other single magnetic complex completely different.

1. Introduction

Among the possibilities offered by the coordination chemistry, obtaining molecules loving (Single Molecule Magnets, SMM) is probably the most significant progress. In fact, a bit of information could be attributed to a single molecular entity. Many strategies have been developed to synthesize such molecules must involve many carriers spin to have a high magnetic moment and have a strong magnetic anisotropy [1-6].

One of the strategies developed by the team based on the synthesis of ligands which are simple Schiff bases of β -diketone. Attractive, these ligands have the advantage of being shaped to perfection with a multitude of functions and chemical donating groups depending on the application required. The use of these ligands for the complexation of transition metals such as copper or cobalt, for example, yielded tetra nuclear complex $[\text{CuII}_4]$ or tetra nuclear mixed-valence $[\text{CoII}_3\text{CoIII}_4]$.

2. Results and discuss

2.1 Materials and methods

The unit cell determination and data reduction were performed using the CrysAlis program (Oxford Diffraction., 2006) on the full set of data.

Calculations were carried out using the WinGX software package [7]. The crystal structure was solved by direct methods using SIR2004 [8] and refined by full-matrix least-squares against F^2 using all data (SHELX97) [9].

All non-H atoms were modelled with anisotropic displacement parameters. The H atoms attached to $-\text{CH}_3$ were located in difference Fourier maps refined as riding atoms (isotropically with a restrained bond distance) with distances constraints of methyl C-H = 0.96 Å and $U_{\text{iso}}(\text{H}) =$



1.5Ueq(C). Aromatic H atoms were positioned geometrically and were allowed to ride on their parent C atoms with C-H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Crystal structure was visualized using ORTEP3 [10] and MERCURY [11]. Analyses were carried out using the program PLATON [12], as incorporated in the WinGX [13].

2.1- Crystal Structure Analysis

2.1.1 Complex of copper (I). The complex (I) crystallizes in the monoclinic space group $P2_1/n$. The molecular structure of the complex (I) and the atom-labeling scheme are shown in (Figure 1). After several cycles of refinement until convergence, we obtained factors reliability $R = 4.5\%$ and $R_w = 7.1\%$. The asymmetric unit corresponds to four copper ions, two ligand type (D) and two other ligand type (L). The formula of the complex is refined $[Cu_4(L-L)_2(D-L)_2]$. The metal cluster in turn can be described as a square Cu_4 in which each copper ion (II) is coordinated to a ligand type (L) and ligand type (D) coordinate two metals at a time.

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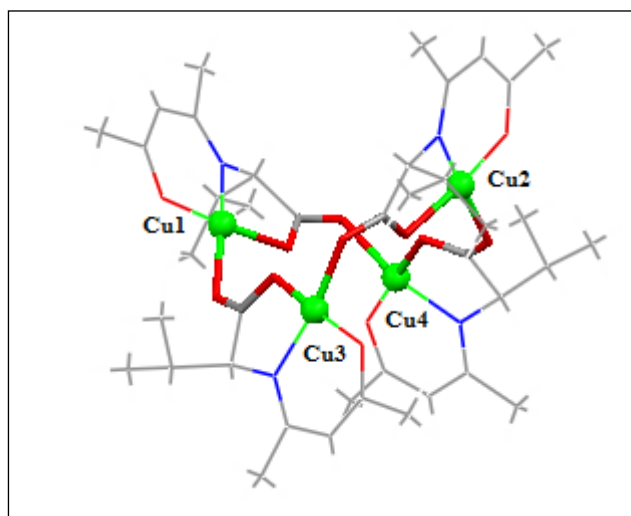


Figure 1: Asymmetric unit and atom-numbering scheme of (I)

