



Synthesis, characterization and crystal structure of new cobalt (III) complex: [Tris(1,10-phenanthroline- κ^2N,N') Cobalt (III)] trinitrate monohydrate [Co(C₁₂H₈N₂)₃](NO₃)₃.H₂O

Jawher Abdelhak*, Saoussen Namouchi Cherni and Mohamed Faouzi Zid

Laboratoire de Matériaux et Cristallographie, Département de Chimie, Faculté des Sciences de Tunis, Université de Tunis El Manar 2092 Tunis, Tunisie

Abstract: We report herein the synthesis and the physicochemical characterization of a new cobalt(III) complex of formula [Co(C₁₂H₈N₂)₃](NO₃)₃.H₂O. This compound has been prepared by slow evaporation at room temperature and characterized by single crystal X-ray diffraction, IR, UV-VIS spectra and thermal analysis (TG and DTA). Structural cohesion is established essentially by π - π interactions between the rings of phenanthroline groups and intermolecular hydrogen bonds connecting the nitrate entities and uncoordinated water molecules.

Keywords: Synthesis; Crystal structure; Thermal behavior; Electronic Spectra; Cobalt complex.

Introduction

Investigation of novel inorganic-organic hybrid framework assemblies represents the intense interest of chemical research; this is driven to a large extent by their interesting properties and their potential practical applications, such as magnetism, catalysis and electrical conductivity¹. In addition, mixed ligand-metal complexes of some organic nitrogen-donors ligand continue to attract attention because it plays an important role in biological systems² and has also been used extensively in analytical chemistry³. Several bifunctional ligands have proven to be well suited building blocks for the assembly of one, two or three-dimensional network structures.

Metal complexes of the type [M(LL)₃]ⁿ⁺, where LL is either phenanthroline (phen) or modified phen, are particularly attractive because they can effectively bind to DNA in different modes of interactions. The central metal or the ligands in these complexes may be varied in easily controlled manner to facilitate a certain applications, which provides an easy access for the detailed study of DNA-binding mechanisms⁴.

The organic ligands containing multiple heterocyclic rings are very useful tools in the self-assembly of metallo supramolecular compounds⁵. At that respect, the 1,10-phenanthroline (phen) has been frequently used in transition metal chemistry⁶. This ligand is especially relevant because they exhibit significant biological activities apart from being used as catalysts in some organic reactions^{7,8}. Phen can be seen as a bifunctional ligand because in addition to its potential chelating character, it can be involved in π - π type interactions necessary for the structural stability of materials⁹.

*Corresponding author:

E-mail address: jawher.abdelhak@ipein.rnu.tn

DOI: <http://dx.doi.org/10.13171/mjc.3.1.2014.26.03.22>

In this paper, we reports its synthesis and structural characterization as well as the spectroscopic and thermal properties of a new compound $[\text{Co}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (**1**).

Experimental Section

Materials and physical measurements

All chemicals were commercially available and were used without further purification. TG/DTA 92 SETARAM thermal analyzer was employed for the investigation of the thermal behavior in Ar atmosphere from room temperature to 600°C at a heating rate 5° min⁻¹. UV-Vis spectrum was recorded on an 1800 UV-Vis spectrophotometer - Shimadzu in the range 200-800 nm. Infrared absorption spectrum was recorded on a Perkin Elmer Spectrum Two over the wave-number range 4000 – 400 cm⁻¹.

Synthesis

This compound, was prepared as good quality pink single crystals from a mixture of cobalt(III) nitrate hydrate, phenanthroline monohydrate and phosphoric acid, respectively (2:6:1) molar ratio in water. H₃PO₄ is used to acidify the reaction mixture with a pH of about 2.5.

An aqueous solution (20 cm³) of phenanthroline (0.06 g, 0.3 mmol) was added drop wise to another aqueous solution (30 cm³) containing cobalt (III) nitrate hexahydrate (0.035 g, 0.1 mmol) with continued stirring. The resulting solution was acidified with phosphoric acid then it is left to evaporate under a hood at room temperature. Red single crystals of parallelepiped shape are separated after ten days. They were collected, washed with small amounts of oil and Vaseline dried on filter paper.

