

## КРАТКИЕ СООБЩЕНИЯ

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STRUCTURAL CHARACTERIZATION OF A NEW METALLOPOLYMER COMPLEX  
OF 1,10-PHENANTHROLINE AND NITRATE  $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{NO}_3)_2]_n$ S.N. Cherni<sup>1</sup>, A. Driss<sup>1</sup>

Crystal Chemistry and Materials Laboratory, Department of Chemistry, Faculty of Sciences, Tunis, Tunisia  
E-mail: saoussencher@yahoo.fr

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A new mixed-ligand copper(II) complex of 1,10-phenanthroline and nitrate ligands  $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{NO}_3)_2]_n$  is prepared and its crystal structure is determined by X-ray diffraction. The complex crystallizes in the monoclinic space group  $P21/n$ , with unit cell dimensions  $a = 8.8226(3) \text{ \AA}$ ,  $b = 9.1462(1) \text{ \AA}$ ,  $c = 17.2507(4) \text{ \AA}$ ,  $\beta = 101.680(2)^\circ$ ,  $Z = 4$ ,  $V = 1363.19(6) \text{ \AA}^3$ . The crystal structure is solved by the Patterson method and refined by full-matrix least squares treatment on  $F^2$  to final values  $R1 = 0.0447$  and  $wR2 = 0.1053$ . The  $\text{Cu}^{\text{II}}$  ions are five-coordinated in a  $\text{CuO}_3\text{N}_2$  environment, giving a distorted square-based pyramidal geometry. The  $\text{Cu}\dots\text{Cu}$  distance in the  $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{NO}_3)_2]_n$  zigzag polymeric chain is  $5.258(1) \text{ \AA}$ . The structure of the title compound is polymeric and consists of layers running parallel to  $(10\bar{1})$ , interconnected by  $\pi\text{---}\pi$  interactions, strong enough to form a three-dimensional framework with tunnels along the  $a$  axis.

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**Keywords:** mixed-ligand copper(II) complex, X-ray diffraction,  $\pi\cdots\pi$  stacking interactions, five-coordination of Cu(II), zigzag polymeric chain complex.

The design and synthesis of discrete and polymeric metal-organic complexes based on 1,10-phenanthroline derivatives have received much interest because of their structure and topology-directing properties and wide applications [ 1–5 ].

These complexes can be specially designed by a careful selection of metal cations with preferred coordination geometries, considering also the nature of the anions, the structure of the connecting ligands and the reaction conditions [ 6, 7 ]. Usually, two different types of interactions, such as covalent bonds and noncovalent intermolecular forces, are used to construct various supramolecular architectures [ 8 ]. To date, much research has been focused on controlling motifs of metal-organic complexes through coordination bonds. However, less attention has been given to noncovalent  $\pi\text{---}\pi$  interactions [ 9 ].

The  $\pi\text{---}\pi$  interaction can be one of the most powerful noncovalent intermolecular interactions for directing supramolecular architectures [ 10, 11 ]. It plays vital roles in highly efficient and specific biological reactions and controls many molecular-recognition and self-assembly processes in the solid state and crystal engineering [ 12–16 ]. In particular, conjugated  $\pi$  systems can strongly influence the physical properties of coordination compounds. Therefore, the design of versatile functional ligands capable of coordinating to a metal atom with providing the  $\pi$ -conjugated system for organizing their complexes into an extended network through  $\pi\text{---}\pi$  interactions is quite desirable. The 1,10-phenanthroline ligand has been widely used to construct supramolecular architectures owing to its excellent coordinating ability and large conjugated system that can easily form  $\pi\text{---}\pi$  interactions.

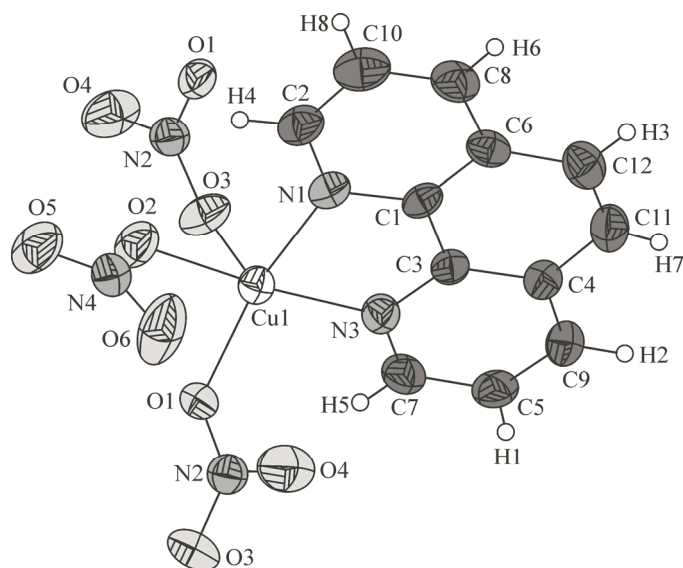


Fig. 1. Molecular structure of (**I**) with atom numbering scheme. Thermal ellipsoids are drawn at the 50 % probability level

We report here the structural characterization of one such complex  $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{NO}_3)_2]$  (**I**) Fig. 1.

