



## Synthesis and characterization of a new Organic – Inorganic sulfate (C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O)<sub>2</sub>[Co(H<sub>2</sub>O)<sub>6</sub>]<sub>3</sub>(SO<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O

M.Mathlouthi<sup>a</sup>, S.Benmansour<sup>b</sup>, M.Rzaigui<sup>a</sup> and W.Smirani Sta<sup>\*,a</sup>

a- Laboratoire de chimie des matériaux, Faculté des sciences de Bizerte, 7021, Zarzouna, Tunisia

b- Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, C/Catedrático José Beltrán, 246980 Paterna, Spain.

\*Corresponding author: wajda\_sta@yahoo.fr

### ABSTRACT

Crystals of a new hybrid compound, (C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O)<sub>2</sub>[Co(H<sub>2</sub>O)<sub>6</sub>]<sub>3</sub>(SO<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O, were synthesized in aqueous solution and characterized. This compound crystallizes in the triclinic system with the space group P-1, the unit cell :a=6.632(3) Å, b=11.769(5) Å, c=14.210(6) Å, α=67.86(4)°, β=81.32(4)°, γ=85.18(4)° and V=1015.14(8) Å<sup>3</sup>. Its crystal structure can be described as a packing of alternated inorganic and organic layers. The different components are connected by a three-dimensional network of O-H...O and N-H...O hydrogen bonds.

### Indexing terms/Keywords

Organic-inorganic hybrid; Crystal structure; IR Spectroscopy; Band-gap.



# Council for Innovative Research

Peer Review Research Publishing System

**Journal:** Journal of Advances in Chemistry

Vol. 10, No. 4

[editorjaconline@gmail.com](mailto:editorjaconline@gmail.com)

[www.cirjac.com](http://www.cirjac.com)

## 1. INTRODUCTION

Research activities in the area of chemical diversity of inorganic compounds templated by organic amines have been growing enormously during the past few years [1]. Most of those compounds are based on oxygen containing materials consisting of elements from the main block of the periodic table and the transition metals. Those materials are of great interest to both industrial and academic fields due to their catalytic, adsorption and ion-exchange properties [2,3]. Particularly, the open-framework sulfates combining transition metal and organic groups are of great interest not only for their potential as model compounds of ferroelectric and ferroelastic domains, but also for their promising application in the field of molecular magnetism [4]. A variety of amines have been used previously in the preparation hybrid metal sulfates including aliphatic [5], aromatic [6] and cyclic amines [7]. We have focused our attention on the 2-amino-6-hydroxypyridine which used in the manufacture of pharmaceuticals, especially antihistaminic drugs and we report here the crystal structure of  $(C_5H_6N_2O)_2[Co(H_2O)_6]_3(SO_4)_4 \cdot 2H_2O$ .

## 2. EXPERIMENTAL

### 2.1 Material Preparation

To an aqueous solution of 2-amino-6-hydroxypyridine (0,41g; 3,76mmol) was added cobalt (II) Acetate (1g; 5,65mmol) dissolved in 15 ml of water. The resulting solution was added to an aqueous solution of sulfuric acid (0,1M). The mixture was stirred for 20 min at room temperature. After slow evaporation during a few days at ambient temperature, pink single crystals of the title compound appeared in the solution.

### 2.2 Physical measurement

Single crystals of the compound was mounted on a glass fibre using a viscous hydrocarbon oil to coat the crystal and then transferred directly to the cold nitrogen stream for data collection. X-ray data were collected at 120 K on a Supernova diffractometer equipped with a graphite-monochromated Enhance (Mo) X-ray Source ( $\lambda = 0.71073 \text{ \AA}$ ). A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of  $0.77 \text{ \AA}$ . The structure was solved and refined using SHELXL-97 [8]. A direct-methods solution was calculated that provided most of the non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed that located the remaining nonhydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The final refinement cycles led to  $R_1 = 0.038$  and  $wR_2 = 0.092$ .

The infrared spectrum of solid  $(C_5H_6N_2O)_2[Co(H_2O)_6]_3(SO_4)_4 \cdot 2H_2O$  was recorded on a Nicolet IR200 FT-IR Spectrometer at ambient temperature.

The UV-Vis absorption (water solution) and optical diffuse reflectance spectra were measured at room temperature with a Perkin Elmer Lambda 11 UV/Vis spectrophotometer in the range of 200-800 nm.

## 3. RESULTS AND DISCUSSION

### 3.1 X-ray diffraction analysis

Crystal data summary of intensity data collection and structure refinement are reported in Table 1. Interatomic distances and bond angles are given in Table 2. First of all, an examination of this table shows that the distance value of C3X-O3X ( $occ(O3X) = 0.5$ ) indicate a double bond, a similar short bond length was observed in 3-ethoxycarbonyl-2-phenyl-6-methoxycarbonyl-5,6-dihydro-4-pyridone [9]. There is a keto-enol tautomerism which has been known since 1907 [10]. Various theoretical studies have also been reported and show that substituents at position 6 have the greatest effect; electron-withdrawing substituents are seen to drive the equilibrium towards the pyridinol tautomer, whereas electron-donating substituents favour the pyridone tautomer. The rationale behind this has already been explained in terms of resonance stabilization and destabilization by the substituent [11].