Crystal structure determinations and refinements

A prismatic red crystal (0.23×0.31×0.24 mm) is selected for the structural analysis. Diffraction data were collected at 293(2) K with Enraf–Nonius CAD4 automatic four-circle equipped with graphite monochromator using Mo K_α ($\lambda=0.71073\text{Å}$) radiation with the $w-2\theta$ technique. Unit-cell parameters and orientation matrix of title compound were determined by least squares treatment of the setting angles of 25 reflections on the range $10^\circ < \theta < 15^\circ$.

The structure is solved by standard Patterson methods and refined by the full-matrix least-squares method on F² for 715 refined parameters. The computations were performed with SHELXS 97¹⁰ and SHELXL 97¹¹. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms of the phen ligand were located from a difference synthesis. The molecular plots were drawn with the Diamond program3.0¹².

Results and Discussion

Crystal structure description

In the present work, we report the structure of tris(phenanthroline-*N,N'*)cobalt(III) complex with three nitrate anions, as well as one water molecule of crystallization.

This compound crystallized in the monoclinic space group *C2/c*. pertinent details for the structure determination and refinement are listed in Table 1. The perspective view of the complex anion is depicted in Fig. 1 with atom labeling scheme, selected bond lengths and bond angles are given in Table 2.

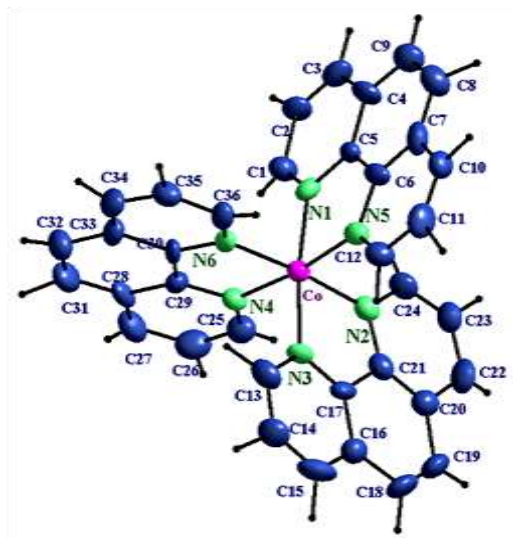


Figure 1. Molecular structure of mononuclear cation of $[\text{Co}(\text{phen})_3]^{3+}$ (at 50 % probability level of the Co(III) center), showing the labeling scheme. The equatorial plan is defined by nitrogen atoms N2, N4, N5 and N6. Water molecules and nitrate groups are not included for clarity.

Table 1. Crystal data and structure refinement for (1)

Formula	$\text{C}_{30}\text{H}_{26}\text{CoN}_9\text{O}_{10}$
Formula weight ($\text{g}\cdot\text{mol}^{-1}$)	820.60
Crystal system	Monoclinic
Space group	$C2/c$
a (\AA)	12.159(1)
b (\AA)	16.041(1)
c (\AA)	35.696(2)
β ($^\circ$)	97.78(1)
Volume (\AA^3)	6898.2(9)
Z	8
ρ ($\text{g}\cdot\text{cm}^{-3}$)	1.580
μ (mm^{-1})	0.577
θ Range ($^\circ$)	2.10 – 26.97
Index ranges	$-14 \leq h \leq 0$ $-1 \leq k \leq 19$ $-43 \leq l \leq 44$
Total data collected	9342
Independent reflections	8215
Reflections with $I > 2\sigma(I)$	7122
R_{int}	0.0195
Goodness-of-fit on F^2	1.022
$R [I > 2\sigma(I)]^a$	0.0393
$R_w [I > 2\sigma(I)]^b$	0.1003
Largest difference peak and hole ($e \text{\AA}^{-3}$)	0.364 and -0.288

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR = \left[\frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w|F_o|^2} \right]^{1/2}$$

Table 2. Selected bond lengths (Å) and angles (°) for [Co(C₁₂H₈N₂)₃]³⁺

Co – N1	2.000(7)	N5 – Co – N6	82.79(6)
Co – N2	1.984(3)	N5 – Co – N4	173.05(6)
Co – N3	2.008(7)	N6 – Co – N3	92.66(6)
Co – N4	1.983(7)	N5 – Co – N1	93.41(6)
Co – N5	1.967(4)	N6 – Co – N2	174.34(5)
Co – N6	1.972(6)	N2 – Co – N4	91.51(6)
		N5 – Co – N2	91.81(6)
		N6 – Co – N1	93.68(7)
		N3 – Co – N2	93.72(6)
		N1 – Co – N2	82.21(7)
		N5 – Co – N3	92.59(6)
		N6 – Co – N4	91.53(7)
		N3 – Co – N4	82.26(6)
		N1 – Co – N4	92.83(7)
		N1 – Co – N3	173.56(5)