**Experimental. Synthesis of the complex and spectroscopy.**  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.5 mmol, 0.12 g) and 1,10-phenanthroline (0.5 mmol, 0.1 g) were mixed and magnetically stirred in an ethanol-water solution (v: 1/1) (20 ml) for 30 min. Then, an ethanol solution (20 ml) containing phosphoric acid (5 mmol, 0.49 g) and oxalic acid (2.5 mmol, 0.32 g) were added dropwise to the solution. The final mixture was further stirred at room temperature for 30 min. The resulting mixture was filtered and the filtrate was left undisturbed at room temperature. In a few days blue prismatic crystals of the complex, suitable for the X-ray crystal structural determination, were formed by slow evaporation of the solvent. The crystals were isolated, washed three times with ethanol, and dried in the air. The C, H, and N contents in (**I**) were calculated, %: C 39.15, H 2.17, and N 15.23.  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{H}_3\text{PO}_4$  acids were added in order to prepare a complex bearing the oxalate and phosphate ligands, which was, however, not found in this reaction. The title  $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{NO}_3)_2]_n$  complex appeared instead. We attempted to repeat the experiment without these two acids to see what would happen, but that did not lead to the crystallization of the title complex. Therefore, we can conclude that the two acids are somehow necessary for this crystallization.

The spectra of (**I**) and 1,10-phenanthroline were recorded in KBr pellets using a PerkinElmer FT-IR Paragon 1000 PC Fourier IR spectrophotometer in the range  $400\text{--}4000\text{ cm}^{-1}$ .

The selected IR frequencies of the free ligand (1,10-phenanthroline) and the copper(II) complex are given in Table 1. The spectrum shows two strong bands at  $1384\text{ cm}^{-1}$  and  $1323\text{ cm}^{-1}$  attributable to  $\nu(\text{NO}_3)_{\text{as}}$  and  $\nu(\text{NO}_3)_{\text{s}}$ , respectively, which is in agreement with the coordinating nitrate anions [17–19]. The C—H stretching bands are observed at  $3063\text{ cm}^{-1}$ . The peaks at  $452\text{ cm}^{-1}$  and  $508\text{ cm}^{-1}$  are due to Cu—N and Cu—O stretching vibrations. The presence of  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{C})$  bands of phen around  $1600\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$ , respectively, also indicates the coordination of the phenanthroline ligand to the metal [20].

Table 1

<i>Selected IR frequencies (<math>\text{cm}^{-1}</math>) of the free ligand and the title complex</i>				
Species	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{NO}_3)_{\text{as}}$	$\nu(\text{NO}_3)_{\text{sym}}$
Phen	1560, 1616	1421, 1505	—	—
$[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{NO}_3)_2]_n$	1587, 1630	1427, 1517	1384	1323

Table 2

Selected bond lengths (Å) and angles (deg.) for the complex

Cu1—O2	1.966(3)	O2—Cu1—O1	90.29(12)	N3—Cu1—N1	82.26(13)
Cu1—O1	2.005(3)	O2—Cu1—N3	174.50(14)	O2—Cu1—O3	82.76(12)
Cu1—N3	2.009(3)	O1—Cu1—N3	93.59(12)	O1—Cu1—O3	86.52(11)
Cu1—N1	2.012(3)	O2—Cu1—N1	94.84(14)	N3—Cu1—O3	93.59(12)
Cu1—O3	2.351(3)	O1—Cu1—N1	166.07(13)	N1—Cu1—O3	106.95(12)

**X-ray structure determination.** Crystals suitable for single crystal X-ray diffraction were selected directly from the mother liquor. A suitable crystal with dimensions  $0.3 \times 0.3 \times 0.2$  mm<sup>3</sup> was chosen for X-ray diffraction studies. The measurements were made on an Enraf—Nonius CAD-4 diffractometer with graphite-monochromated radiation (MoK $\alpha$ ) at 293 K in the  $\theta$  range 2.41—25.97°. Lorentz and polarisation corrections were applied. 2830 reflections were collected. Crystallographic data: space group  $P2_1/n$ ,  $a = 8.8226(3)$  Å,  $b = 9.1462(1)$  Å,  $c = 17.2507(4)$  Å,  $\beta = 101.680(2)^\circ$ ,  $V = 1363.19(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calc}} = 1.792$  g/cm<sup>3</sup>. The structure was solved by the heavy-atom Patterson method expanded using Fourier techniques, and refined with anisotropic temperature factors for non-hydrogen atoms by full matrix least-squares on  $F^2$  using SHELXL. A  $\psi$ -scan absorption correction was applied, which resulted in transmission factors ranging from 0.7944 to 0.9093. The final refinement on 2651 ( $R_{\text{int}} = 0.0452$ ) independent reflections gave  $R1 = 0.0836$  ( $wR2 = 0.1053$ ). For 1790 reflections with  $I \geq 2\sigma(I)$   $R1 = 0.0447$  ( $wR2 = 0.0918$ ); the goodness of fit on  $F^2$   $S = 1.018$ ; the number of refined parameters is 240 and the residual electron density is 0.335 e/Å<sup>3</sup> and  $-0.387$  e/Å<sup>3</sup>. CCDC-1412801 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

