Original Article

Crystal structure, magnetic and IR spectroscopic studies of a novel non centrosymmetric copper(II) complex [Cu(AMP)(H₂O)₃]SO₄

$[Cu(AMP)(H_2O)_3]SO_4$

M.Ben Nasr[1]*, E.Aubert[1], E.Espinosa[1], M.Zeller[2], L.C.J.Pereira[3], M.R.Silva[4], P.S.Pereira Silva[4]

[1]**Laboratoire CRM2 (Cristallographie, Résonance Magnétique et Modélisations) Université de Lorraine BP 70239 - 54506 Vandoeuvre lès Nancy Cedex, (FRANCE)**
[2]**Youngstown State University, Department of Chemistry, One University Plaza, Youngstown, Ohio 44555-3663, (USA)**
[3]**Solid State Group, UCQR, IST/CTN, Instituto Superior Técnico, UTL, Estrada Nacional 10, 2695-066 Bobadela LRS, (PORTUGAL)**
[4]**CEMDRX, Physics Department, University of Coimbra, P-3004-516 Coimbra, (PORTUGAL)**
E-mail : mahjouba_bennasr@yahoo.fr

Abstract : A new Cu (II) complex with the bidentate ligand 4-amino-6-methoxypyrimidine (AMP), $[Cu(AMP)(H_2O)_3]SO_4$, has been prepared and was characterized by single crystal X-ray diffraction, IR spectroscopy and magnetic measurements. It crystallizes in the chiral orthorhombic space group $P2_12_12_1$. In the complex, the Cu(II) cation is penta-coordinated in a distorted trigonal bipyramidal fashion by two nitrogen atoms of two 4-amino-6-methoxypyrimidine ligands and three oxygen atoms of water molecules. In the molecular arrangement, each 4-amino-6-methoxypyrimidine molecule is coordinated to two Cu(II) cations through its two aromatic nitrogen atoms to form uniformly spaced chains spreading along the *b*-direction of the crystal lattice. The sulfate anions are located between these chains, and linked to them *via* N–H⋯O and OH⋯O hydrogen bonds. The magnetic susceptibility data of $[Cu(AMP)(H_2O)_3]SO_4$ shows an antiferromagnetic interaction of the metallic magnetic moments, through the Cu(II) chains, with an exchange integral of -35.7 K. **© Global Scientific Inc.**

Keywords : Noncentrosymmetric copper(II) complex; Crystal structure; Magnetism; IR spectroscopy.

INTRODUCTION

In recent years, there has been a growing interest in the development of functional metal-organic coordina-

tion materials[1]. This arises from both their fundamental properties such as their intriguing topological frameworks, but also their – initially often unexpected –potential applications in a wide range of various fields of

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engineering, device manufacturing, materials science, and many others[2-5]. When dealing with polynuclear metal-organic coordination materials that incorporate transition metal or lanthanide cations, structural features do correlate with magnetic properties of the coordination materials. Understanding of structural and chemical features that govern electronic exchange coupling of the metal ions through multi-atom bridging ligands[6-8], and the possibility for magnetic interaction between the metal ions can be used for the design of functional molecular magnetic materials[9]. In the construction of such materials, pyrimidine-based ligands can be used as versatile linkers with multiple potential binding sites for metals. The coordination properties of pyrimidines, which count the DNA bases cytosine, thymine, and uracil, thiamine (vitamin B1) and many other biologically relevant molecules among them, are also important for understanding the role and function of metal ion in biological systems[10,11] and the chemistry of e.g. transition metal complexes with ligands of biological relevance in which the metal centers are at close proximity to another is one of the central themes of current research. This is especially true for copper complexes[12,13] due to their versatile structural chemistry, their electrochemical and magnetic properties[14] and also because of their relevance as synthetic models[15,16] for active sites of several metalloenzymes[17]. For the Cu ions, coordination numbers vary between 4 and 6 for Cu(II), and 2 (sometimes even 1) and four for Cu(I). For the Cu(II) ion, the d^9 configuration is Jahn-Teller active: a single unpaired d-electron occupies one of the d orbitals, which gives rise to structural flexibility and often highly distorted ligand coordination geometries. In Cu(I) complexes, the d^{10} configuration does not impart any specific preferred geometry. Copper complex geometries are highly flexible with varying coordination geometries.

In order to better understand the correlation between molecular structure and magnetic behavior in copper complexes, we have undertaken a systemic study of several copper complexes of multidentate ligands[18,19]. As a part of this program, we have investigated structure and properties of the noncentrosymmetric copper (II) complex [Cu(AMP)(H$_2$O)$_3$]SO$_4$ (where AMP = 4-amino-6-methoxypyrimidine), which could act as a promoter material for quadratic non-linear optical applications.

MATERIALS AND METHODS

Chemical preparation

A solution of CuSO$_4$ (16 mg, 0.1 mmol) in water was added dropwise to a solution of 4-amino-6-methoxypyrimidine (13 mg, 0.1 mmol) in ethanol (6 mL). After stirring for 30 min, the mixture was filtered. Crystals suitable for X-ray analysis were obtained after five days by slow evaporation of the filtrate at room temperature (yield = 70 %).