The coordination environment of Co^{III} ion involves six nitrogen atoms from three phen molecules to form a distorted octahedron, the three diagonal angles of the polyhedron average 173.05(6)° and 174.34(5)°, indicating a slightly distorted octahedron around cobalt ion. The Co–N bond distances are in the range from 1.967(4)Å up to 2.008(7)Å. These bonds are comparable with those reported for Co(III) compounds, such as [Co(SPh)₂(phen)₂]ClO₄ and [Co(ox)₂(phen)₂](NO₃).3.88H₂O^{13,14}.

The central Co atom in complex is very close to coplanarity with the four surrounding N atoms, the largest deviation is 0.11 Å from the plane defined by N2, N4, N5 and N6, the central atoms are 0.14 Å out of this plane that shows a slight distortion. The N-Co-N (82.21(7)° up to 93.72(6)°) bite angles are far from the ideal one of 90° because of the usual small bite size of five-member planar chelate rings formed by the bidentate phenanthroline ligand¹⁵.

Otherwise, we can say, since the resulting coordination sphere is not a perfect octahedral, it is appropriate to use the angular structural parameter, τ , as suggested in Ref.¹⁶. τ , is defined as the ratio of the two basal angles difference and 60°: for pure octahedral $\tau = 0$ and for a trigonal-bipyramid $\tau = 1$. In the case of this compound $\tau = 0.19$ indicating a slightly distorted octahedron around the cobalt.

The phen ligands are planar and the average C-C (1.372 Å) and C-N (1.326 Å) bond lengths, the average angles (120°) within the rings are in good agreement with those currently given in the literature for phen-coordinated metal complexes^{17,18}. All the atoms in the phen ligand were used with the following equation:

$$0.2243(0.0073)x + 6.9658(0.0043)y + 12.8838(0.0068)z = 5.4729(0.0021)$$

The nitrate group exhibits substantial deviation for the D_{3h} symmetry. The N–O band range from 1.200(3) to 1.305(1)Å, in perfect accord within similar compounds.

The structure of title compound is consisted by layers of complex cation formed by {[Co(phen)₃]³⁺; one nitrate anion and water molecules H₂O} parallel to [01 $\bar{1}$] intercalated by sheet for two nitrate anions and interconnected via O–H...O hydrogen bonds.

In this compound, the complex cations and nitrate entities are joined through N–H...O hydrogen bonds [length d(D...A) and angle <(D–H...A) are from 2.736(3)Å up to 2.770(3)Å and from 151(3)° up to 168(3)°, respectively] into 3D supramolecular networks

(Fig. 2 (a) and (b), Table 3). In fact, the uncoordinated water molecules OW1 play a role as donors. As for the nitrate groups, the oxygen atoms O3 and O5 are only acceptors.

Table 3. Selected hydrogen–bond parameters for (1)

D	H	A	D–H	H...A	D...A	D–H...A
Ow1	Hw1	O3	0.96(4)	1.79(4)	2.736(3)	168(3)
Ow1	Hw2	O5 ⁱ	1.05(5)	1.81(5)	2.770(3)	151(3)

D: donor; A: acceptor

Codes of symmetry **i** : -x,y+1,-z+3/2

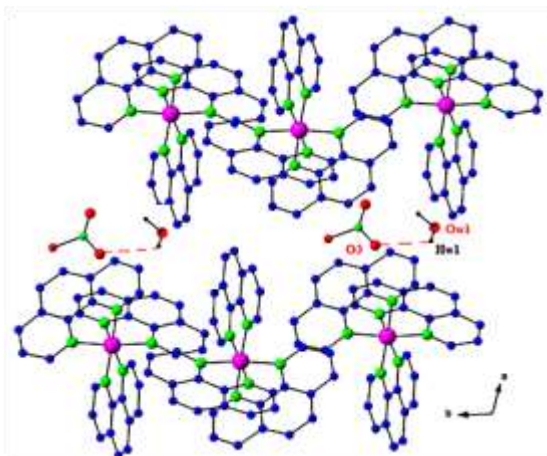


Figure 2 (a). Fragments of the molecular structure of cation complex $\{[\text{Co}(\text{phen})_3](\text{NO}_3)\cdot\text{H}_2\text{O}\}^{2+}$ showing well-directional hydrogen bonding interactions. Hydrogen atoms are not included for clarity.