All H atoms were identified from a difference Fourier map and were refined with an isotropic temperature factor. Selected bond lengths and bond angles are compiled in Table 2. An ORTEP drawing of the complex is illustrated in Fig. 1. A packing diagram is shown in Fig. 2.

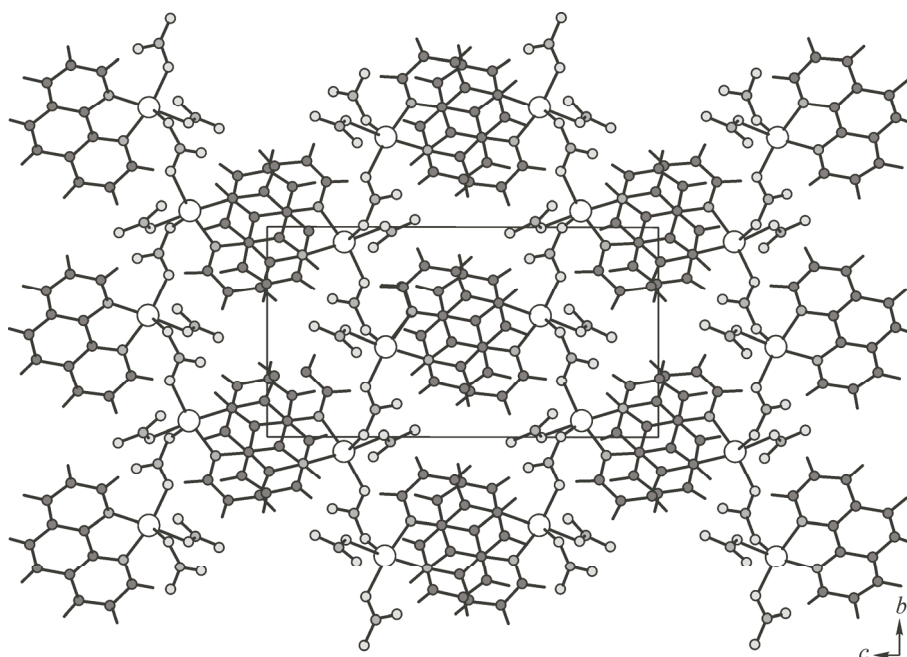


Fig. 2. Metallopolymer chains in the crystal of (I)

## RESULTS AND DISCUSSION

The Cu atom of the  $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{NO}_3)_2]$  unit is in a square pyramidal coordination, with two N atoms of the phen molecule and two O atoms of nitrate groups defining the basal plane, and with another O atom of a nitrate group occupying the apical position (Fig. 1). The Cu atom lies  $0.077(2)$  Å off the least-squares plane defined by the four basal donor atoms in the direction of the apical ligand. The degree of distortion of the square pyramidal geometry can be measured by the bond angles ranging from  $82.76(12)^\circ$  to  $106.95(12)^\circ$  for the apical and basal donors, and from  $82.26(13)^\circ$  to  $94.84(14)^\circ$  for the basal donors. The question arises as to whether the coordination polyhedron around the Cu atom can be described as a distorted square pyramid or a trigonal bipyramid. The answer can be obtained by determining the structural index  $\tau$  [21–23], which represents the relative amount of trigonality (square pyramid,  $\tau = 0$ ; trigonal bipyramid,  $\tau = 1$ );  $\tau = (\beta - \alpha)/60^\circ$ ,  $\alpha$  and  $\beta$  being the two largest angles around the central atom. The  $\tau$  value is  $0.14(1)$ . Thus, the coordination geometry of Cu is best described as a square pyramid.