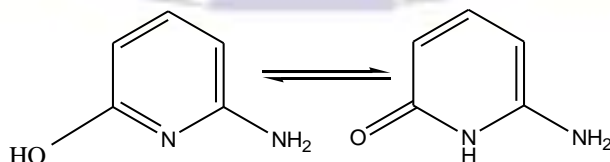
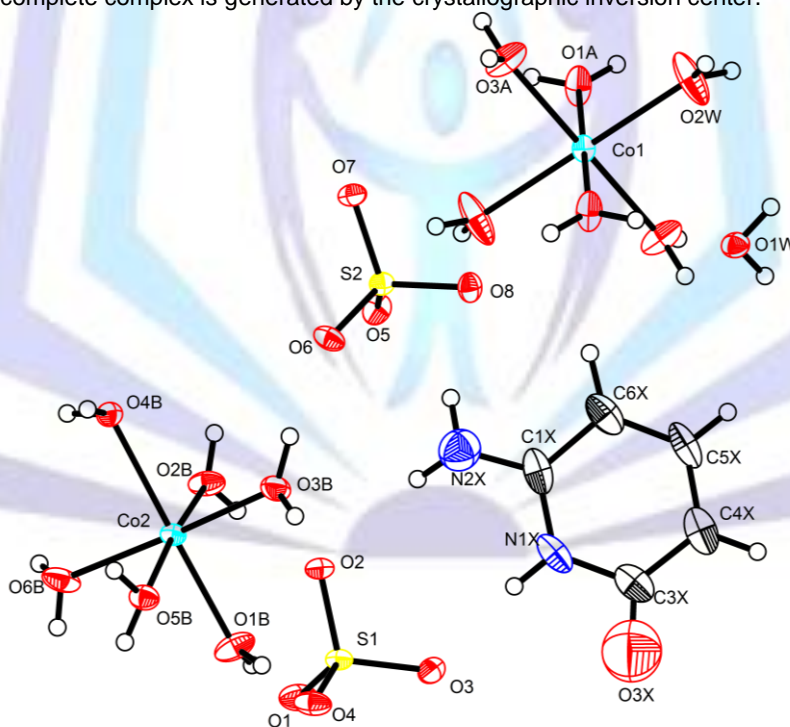


Table 1. Crystal data and structure refinement

|                                      |                                |
|--------------------------------------|--------------------------------|
| Empirical formula                    | $C_{10}H_{25}N_4O_{37}S_4Co_3$ |
| Formula weight( $g \cdot mol^{-1}$ ) | 1125.58                        |
| Wavelength ( $\text{\AA}$ )          | 0.71075                        |
| Crystal system                       | triclinic                      |
| Space group                          | P-1                            |
| $a$ ( $\text{\AA}$ )                 | 6.632(3)                       |