Crystal structure determination

Diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer at 100 K using monochromatic Mo Kα radiation with the omega scan technique. Data were collected, the unit cell determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs[20]. The structure was solved by direct methods using Shelxs and refined by full matrix least squares against F^2 with all reflections using Shelxl[21] and Shelxle[22]. Non hydrogen atoms were refined anisotropically. Carbon bound H-atoms were placed in calculated positions guided by difference electron density maps and were assigned U_{iso}(H) values a multiple of U_{eq}(C) of their respective carrier atom (1.5 times for methyl C-atoms, 1.2 for all others). Water and nitrogen bound H-atoms were located in difference density maps and were refined with U_{iso}(H$_{H2O}$) set to 1.5 U_{eq}(O) and U_{iso}(H$_{NH2}$) to 1.2 U_{eq}(N). All O–H and N–H bonds were each restrained to have the same length within an esd of 0.02 Å. Experimental details are given in TABLE 1, selected bond distances and angles in TABLE 2, and hydrogen bonding interactions in TABLE 3.

Infrared spectroscopy

The infrared spectrum was recorded in the range 4000 - 400 cm^{-1} with a "Perkin-Elmer FTIR" spectrophotometer 1000 using a sample dispersed in spectroscopically pure KBr pressed into a pellet.

Magnetic measurements

Magnetic data on a powder sample were collected using a S700X Cryogenic Ltd. superconducting quan-

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tum interference device (SQUID) magnetometer. The temperature dependence of the magnetic susceptibility curves were measured over the temperature range 5-300K, after zero field cooling. A small magnetic field (500 Oe) was applied during susceptibility measurements.

RESULTS AND DISCUSSION

Crystal structure description

A depiction of the structure of [Cu(AMP)(H$_2$O)$_3$] SO$_4$, determined by single crystal X-ray diffraction, is shown in Figure 1. The crystallographic data and the structure refinement parameters of the title compound are summarized in TABLE 1. The selected bond lengths and angles are given in TABLE 2.

In the repeating unit of the [Cu(AMP)(H$_2$O)$_3$]SO$_4$ coordination polymer, the copper atoms are coordinated by two nitrogen atoms from two 4-amino-6-methoxypyrimidine ligands and three oxygen atoms of water molecules to yield a penta-coordination for the metal ion (Figure 2). Both AMP nitrogen atoms are metal-coordinated, with the AMP ligands connecting the copper ions into infinite chains. The coordination environment of the copper ion can be described as a distorted trigonal bipyramidal, with the equatorial ligands consisting of the two N-coordinated AMP molecules and one water molecule, and the apical positions taken

TABLE 1 : Experimental details.

	Cu(AMP)(H$_2$O)$_3$]SO$_4$
Crystal data	
Chemical formula	C$_5$H$_{13}$CuN$_3$O$_4$·O$_4$S
M_r	338.78
Crystal system, space group, Z value	Orthorhombic, $P2_12_12_1$, 4
Temperature (K)	100
a, b, c (Å)	7.9026 (17), 11.137 (2), 12.978 (3)
V (Å^3),	1142.3 (4)
F(000)	692
D_x (Mg m^{-3})	1.970
No. of refl., θ range (°) for cell measurement	9809, 2.4–32.0
μ (mm^{-1})	2.13
Crystal shape, colour	Block, blue
Crystal size (mm)	0.55 × 0.50 × 0.36
Data collection	
Diffractometer	Bruker AXS *SMARTAPEX* CCD diffractometer
Radiation source, type	fine-focus sealed tube, graphite monochr. Mo *K*α
Scan method	ω scans
Absorption correction	Multi-scan, Apex2 v2011.2-0 (Bruker, 2011)
exptl. T_{min}, T_{max}	0.595, 0.746
No. of meas., indep. and obs. [$I > 2\sigma(I)$] refl.	13361, 3673, 3622
R_{int}	0.019
θ values (°)	$\theta_{max} = 32.1$, $\theta_{min} = 2.4$
(sin θ/λ)$_{max}$ (Å^{-1})	0.748
Range of h, k, l	$h = -11 \rightarrow 11$, $k = -16 \rightarrow 16$, $l = -18 \rightarrow 18$
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.016, 0.043, 1.09
No. of refl., parameters, restraints	3673, 188, 16
H-atom treatment	Mixture of independent and constrained refinement
Δρ$_{max}$, Δρ$_{min}$ (e Å^{-3})	0.34, -0.32
Absolute structure (Flack) parameter[25]	0.018 (6) (based on 1501 Friedel pairs)

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up by the two remaining water molecules. The sum of the angle values between the three equatorial bonds 359.98 (4)° is, within the standard deviation, the value expected for a trigonal bipyramidal coordinated metal center 360° [O8-Cu-N2 = 116.97 (4)°, O8-Cu-N1[ii] = 91.72(4)°, N2-Cu1-N1[ii] = 151.29(4)°, for symmetry codes, see TABLE 2]. The positive charge of the

Cu(II) cation is compensated through the not coordinated sulfate anion. The bond distances around the copper ion (TABLE 2) vary between 1.9419(10) and 2.1666(10) Å for the Cu-O distances, and between 2.0342(10) and 2.0386(10) Å for the Cu-N distances, being similar to those observed in related copper(II) complexes[23].