2.1.2 The Complex of cobalt. The complex (II) crystallizes in the triclinic, $P-1$ space group. The final refinement of the structural model performed using the SHELXL97 program led to the reliability factors $R = 0.13$ unweighted and weighted $R_w = 0.44$ with a $goof = 1.119$. The molecular structures of (II) and the atom-labeling scheme are shown in (Figure 2). The four cobalt atoms form a rhombus whose center is the center of inversion of the molecule (Figure 3). The atom Co (1) is in a hexacoordinate pseudo-octahedral surrounded by oxygen of the acid function, an oxygen atom of the acac and a nitrogen atom of the same ligand (L) configuration, oxygen a methanolate type (μ_3 -OMe) and one oxygen methanolate another type (μ_2 -OMe), as well as a methanol. The base of the octahedron is formed by three atoms of oxygen and a nitrogen atom, the two peaks are the two oxygens of the

ligand. The Co atom (2) is in a second position hexacoordinate crystallographic in a distorted octahedral environment by effect of the two intramolecular hydrogen bonds. This atom (Co2) is surrounded by: two two oxygens methanolates type (μ_2 -OMe), a third oxygen methanolate type (μ_3 -OMe), an oxygen of the carboxyl function of the ligand configuration (D) and two two molecules of methanol oxygens. The base of the octahedron is formed by four oxygen atoms attributed to: methanolate type (μ_2 -OMe), methanolate type (μ_3 -OMe), methanol, and a carboxylic function and the two peaks are of a methanol oxygen and another oxygen from a methanolate(μ_3 -OMe).

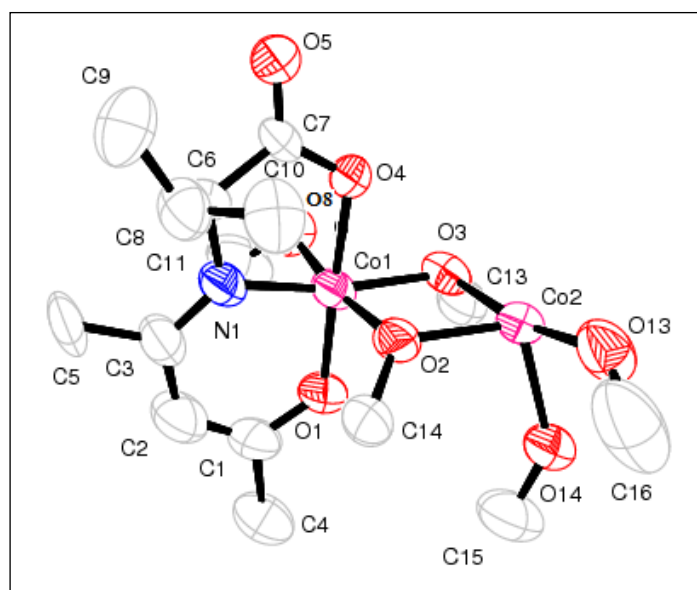


Figure 2: Asymmetric unit and atom-numbering scheme of (II) . Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small sphere of arbitrary radii.

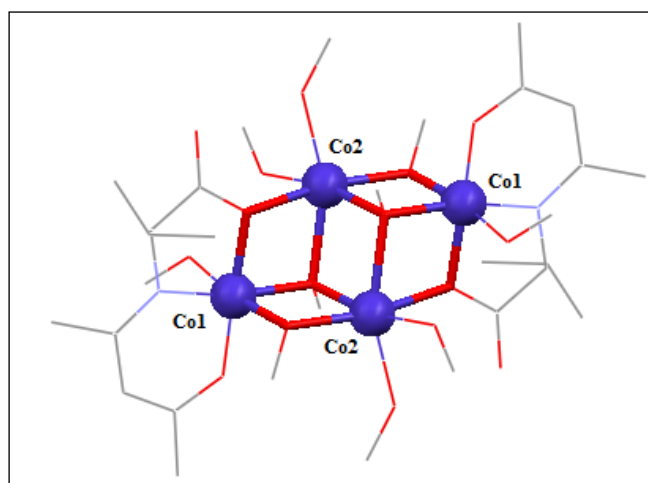


Figure 2: Complex of Cobalt

2.2. Magnetism:

2.2.1. *Complex of copper (I)*. Studies of the magnetic properties were carried out for this compound; the thermal variation of the product of the magnetic susceptibility in the temperature of the complex is shown in **figure (4)**.