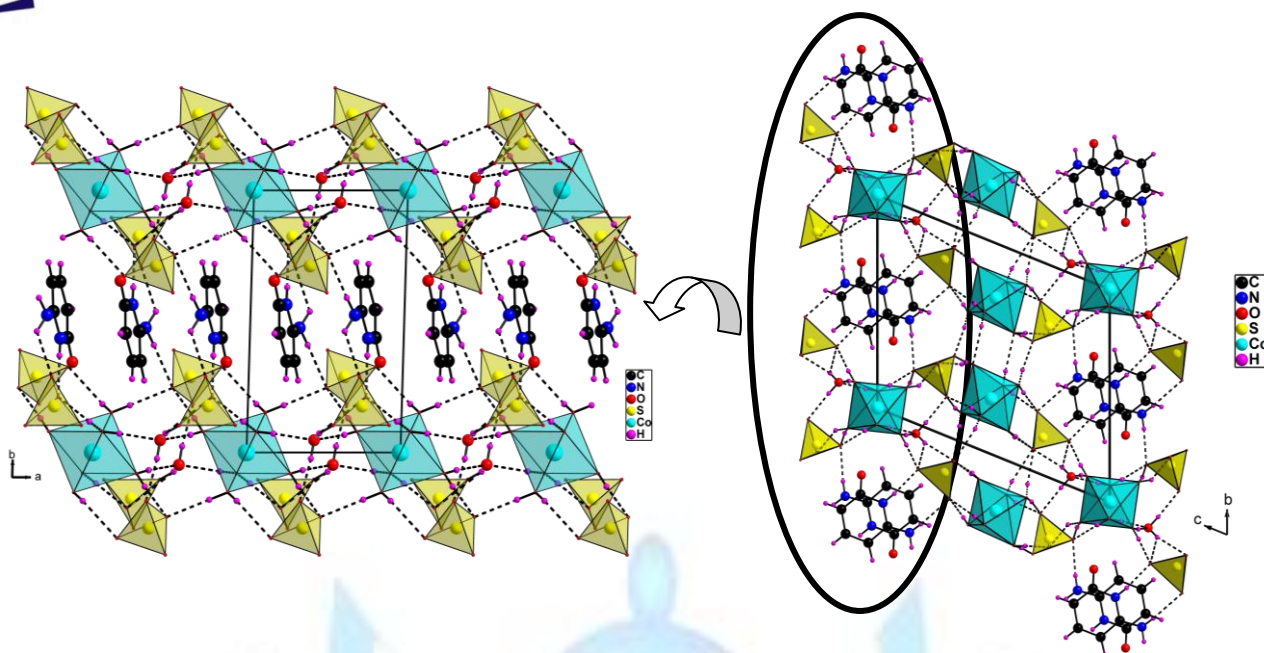
|  |                              |
|--|------------------------------|
| $b$ (Å)  | 11.769(5)                    |
| $c$ (Å)  | 14.210(6)                    |
| $\alpha$ (°)                                     | 67.86(4)                     |
| $\beta$ (°)                                      | 81.32(4)                     |
| $\gamma$ (°)                                     | 85.18(4)                     |
| Volume (Å <sup>3</sup> )                         | 1015.14(8)                   |
| $Z$  | 2                            |
| $D_{\text{calc}}$ (g/cm <sup>-3</sup> )          | 1.842                        |
| Absorption coefficient (cm <sup>-1</sup> )       | 1.535                        |
| $F(000)$   | 581                          |
| Crystal size (mm <sup>3</sup> )                  | 0.35 × 0.20 × 0.15           |
| Reflections collected                            | 13083                        |
| Unique reflections / No. Variables               | 4263/361                     |
| Goodness-of-fit on $F^2$                         | 1.026                        |
| Final R indices [ $I > 2$ sigma ( $I$ )]         | $R_1=0.038$ and $wR_2=0.092$ |
| Largest diff. peak and hole (e/Å <sup>-3</sup> ) | 0.83 and -0.64               |

The asymmetric unit of the title complex,  $(\text{C}_5\text{H}_6\text{N}_2\text{O})_2[\text{Co}(\text{H}_2\text{O})_6]_3(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$  (Figure 1), comprises of one and a half of hexaaquacobalt(II) cations, one 2-amino-6(1H)-pyridone cation, two isolated sulfate anions and one water molecule of crystallization. The complete complex is generated by the crystallographic inversion center.



**Figure 1. ORTEP view of  $(\text{C}_5\text{H}_6\text{N}_2\text{O})_2[\text{Co}(\text{H}_2\text{O})_6]_3(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ , showing 50% probability ellipsoids**

In the crystal structure, the ions and molecules are linked into a layered three-dimensional supramolecular network, via O—H...O, N—H...O hydrogen bonds and weak intermolecular  $\pi$ — $\pi$  interactions [centroid—centroid distance = 3.658(4)Å], forming channels in which the 2-amino-6(1H)-pyridone cations play a templating role (Figure 2).



**Figure 2. Crystal packing of the complex  $(C_5H_6N_2O)_2[Co(H_2O)_6]_3(SO_4)_4 \cdot 2H_2O$**

There are two independent transition metal ions: Co(1) is located in special position on crystallographic inversion center and the second Co(2) in a general position. Both are coordinated by six water-molecules. There are three crystallographically independent for Co(1). These  $[CoII(H_2O)_6]^{2+}$  octahedra are slightly distorted. The metal–oxygen distances vary from 2.051(5) to 2.205(7) Å for  $[Co(1)(H_2O)_6]^{2+}$  and from 2.035(7) to 2.178(4) Å for  $[Co(2)(H_2O)_6]^{2+}$ . Bond angles fall in the range 89.13(11)–90.87(11)° for O–Co(1)–O and 81.21(10)–177.73(10)° for O–Co(2)–O, analogous with other organically template metal sulfates [12] (Table 3).

There are two independent  $SO_4^{2-}$  anions in this structure. The geometrical characteristics of these anions are comparable and are not very distinct from these observed in other cobalt-organic complex [12]. These sulfate anions compensate the positive charges of the tris-hexaaquacobalt (II) and ensure the cohesion of the packing. Indeed, all oxygen atoms of the  $SO_4$  groups participate as acceptor in hydrogen bonds accepting hydrogen atoms of the organic moiety and the complex  $Co(H_2O)_6^{2+}$  (Table 3).