In the structural arrangement, each of the 4-amino-6-methoxypyrimidine molecules is coordinated to Cu(II) cations through both of its two aromatic nitrogen atoms to form uniformly spaced chains that run in a *zig-zag* pattern parallel to the *b*-axis direction (Figure 3). The space between the chains is taken up by the sulfate anions, which are connected to the coordination polymer

TABLE 2 : Selected geometric parameters (Å, °).

C1—N1	1.3220 (14)	C5—O1	1.4428 (17)
C1—N2	1.3383 (14)	N1—Cu1[i]	2.0386 (10)
C2—N3	1.3354 (17)	N2—Cu1	2.0342 (10)
C2—N2	1.3603 (15)	O6—Cu1	1.9419 (10)
C2—C3	1.4083 (18)	O7—Cu1	1.9554 (10)
C3—C4	1.3742 (17)	O8—Cu1	2.1666 (10)
C4—O1	1.3383 (14)	Cu1—N1[ii]	2.0385 (10)
C4—N1	1.3565 (15)		
N3—C2—N2	119.03 (11)	C2—N2—Cu1	127.72 (8)
N3—C2—C3	120.44 (12)	C4—O1—C5	116.76 (10)
N2—C2—C3	120.53 (11)	O6—Cu1—O7	176.57 (4)
C4—C3—C2	117.01 (11)	O6—Cu1—N2	88.38 (4)
O1—C4—N1	111.76 (10)	O7—Cu1—N2	88.80 (4)
O1—C4—C3	125.91 (11)	O6—Cu1—N1[ii]	91.09 (4)
N1—C4—C3	122.33 (11)	O7—Cu1—N1[ii]	92.32 (4)
C1—N1—C4	116.88 (10)	N2—Cu1—N1[ii]	151.29 (4)
C1—N1—Cu1[i]	126.83 (8)	O6—Cu1—O8	89.17 (4)
C4—N1—Cu1[i]	116.20 (8)	O7—Cu1—O8	90.36 (4)
C1—N2—C2	117.26 (10)	N2—Cu1—O8	116.97 (4)
C1—N2—Cu1	114.78 (8)	N1[ii]—Cu1—O8	91.72 (4)

Symmetry code(s): (i) *-x, y-1/2, -z+3/2*; (ii) *-x, y+1/2, -z+3/2*.

TABLE 3 : Selected hydrogen-bond interactions.

D–H⋯*A*	*D*–H (Å)	H⋯*A* (Å)	*D*⋯*A* (Å)	*D*–H⋯*A* (°)
N3–H3A⋯O4	0.794 (15)	2.477 (18)	3.0253 (17)	127 (2)
N3–H3A⋯O5[iii]	0.794 (15)	2.582 (18)	3.2086 (17)	137 (2)
N3–H3B⋯O2	0.751 (15)	2.425 (18)	3.0585 (17)	143 (2)
O6–H6A⋯O3[iv]	0.771 (13)	1.949 (13)	2.7157 (14)	173 (2)
O6–H6B⋯O5[v]	0.780 (13)	1.866 (13)	2.6400 (14)	172 (2)
O7–H7A⋯O3[vi]	0.750 (13)	1.953 (13)	2.7004 (14)	174 (2)
O7–H7B⋯O4[vii]	0.778 (13)	1.899 (13)	2.6721 (14)	173 (2)
O8–H8A⋯O2[v]	0.779 (13)	1.980 (13)	2.7463 (14)	168 (2)
O8–H8B⋯O2	0.804 (13)	1.914 (13)	2.6956 (14)	164 (2)