The five Cu—N distances and the Cu—O bond lengths range from  $2.009(3)$ – $2.012(3)$  Å and  $1.966(3)$ – $2.351(3)$  Å, respectively, which are comparable to those found in other crystallographically characterized complexes with 1,10-phenanthroline ligands [20, 24–29]. The basal Cu—O bond distance is considerably shorter than the axial Cu—O bond distance. This is, in part, because the fifth coordination position in square-pyramidal arrangements is usually longer [30, 31]. The plane defined by the four donor atoms from the chelating phenanthroline ligand and the two nitrate ligands has an r.m.s deviation of  $0.1521$  Å (distances: O1  $0.147(2)$  Å, O2  $-0.147(2)$  Å, N1  $0.157(2)$  Å, and N3  $-0.157(2)$  Å). The distance from the Cu atom to the axial O atom, which is indicative of a typical Jahn—Teller distortion, is elongated and very different from each other, while O3 is  $2.351(3)$  Å from the metal Cu center, which is about  $0.365(3)$  Å longer than the mean Cu—O(eq) bond distance.

The angles subtended at the Cu atom by the phen ligand and the nitrate ligands are  $82.26(13)^\circ$  and  $90.29(12)^\circ$ , respectively, which are in agreement with those found in other complexes containing  $\text{Cu}^{\text{II}}$  or  $\text{Ni}^{\text{II}}$  [32–36]. The N1—Cu—N3 angle is far from the ideal value of  $90^\circ$  because of the constrained geometry of the phen ring systems. There is also a significant tetragonal distortion of the equatorial plane (the maximum atomic deviation of  $0.1569(16)$  Å out of this mean plane). The dihedral angle between the square plane and the phen mean plane is  $13.21(11)^\circ$ . The 1,10-phenanthroline molecule is almost planar (the largest deviation of atoms from the mean plane is  $-0.087(4)$  Å for the C5 atom). The average C—C ( $1.284(5)$  Å) and C—N ( $1.348(5)$  Å) bonds and  $120.29(4)^\circ$  angles within the rings are in agreement with those previously reported for 1,10-phenanthroline-coordinated  $\text{Cu}(\text{II})$  and  $\text{Ni}(\text{II})$  complexes [31, 32, 37, 38].

The analysis of the crystal packing of the complex shows that each pair of adjacent  $\text{Cu}^{\text{II}}$  centres is bridged by a nitrate group to form zig-zag polymeric chains [39–41] running along the *b* axis with a Cu...Cu separation of  $5.258(1)$  Å.

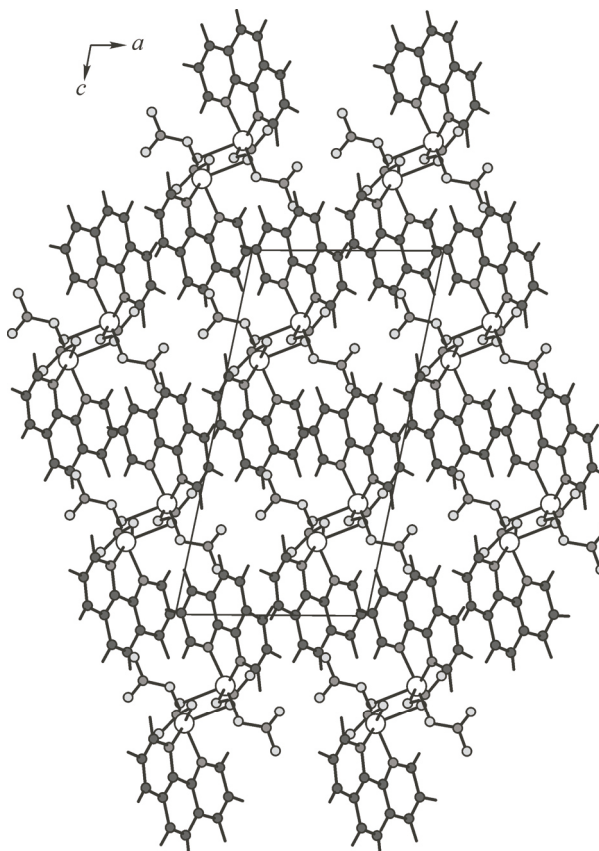


Fig. 3. Molecular packing of the complex, viewed along the *b* axis

Additional stabilization of the structure may come from face-to-face  $\pi$ — $\pi$  interactions between stacked 1,10-phen molecules. There is a stacking interaction involving the benzene rings of the phen ligands from the neighbouring chains parallel to the [010] direction (Fig. 2) with a centroid-to-centroid distance of 4.780(1) Å, to form a two dimensional layer parallel to (10 $\bar{1}$ ). Another stacking interaction involves the benzene rings of the phen ligands from the neighbouring layers (Fig. 3) with a centroid-to-centroid distance of 4.024(1) Å. Therefore, the complex can also be viewed as a three-dimensional supramolecular architecture extended via the  $\pi$ — $\pi$  stacking interactions which delimit elliptic tunnels along the *a* axis ( $r_{\min} = 2.728(1)$  Å,  $r_{\max} = 5.655(4)$  Å).

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