**Table 2. Selected bond distances (Å) and angles (°) for  $(C_5H_6N_2O)_2[Co(H_2O)_6]_3(SO_4)_4 \cdot 2H_2O$**

| Co(1)O <sub>6</sub> octahedron |               |  |            |
|--------------------------------|---------------|--|------------|
| Atoms                          | Distances (Å) | Atoms                                  | Angles (°) |
| Co1—O1A                        | 2.068(4)      | O3A—Co1—O3A <sup>i</sup>               | 179.99(12) |
| Co1—O3A                        | 2.051(5)      | O3A—Co1—O1A                            | 90.16(11)  |
| Co1—O3A <sup>i</sup>           | 2.051(5)      | O3A <sup>i</sup> —Co1—O1A              | 89.84(11)  |
| Co1—O1A <sup>i</sup>           | 2.068(4)      | O3A—Co1—O1A <sup>i</sup>               | 89.84(11)  |
| Co1—O2W <sup>i</sup>           | 2.105(7)      | O3A <sup>i</sup> —Co1—O1A <sup>i</sup> | 90.16(11)  |
| Co1—O2W                        | 2.105(7)      | O1A—Co1—O1A <sup>i</sup>               | 179.99(10) |
|                                |               | O3A—Co1—O2W <sup>i</sup>               | 89.13(11)  |
|                                |               | O3A <sup>i</sup> —Co1—O2W <sup>i</sup> | 90.87(11)  |
|                                |               | O1A—Co1—O2W <sup>i</sup>               | 89.18(10)  |
|                                |               | O1A <sup>i</sup> —Co1—O2W <sup>i</sup> | 90.83(10)  |
|                                |               | O3A—Co1—O2W                            | 90.87(11)  |
|                                |               | O3A <sup>i</sup> —Co1—O2W              | 89.13(11)  |
|                                |               | O1A—Co1—O2W                            | 90.82(10)  |
|                                |               | O1A <sup>i</sup> —Co1—O2W              | 89.18(10)  |



| Co(2)O <sub>6</sub> octahedron |               | O2W <sup>1</sup> —Co1—O2W |            |
|--------------------------------|---------------|---------------------------|------------|
|                                |               | 179.99(12)                |            |
| Atoms                          | Distances (Å) | Atoms                     | Angles (°) |
| O2B—Co2                        | 2.104(5)      | O3B—Co2—O6B               | 171.53(10) |
| O4B—Co2                        | 2.178(4)      | O3B—Co2—O1B               | 90.97(10)  |
| O5B—Co2                        | 2.108(5)      | O6B—Co2—O1B               | 92.54(10)  |
| Co2—O3B                        | 2.035(7)      | O3B—Co2—O2B               | 94.99(10)  |
| Co2—O6B                        | 2.046(7)      | O6B—Co2—O2B               | 92.51(10)  |
| Co2—O1B                        | 2.062(4)      | O1B—Co2—O2B               | 93.14(10)  |
|                                |               | O3B—Co2—O5B               | 86.23(10)  |
|                                |               | O6B—Co2—O5B               | 86.69(10)  |
|                                |               | O1B—Co2—O5B               | 81.21(10)  |
|                                |               | O2B—Co2—O5B               | 174.25(10) |
|                                |               | O3B—Co2—O4B               | 89.40(9)   |
|                                |               | O6B—Co2—O4B               | 87.40(1)   |
|                                |               | O1B—Co2—O4B               | 177.73(10) |
|                                |               | O2B—Co2—O4B               | 84.59(10)  |
|                                |               | O5B—Co2—O4B               | 101.05(10) |
| S(1)O <sub>4</sub> tetrahedron |               |                           |            |
| Atoms                          | Distances (Å) | Atoms                     | Angles (°) |
| O1—S1                          | 1.472(4)      | O4—S1—O1                  | 110.15(12) |
| O2—S1                          | 1.477(3)      | O4—S1—O2                  | 110.37(14) |
| O3—S1                          | 1.485(3)      | O1—S1—O2                  | 111.17(14) |
| O4—S1                          | 1.467(4)      | O4—S1—O3                  | 108.25(14) |
|                                |               | O1—S1—O3                  | 107.79(14) |
|                                |               | O2—S1—O3                  | 109.03(14) |
| S(2)O <sub>4</sub> tetrahedron |               |                           |            |
| Atoms                          | Distances (Å) | Atoms                     | Angles (°) |
| O5—S2                          | 1.464(3)      | O5—S2—O6                  | 110.70(13) |
| O6—S2                          | 1.469(5)      | O5—S2—O8                  | 110.30(13) |
| O7—S2                          | 1.485(3)      | O6—S2—O8                  | 109.24(13) |
| O8—S2                          | 1.480(4)      | O5—S2—O7                  | 109.38(14) |
|                                |               | O6—S2—O7                  | 109.12(14) |
|                                |               | O8—S2—O7                  | 108.05(13) |
| Organic group                  |               |                           |            |
| Atoms                          | Distances (Å) | Atoms                     | Angles (°) |
| N1X—C5X                        | 1.380(6)      | C5X—N1X—C1X               | 117.44(36) |
| N1X—C1X                        | 1.415(7)      | N2X—C1X—C2X               | 116.97(40) |