Symmetry code(s): (iii) *-x, y-1/2, -z+1/2*; (iv) *-x-1/2, -y+2, z+1/2*; (v) *x-1/2, -y+5/2, -z+1*; (vi): *x+1/2, -y+5/2, -z+1*; (vii) *-x+1/2, -y+2, z+1/2*.
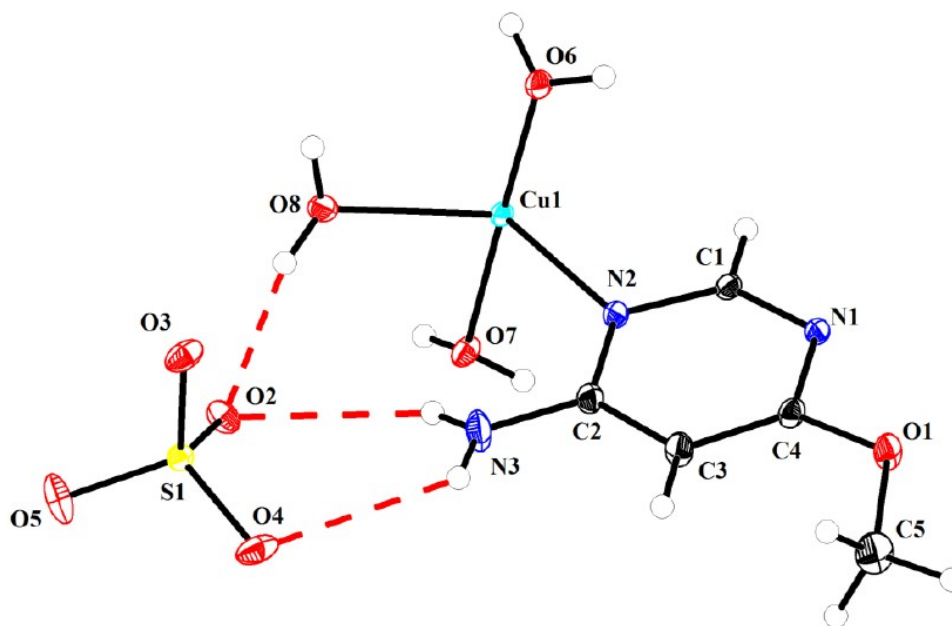

Figure 1 : Asymmetric unit of [Cu(AMP)(H₂O)₃]SO₄ with the atom numbering scheme and thermal ellipsoids at 50 % probability and except for H-atoms, which are represented by spheres of arbitrary radii.
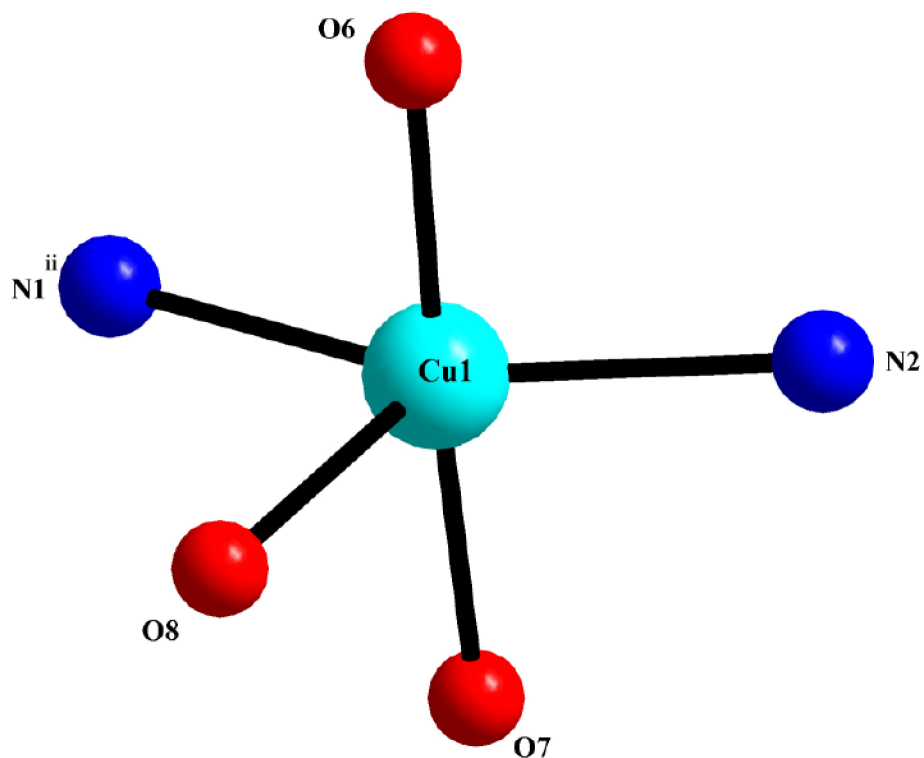
Figure 2 : Coordination geometry around the Cu(II) cation in the crystal structure of [Cu(AMP)(H$_2$O)$_3$]SO$_4$. Symmetry code: (ii) -*x*, *y*+1/2, -*z*+3/2.
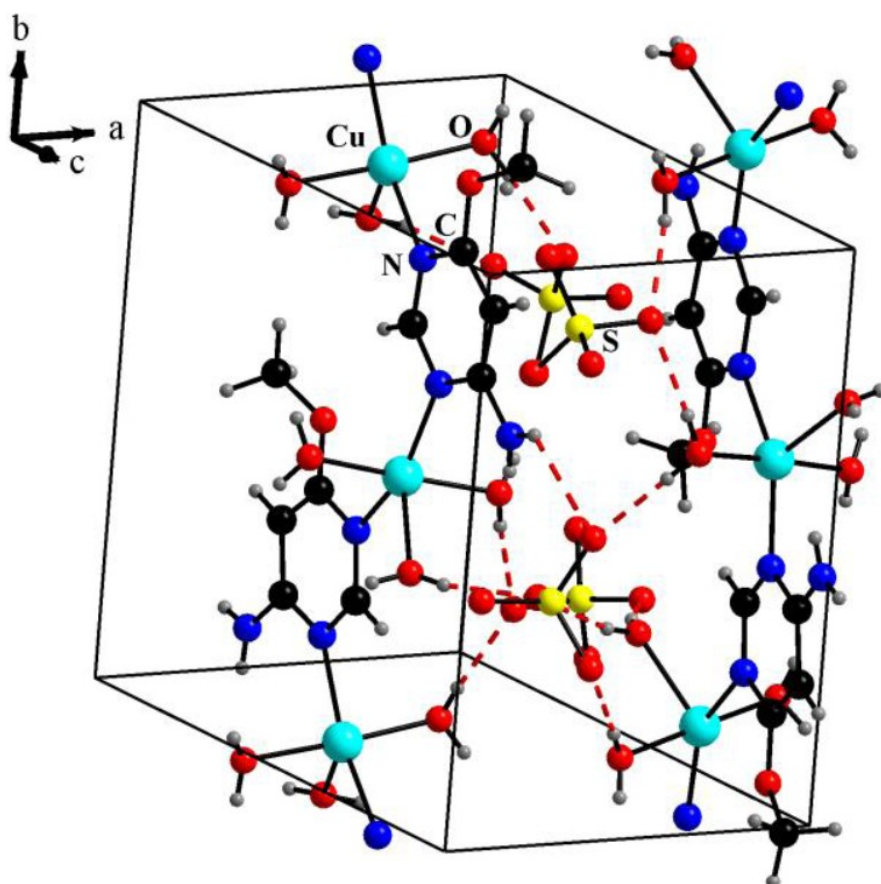
Figure 3 : Inorganic-organic chains in the crystal structure of [Cu(AMP)(H$_2$O)$_3$]SO$_4$.