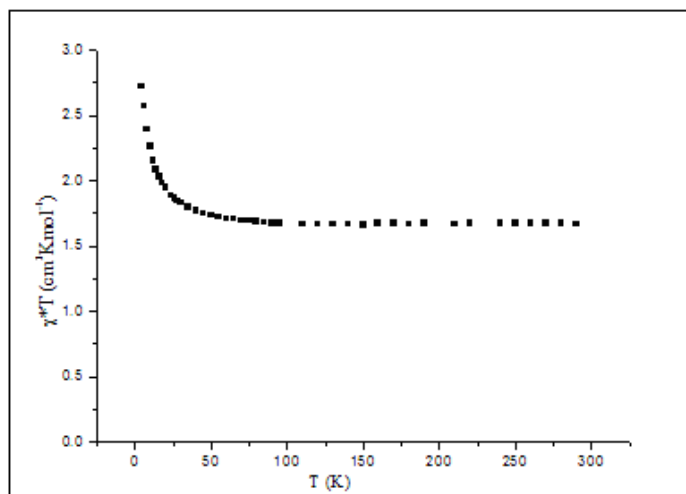


Figure (4): Evolution of temperature χT product.

At 300K, χT has a value of 1.68 cm³.K.mol⁻¹ which is a little higher than the value expected for four copper CuII ($S = 1/2$) magnetically independent from each other ($4 \times 0.375 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$). χT increases steadily when lowering the temperature to the value of 2.72 cm³.K.mol⁻¹ at 4K which is close to the value expected for ferromagnetically coupled four brass ($S = 2$, $\chi T = 3 \text{ mol cm}^3 \cdot \text{K}^{-1}$) this behavior is indicative of dominant ferromagnetic interactions within the complex which is confirmed by the value of the saturation magnetization measured at 2K **figure (5)** tends to the expected value for four copper, namely 4 μ B.

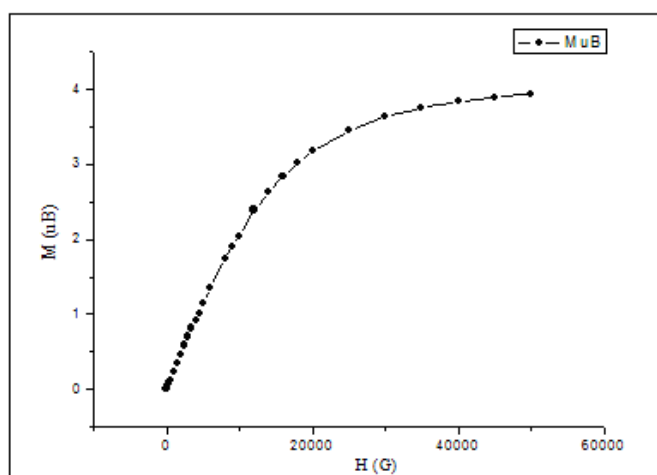


Figure (5): Dependence of the magnetization as a function of the field.

2.2.2. *Complex of Cobal.* In addition to its structural characteristics, the complex also has magnetic properties Figure (6) that we will discuss.