|         |           |             |            |
|---------|-----------|-------------|------------|
| N2X—C1X | 1.293(6)  | N2X—C1X—N1X | 123.03(38) |
| C1X—C2X | 1.323(6)  | C2X—C1X—N1X | 120.00(42) |
| C2X—C3X | 1.336(6)  | C1X—C2X—C3X | 121.45(36) |
| C3X—O9  | 1.076(13) | O9—C3X—C2X  | 108.72(65) |
| C3X—C4X | 1.358(6)  | O9—C3X—C4X  | 129.13(74) |
| C4X—C5X | 1.382(7)  | C2X—C3X—C4X | 122.15(36) |
|         |           | C3X—C4X—C5X | 117.74(44) |
|         |           | N1X—C5X—C4X | 121.21(41) |

The supramolecular crystal structure is built from the alternatively arranged inorganic and organic layers. Layers at  $z=0$  are built from the first  $[\text{Co}(1)(\text{H}_2\text{O})_6]^{2+}$  complex, which occupy the corners of the unit cell (Figure 3), the uncoordinating water molecule and the sulfate anions via OW-H...O-S creating cavities where are located the organic cations. These layers are interconnected through the sulfate anions and the second  $[\text{Co}(2)(\text{H}_2\text{O})_6]^{2+}$  complex layer located at  $z=1/2$  (Figure 4) giving rise a three-dimensional network. The sulfate anions play an important role in the stability of the crystal structure by linking the organic and inorganic cations via hydrogen bonds which are fairly strong, with donor-acceptor distances range between 2.664(4) and 2.998(4)Å (Table 4).

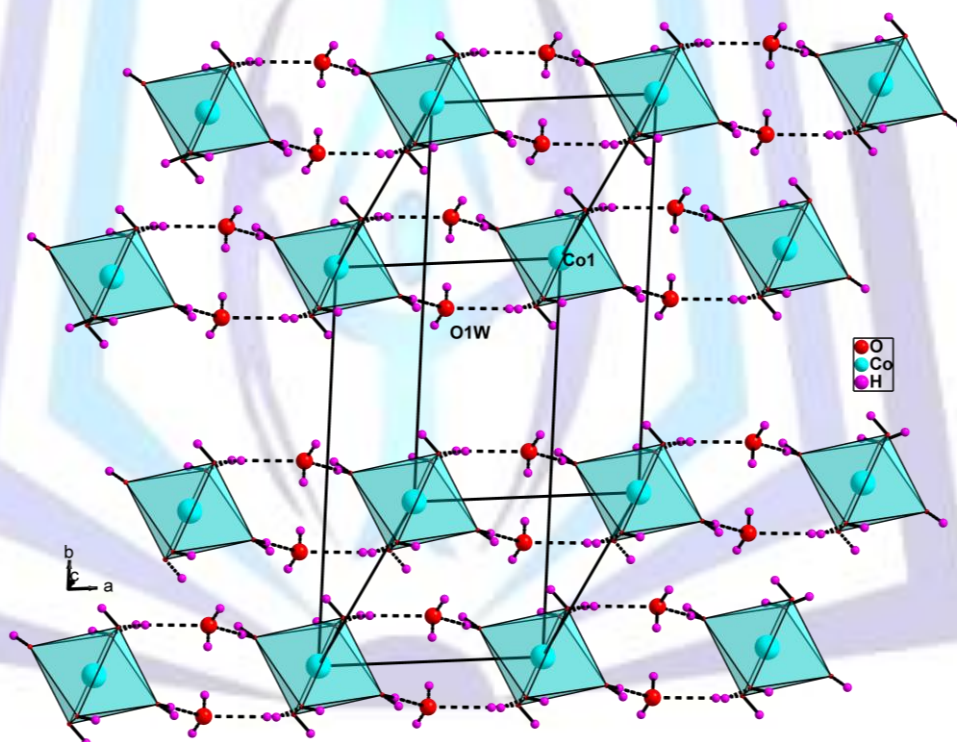
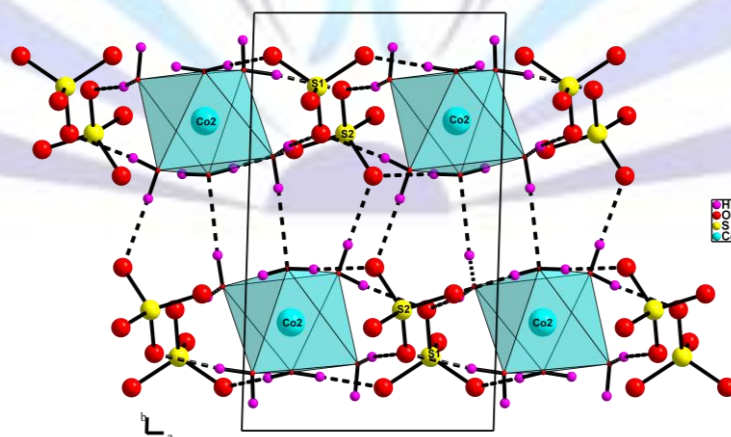