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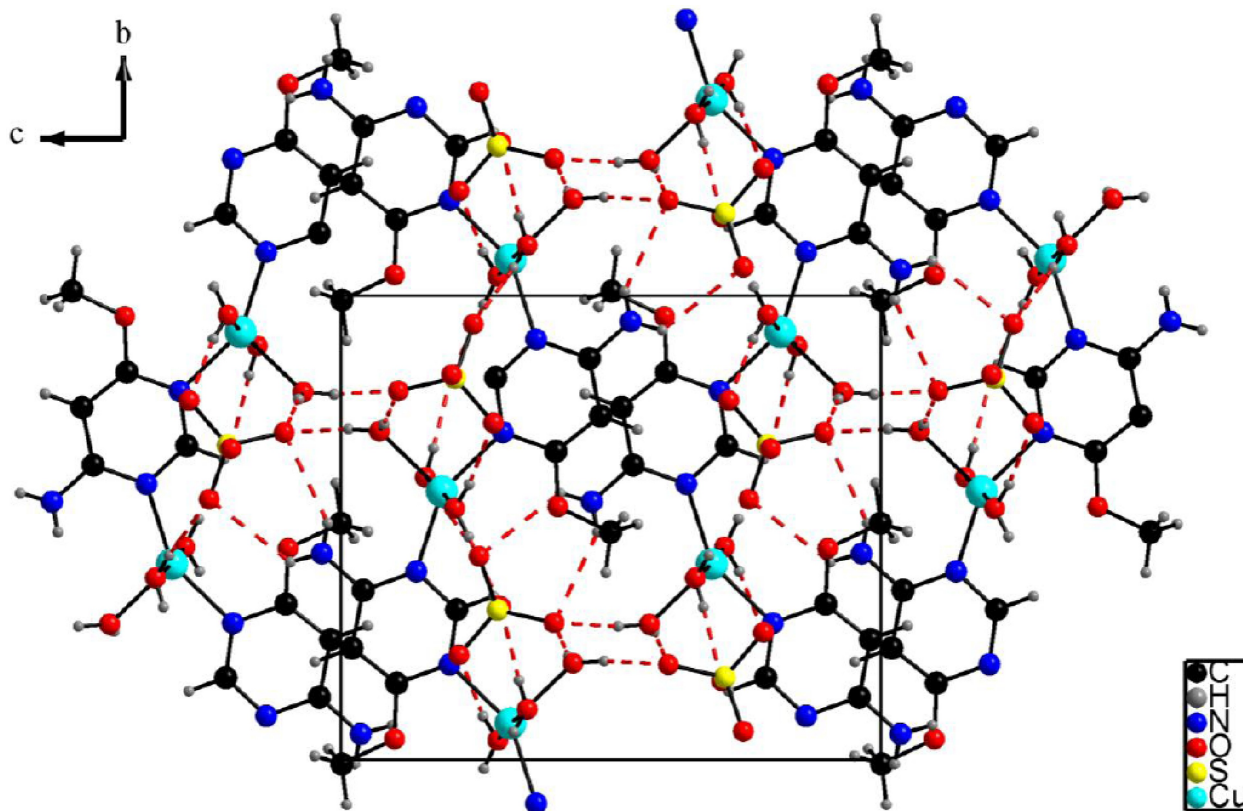
Figure 4 : Projection of the crystal structure of [Cu(AMP)(H$_2$O)$_3$]SO$_4$ along the *a*-axis. The dotted lines indicate hydrogen bonds.