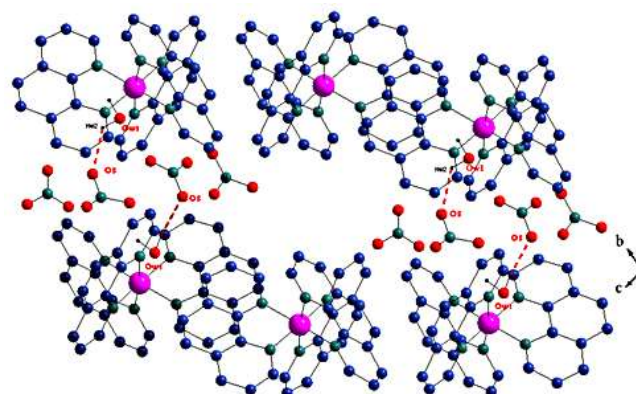


Figure 2 (b). View of the molecular structure of the compound (1), showing the hydrogen bonds between the layers. Hydrogen atoms are not included for clarity.

Along three directions (A, B and C), the $[\text{Co}(\text{phen})_3]^{3+}$ cations are lined up to form columnar chains with the phenanthroline ligands engaged in face-to-face π - π stacking interactions. The interplanar short distance is framed by 3.543 Å and 4.015 Å. A lateral offset of 1.75 Å. The centroid–centroid distance somewhat exceeds the values typical for the π - π interaction 3.909 Å¹⁹ (Fig. 3).

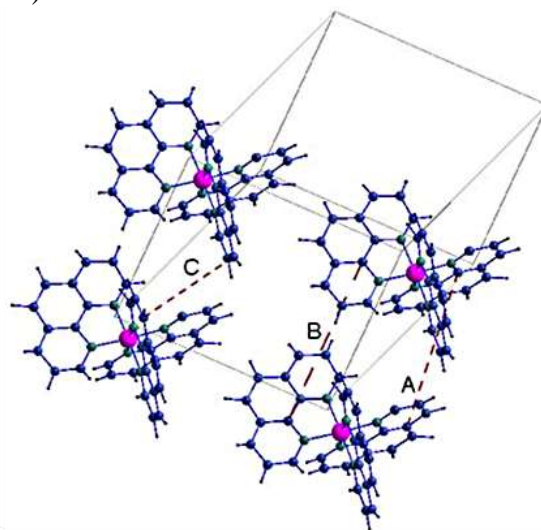


Figure 3. A view of part of a sheet of $[\text{Co}(\text{phen})_3]^{3+}$ cation, linked by π - π stacking interactions (dashed lines) between the neighboring pyridine ligands.

Obviously, the hydrogen bonds and π - π interactions are responsible for the structural stability of the material. For this compound, electrostatic interactions generally play the key role in structure formation²⁰. A structure was complicated by an extensive disorder of oxygen atoms in nitrate anions. The oxygen atoms O3 and O8 of the anion occupy two positions in the independent part of the unit cell with almost equal probabilities.

IR Spectra

The infrared spectra of compound exhibit characteristic bands for phen ligand. It display an intense and broad band centered at 3300 cm^{-1} that can be attributed to the $\nu(\text{OH})$ vibrations of water molecules in the crystal lattice as well as $\nu(\text{C-H})$. The peak located at 497 cm^{-1} are assigned to $\nu(\text{Co-N})$ ²¹. The band around 1380 can be assigned to the vibration of the nitrate group.

Additionally, the bands located in the region $1650 - 1400\text{ cm}^{-1}$ region, are assignable to C-C and C-N stretching vibration of phen groups. Finally, the bands in the region $1250-600\text{ cm}^{-1}$ can be assigned to ring deformation absorptions of phen.

Thermal analysis

Thermal stability of the compound has been studied by differential thermal analysis (DTA) and thermogravimetry (TG), figure 4 shows the TG and DTA analysis of compound. Within this interval, several degradation steps were observed. In the interval between 69 and 117°C , the DTA trace shows an endothermic peak. The loss in weight (calculated 2.53% ; found 2.20%) suggests that the compound loses one water molecules.

The next large step in the decomposition curve, in the temperature range of $220-450^\circ\text{C}$, comprises the removal of phen and nitrate anions as a strongly exothermic process²².

This technique was used to check the number of water molecules as well as the nature of connections to the network of these molecules. These results are in perfect agreement with the structural study.