Figure 3. Organization of the  $[\text{Co}(1)(\text{H}_2\text{O})_6]^{2+}$  complex in  $(\text{C}_5\text{H}_6\text{N}_2\text{O})_2[\text{Co}(\text{H}_2\text{O})_6]_3(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$

Table 4. Principal intermolecular distances (Å) and bond angles (°) of the hydrogen bonding scheme

| Donor | H       | Acceptor | D...A    | D-H      | H...A    | D-H...A |
|-------|---------|----------|----------|----------|----------|---------|
| O(1W) | -H(11W) | ...O(7)  | 0.83(6)  | 1.88(6)  | 2.711(3) | 174(6)  |
| O(1W) | -H(1W)  | ...O(1)  | 0.77(6)  | 2.14(5)  | 2.895(3) | 167(6)  |
| O(1W) | -H(1W)  | ...O(3)  | 0.77(6)  | 2.56(6)  | 3.089(3) | 127(5)  |
| O(1A) | -H(1A)  | ...O(1W) | 0.83(3)  | 1.88(3)  | 2.712(3) | 175(4)  |
| O(1A) | -H(11A) | ...O(8)  | 0.84(3)  | 1.93(3)  | 2.763(3) | 175(3)  |
| O(2W) | -H(2A)  | ...O(5)  | 0.84(4)  | 2.26(6)  | 2.999(3) | 147(6)  |
| O(2W) | -H(22A) | ...O(8)  | 0.84(2)  | 1.98(2)  | 2.823(3) | 175(4)  |
| O(3A) | -H(3A)  | ...O(3)  | 0.85(3)  | 1.90(4)  | 2.745(3) | 176(4)  |
| O(3A) | -H(33A) | ...O(1W) | 0.84(2)  | 1.92(2)  | 2.751(3) | 171(3)  |
| O(1B) | -H(1B)  | ...O(4)  | 0.82(3)  | 1.86(4)  | 2.664(3) | 168(4)  |
| O(1B) | -H(11B) | ...O(1)  | 0.83(3)  | 1.91(3)  | 2.733(3) | 176(5)  |
| O(2B) | -H(2B)  | ...O(4B) | 0.81(6)  | 2.16(6)  | 2.971(3) | 174(5)  |
| O(2B) | -H(22B) | ...O(2)  | 0.83(5)  | 2.05(6)  | 2.876(3) | 175(5)  |
| O(3B) | -H(33B) | ...O(2)  | 0.75(6)  | 2.00(6)  | 2.750(3) | 177(7)  |
| O(3B) | -H(3B)  | ...O(6)  | 0.90(6)  | 1.81(6)  | 2.705(3) | 172(5)  |
| O(4B) | -H(4B)  | ...O(6)  | 0.81(6)  | 1.92(5)  | 2.723(3) | 169(5)  |
| O(4B) | -H(44B) | ...O(5)  | 0.85(5)  | 1.94(5)  | 2.786(3) | 175(5)  |
| O(5B) | -H(5B)  | ...O(1)  | 0.77(7)  | 2.14(7)  | 2.898(3) | 169(5)  |
| O(5B) | -H(55B) | ...O(7)  | 0.82(6)  | 1.90(5)  | 2.700(3) | 165(6)  |
| O(6B) | -H(6B)  | ...O(7)  | 0.89(5)  | 1.80(5)  | 2.686(3) | 173(5)  |
| O(6B) | -H(66B) | ...O(4)  | 0.75(6)  | 1.96(6)  | 2.701(3) | 172(3)  |
| N(1X) | -H(3X)  | ...O(3)  | 0.82(4)  | 1.88(4)  | 2.699(4) | 174(4)  |
| N(2X) | -H(6X)  | ...O(8)  | 0.89(11) | 2.11(11) | 2.966(4) | 162(11) |
| N(2X) | -H(2X)  | ...O(2)  | 0.88(9)  | 2.17(9)  | 2.955(4) | 149(11) |


 Figure 4. Organization of the  $[\text{Co}(2)(\text{H}_2\text{O})_6]^{2+}$  complex in  $(\text{C}_5\text{H}_6\text{N}_2\text{O})_2[\text{Co}(\text{H}_2\text{O})_6]_3(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$

### 3.2 Infrared Spectroscopy

The infrared spectrum of the crystalline complex is shown in Figure 5. To assign the IR peaks to vibrational modes, we examined the modes and frequencies observed in similar compounds [13].

A free  $\text{SO}_4^{2-}$  ion in its ideal  $T_d$  symmetry has four fundamental vibrations, the non-degenerate symmetric stretching mode  $\nu_1$  ( $A_1$ ), the double degenerate bending mode  $\nu_2$  ( $E$ ), the triply asymmetric stretching mode  $\nu_3$  ( $F_2$ ), and triply degenerate asymmetric bending mode  $\nu_4$  ( $F_2$ ).