chains through multiple N–H···O and O–H···O hydrogen bonds originating from the AMP amino groups and the metal coordinated water molecules (Figure 3, TABLE 3). Among these hydrogen bonds, one is a three-centered interaction N3–H3A···(O4, O5^{iii}) (see TABLE 3). Via the O–H···O bonds, the sulfate anions and the water molecules are interconnected to form a hydrogen bonded layered network parallel to the (b, c) plane (Figure 5) that is weaving around the AMP molecules in this layer. Within this layer, R$_2^2$(32) graph set motifs[24] are apparent.

With regard to the arrangement of the organic molecules (Figure 4), the 4-amino-6-methoxypyrimidine groups are not organized *trans* to each other on the metal atom. This is a situation favorable for an arrangement in a non-centrosymmetric setting and space group. Indeed, refinement of the structure in the chiral space group $P2_12_12_1$ gives a Flack parameter value of 0.018(6)[25], indicating resolution of the achiral starting materials into a racemic mixture of chiral crystals during crystallization.

Examination of the geometric features of the or-

ganic moiety (TABLE 2) shows two types of C-O distances, 1.4428(14) Å for the C5–O1 distance involving the methyl carbon atom, and a much shorter 1.3383(14) Å for C4–O1. The small bond distance value of the latter can be attributed to the donor mesomeric effect of the methoxy group attached to the pyrimidinic ring[26]. Furthermore, the C2–N3 distance [1.3354(17) Å] is approximately equal to a C=N double bond length. The sum of the angles around N2 is 359.3(14)°. All these geometrical features are consistent with enamine-imine tautomerism[27] and suggest a great contribution from such resonance to the title compound. It is worth noticing that no π–π stacking interactions between neighboring pyrimidinic rings or C-H…π interactions towards them are observed.

IR spectroscopy

The IR spectrum of the crystalline complex [Cu(AMP)(H$_2$O)$_3$]SO$_4$ is shown in Figure 6. The characteristic vibrational modes of the title compound can be compared to those of similar materials[30].