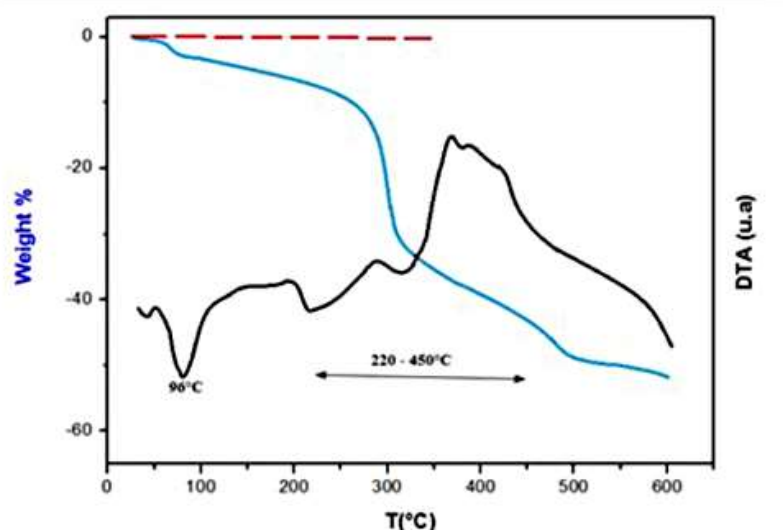


Figure 4. TG-DTA thermogram of compound (1) from room temperature to 600°C .

Electronic Spectra

For a Co^{3+} ion with a d^6 configuration in an O_h crystal field and assuming a low-spin electronic configuration of complex, the ${}^1\text{A}_{1g}$ term is the ground state. Two lower energy ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$ transitions exhibit symmetry- and spin-forbidden character²³⁻²⁶.

Electronic spectroscopic is obtained from water solution. Figure 5 shows the electronic spectrum of compound. The absorption spectra of the complex show very intense bands in UV. The peaks at 642 nm and 411 nm correspond to the two $t_{2g} \rightarrow e_g$ transitions. These represent respectively the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions. It is also found the presence of an additional transition assigned to charge transfer metal-ligand (MLCT) at a maximum wavelength of 539 nm^{27,28}.

In the bibliography, two intense bands (not shown) are found at 250 and 215 nm, which can be assigned to phen $n-\pi^*$ and $\pi-\pi^*$ transitions^{29,30}. For a complex of Co (III), these transitions are due to the excitonic effect under the p band of phenanthroline³¹⁻³³.

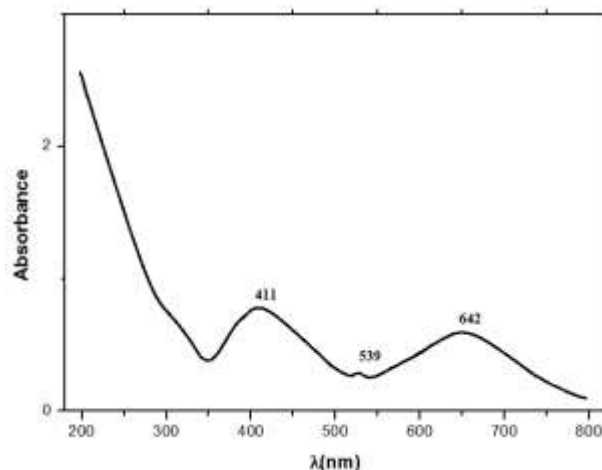


Figure 5. Uv- vis spectra of compound (1) in Water

Conclusion

In conclusion, this paper is a study of a new compound containing phen bridging ligands. The single-crystal X-ray data show elongated tetragonal-bipyramidal coordination around cobalt(III) atoms of $[\text{Co}(\text{phen})_3]^{3+}$ cations. In addition to $\pi-\pi$ interactions between the rings of phen groups, the nitrate anions and uncoordinated water molecules are connected through hydrogen bonds into 3D supramolecular frameworks.

Thermal analysis allows confirming the number of water molecules as well as the nature of connections to the network of these molecules, these results is in perfect agreement with the structural study. Well, Uv-vis spectroscopy we confirmed the oxidation state and to elucidate the coordination sphere of the cobalt. Further work is in progress, using mixed bridging ligands, to build up novel polymeric, with interesting properties.

Supplementary material

Crystallographic data and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 974794. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, CAMBRIDGE CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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