The average frequencies observed for these modes are 981, 451, 1104 and 614  $\text{cm}^{-1}$ , respectively [13].

In the crystal, the  $\text{SO}_4^{2-}$  ion occupies lower site symmetry  $C_1$ . As a result the IR inactive  $\nu_1$  and  $\nu_2$  modes may become active and the degeneracy's  $\nu_3$  and  $\nu_4$  modes may be removed. The triply asymmetric stretching modes  $\nu_3$  appears as one intense band at 1076.08  $\text{cm}^{-1}$ . The  $\nu_4$  mode appears as one band at 599.75  $\text{cm}^{-1}$ .

The most typical features in this respect are the characteristic band of the 2-amino-6(1H)-pyridone skelet on vibrations at 1679 $\text{cm}^{-1}$ , 1637 $\text{cm}^{-1}$  and 3234 $\text{cm}^{-1}$ . Frequencies in the range 1486, 1388 and 1332  $\text{cm}^{-1}$  are attributed to the aromatic C=C and O-H associated [14].

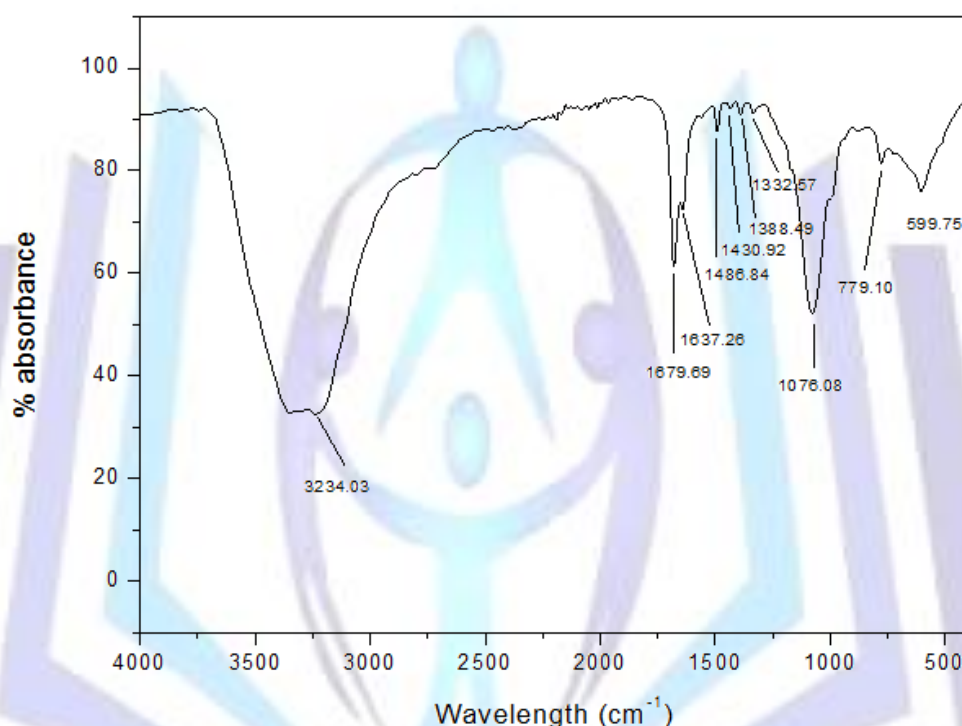


Figure 5. IR absorption spectrum of  $(\text{C}_5\text{H}_6\text{N}_2\text{O})_2[\text{Co}(\text{H}_2\text{O})_6]_3(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$

### 3.3 UV-Vis Absorption and Diffuse Reflectance

The UV-Visible spectrum of the cobalt complex (Figure 6) presents an intense and broad absorption with a maximum absorption at 570 nm and a shoulder of which the wavelength is less than 570 nm bands. These bands are attributed to d-d electron transitions and the charge transfer  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  et  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  indicating the octahedral geometry of the cobalt atom [15]. The little intensity band at 300 nm indicates the  $n \rightarrow \pi^*$  transition of the  $\text{Co}(\text{H}_2\text{O})_6$  cations. These observations are in good agreement with the results of the XRD study on the octahedral geometry and the valence state of the cobalt metal. Moreover the electronic spectrum of the compound provided by using the Tauc model, optical band gaps of 3.86 eV as reported in Figure 7, suggesting that the material is a wide-band-gap of dielectric material.