In the high-frequency region, the very large band spreading between 3600-2200 cm^{-1} corresponds to the
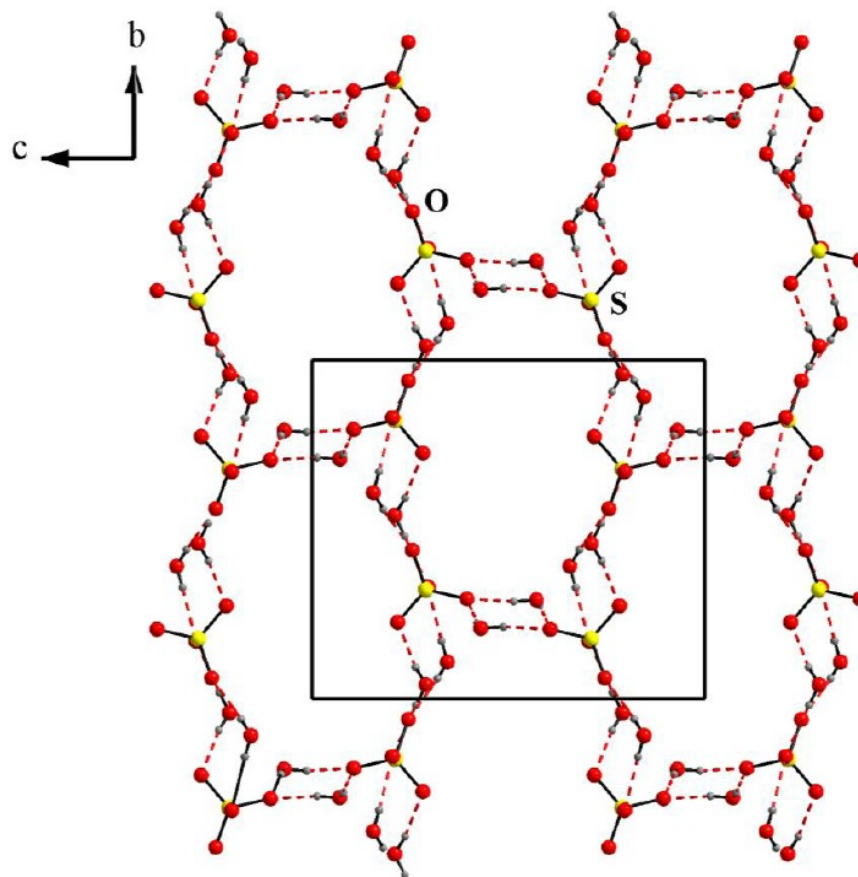
Figure 5 : Projection of the inorganic layers in the crystal structure of [Cu(AMP)(H$_2$O)$_3$]SO$_4$ along the *a*-axis.
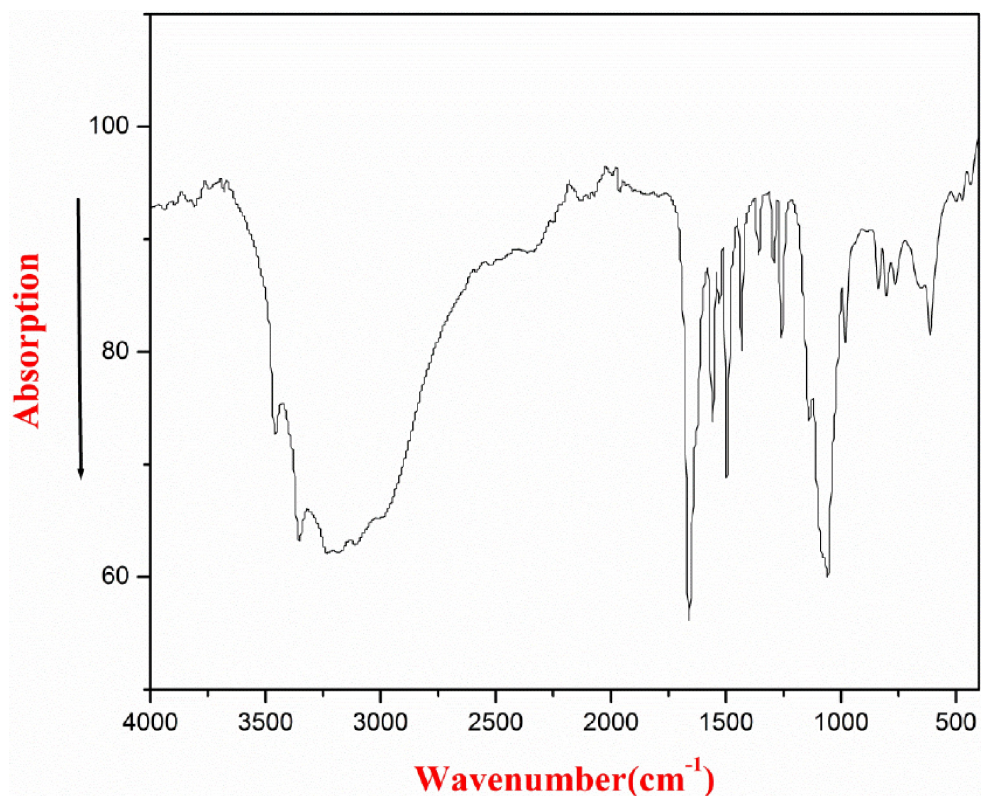
Figure 6 : IR absorption spectrum of [Cu(AMP)(H$_2$O)$_3$]SO$_4$.

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valence vibrations of C–H, O–H and N–H groups interconnected by a system of hydrogen bonds in the crystal[31,32].

- Bands in the 1620-1100 cm^{-1} region correspond the O–H bending vibration and to the valence vibrations of C=C and C=N groups[33,34].
- Between 1200 and 400 cm^{-1} various valence and bending vibration bands are characteristic of the sulfate group[35]. In the crystal, the SO_4 tetrahedron gives two stretching vibrations ν_s and ν_{as}, the symmetric and asymmetric bands, respectively, and the bending modes δ_s and δ_{as} [35]. In the spectrum of the title compound, the δ_s mode of the sulfate ion is found to be split into two components around 468 and 433 cm^{-1}. The stretching mode ν_s appears as one band at 981 cm^{-1}. The ν_{as} mode appears as one intense band at 1058 cm^{-1} with two shoulders at 1098 and 1138 cm^{-1}. The δ_{as} mode is observed as two bands at 655 and 613 cm^{-1}.

Magnetic susceptibility measurements

The temperature dependence of the magnetic susceptibility of the title compound was measured under an applied field of 500 Oe in the temperature range 5-300 K, in the zero field-cooled regime.

The plot of the molar susceptibility versus T is shown in Figure 7. It shows an increase of the susceptibility as the temperature decreases with a broad maximum around 20 K. The overall magnetic behavior corresponds to an antiferromagnetic coupled system. The room temperature χT value is close to that expected for non-interacting copper(II) ions (0.375 cm^{3}mol^{-1} with g = 2.0).

The data over the entire temperature range are best fitted by the Bonner–Fisher model for an uniformly spaced chain of S=1/2 spin[36],

$$\chi = \frac{Ng^2\mu_B^2}{k_BT}\frac{0.25 + 0.074975z + 0.075235z^2}{1.0 + 0.9331z + 0.172135z^2 + 0.757825z^3}$$

with $z = |J|/(k_BT)$ and $\langle g \rangle = 2.1$, for $H = -2J\backslash_1\cdot\backslash_2$. In addition a low temperature Curie contribution was used to fit the experimental data.