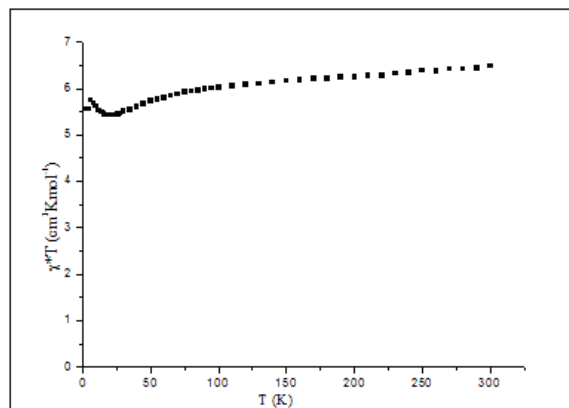


Figure (6): Evolution of temperature χT product.

At 300K, a χT value of $6.45 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ which lower the expected value for two CoIII and CoII two magnetically independent ($9.75 \times 3 = 2 \times 1.875 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ with $g = 2$). χT decreases when the temperature is lowered to a minimum and this 20K-1 $5.42 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, and then increases to a maximum at 6K ($5.74 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$), and then decreases at lower temperature. This behavior is the signature of dominant ferromagnetic interactions; the value of the saturation magnetization measured at 2K tends to $6\mu\text{B}$ **Figure (7)**.

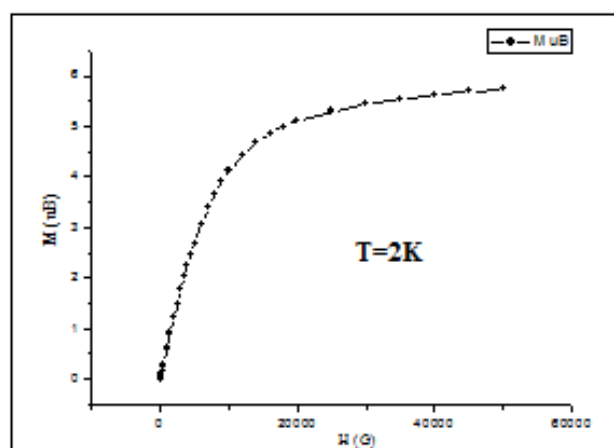


Figure (7): Dependence of the magnetization as a function of the field.

3. Experimental part

3.1 The complex of copper

(1mmol, 237mg) of the ligand (L1HK) is dissolved in 20 ml of methanol, to this solution was added one equivalent of copper chloride (1 mmol, 170 mg) dissolved in 10 ml of ethanol: a green solution is obtained. After ten minutes of stirring, 3 equivalents (0.6 ml) of triethylamine are added the solution

becomes very intense green. Slow evaporation of the latter leads to the production of single crystals of good size and good quality usable in X-ray diffraction after slow evaporation of the solvent.

3.2 *The complexe of cCobalt:*

The ligand L1HK (236mg, 1mmol) was dissolved in 10 ml of methanol. To this solution is added (129mg, 1 mmol) of cobalt chloride (CoCl₂) previously dissolved in methanol: a brown solution is obtained. 0.6 ml of triethylamine dissolved in 10 ml of methanol was added and the solution becomes orange-brown. Slow evaporation of the latter leads to the production of single crystals after some days of acceptable size, usable in X-ray diffraction

4. Conclusion:

In general this work contributed to new approaches for the development of new molecular-based materials; We therefore conducted a study crystallographic and magnetic susceptibility measurements on a complex tetra nuclear of copper. Such complexes are currently intensively are studying because it has an interest in biological processes and in the design of inorganic materials⁽⁴⁻⁶⁾. One of our goals is the synthesis of heterometallic using tetramer as brick departure. More we can synthesize a new complex "cubane mixed valence cobalt based" rather than a wheel (similar to copper) although we used the same ligand because of the chemistry of cobalt complexes it involves complicated processes which which most crystallographically characterized compounds are not the only product present in the solution. The synthesis included the protonation / deprotonation redox chemistry and understanding of several species simultaneously. (The source of cobalt ions is a cobalt salt with the oxidation state (+ II), some of which go to the oxidation state (+ III) after partial oxidation. Process is very difficult to control because the oxidation proceeds from a part of the use of the base and the other of the water molecules.

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