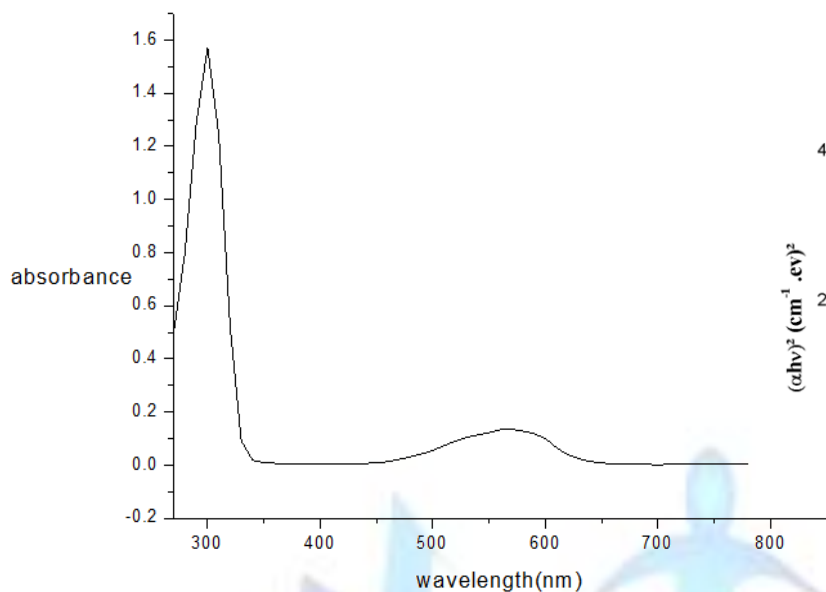


Figure 6. UV diffuse reflectance spectrum

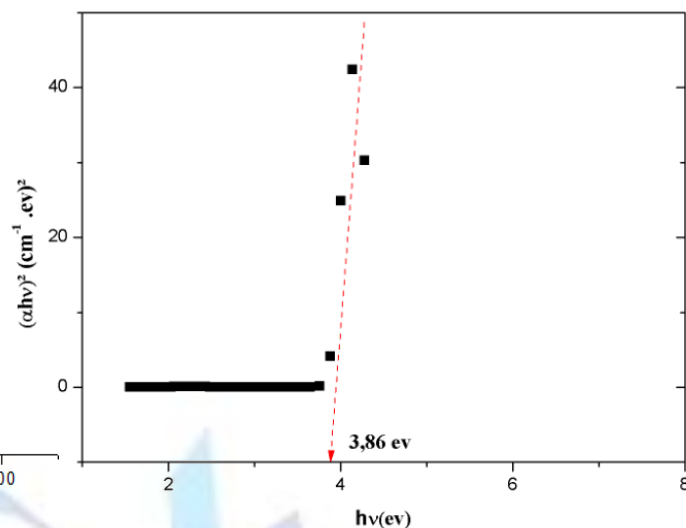


Figure 7. Band gap determination

### 3.4 Conclusion

A new sulfate complex,  $(C_5H_6N_2O)_2[Co(H_2O)_6]_3(SO_4)_4 \cdot 2H_2O$ , has been prepared and structurally characterized. Its crystal structure consists of 3D-supramolecular anionic and water molecule network with cavities in which the organic cations are lodged by means an extensive hydrogen bond scheme. The diffuse reflectance data indicate an energy gap 3.86 eV which is a typical of a dielectric material.

### REFERENCES

- [1] K. Cheetham , G. Ferey , T. Loiseau , *Angew. Chem., Int. Ed.* , 1999, 38 , 3268
- [2] P. B. Venuto, *Microporous Mate.* , 1994, 2 , 297
- [3] X. Cao , Y. Wang , J. Chen, *Chem. Res. Chinese U.* , 2000, 16, 1
- [4] W. Rekik, H. Naili, T. Mhiri, T. Bataille, *Mater. Res. Bull.*, 2008, 43, 2709
- [5] A. J. Norquist, M. B. Doran, D. O'Hare, *Inorg. Chem.*, 2005, 44, 3837.
- [6] C. Y. Chen, K. H. Lii and A. J. Jacobson, *J. Solid State Chem.*, 2003, 172, 252.
- [7] E. A. Muller, R. J. Cannon, A.N. Sarjeant, K.M.Ok, P. S. Halasyamani, A. J. Norquist, *Cryst. Growth Des.*, 2005, 5, 1913.
- [8] SHELX97: Sheldrick, G.M. *Acta Cryst.*, 2008, A64, 112.
- [9] T. Borow, I. Wolska, A. Korzańska, W. Milius, W. Schnick, W. Antkowiak, *Z. Naturforsch.*, 2000, 55 b, 5.
- [10] W. Clegg, G. S. Nichol, *Acta Cryst.*, 2004, E60, o1433
- [11] F. Baker, E. C. C. Baly, 1907, *J. Chem. Soc.*, 1122
- [12] T. Sahbani, W. Smirani, S. S. Al-Deyab, M. Rzaigui, *Acta Cryst.*, 2011, E67, m1079
- [13] G. Hertzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, New York, 1966
- [14] T. Guerfel, M. Bdiri, A. Jouini, *J. Chem. Crystallogr.* , 2000, 30, 799
- [15] S.S. Karapandian, M. Vijay Kumar, *Mat.chem.phys.* , 2003, 80, 29