As observed in Figure 7 the equation provides a good fit of experimental data in the 10-300 K region, yielding an exchange coupling constant of J/k$_B$ =-35.7 K (J=-24.8 cm^{-1}). The Curie term corresponds to about 0.5% of the curve and is probably due to some
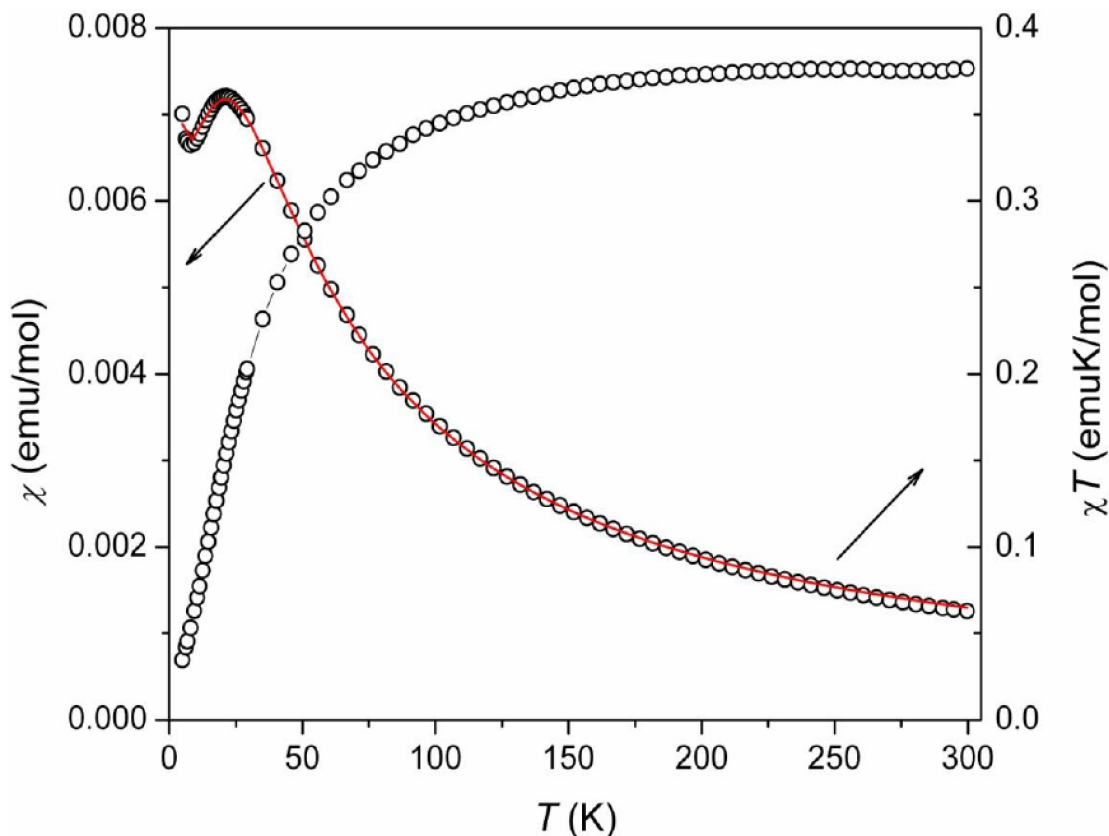

Figure 7 : χ and χT curves of the title complex. The solid line represents a fit as discussed in the text.

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paramagnetic S=1/2 impurities as it is observed by the increasing of the magnetic susceptibility at very low temperatures.

The N-atoms of the pyrimidine ring bridge the metal ions in equatorial positions; such conformation has been found to promote antiferromagnetic interactions, as axial-axial and axial-equatorial support very weak antiferromagnetic and ferromagnetic interactions, respectively[37-39]. It has been argued that an equatorial-equatorial coordination geometry allows the overlap of a copper magnetic orbital with a σ type symmetry with aσ orbital of the coordinated nitrogen, an essential occurrence for the antiferromagnetic interaction to arise through the ring[37,38].

CONCLUSION

A new Cu(II) complex with the bidentate ligand 4-amino-6-methoxypyrimidine, $[Cu(AMP)(H_2O)_3]SO_4$, was synthesized and characterized by various physical and chemical methods. At the structural level, the atomic arrangement of this material consists of chains built by the Cu(II) cation, the organic groups and the water molecules. Between these chains are located the sulfate anions via N–H···O and OH···O hydrogen bonds. In this complex the copper atom has a slightly distorted trigonal bipyramidal environment. This compound, which has a noncentrosymmetric structure, could be a potential candidate material for quadratic non-linear optical applications. From the magnetic measurements the presence of antiferromagnetic intrachain interactions were confirmed.

SUPPLEMENTARY DATA

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No 957888. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the CCDC, 12Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

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