

PREPARATION, STRUCTURE AND PROPERTIES OF BIS (M₂-CHLORO)-(NITRATO-O)-(2,2'-BIPYRIDINE-N.N')COPPER(II): [Cu(2,2'-BP)Cl NO₃]₂

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ABSTRACT

The crystal structure of the compound with empirical formula [Cu (2, 2'-BP)Cl NO₃]₂ (BP: 2,2'-bipyridine) (**1**) has been determined. Crystals are triclinic, space group P₁ with a = 7.5152 (12) Å, b = 9.2531(14) Å, c = 10.2834(16) Å, α = 112.181(2)°, β = 102.155(2)°, γ = 105.617(2)°.

The copper atom displays a (4+1) square pyramidal coordination, with the four in-plane bonds provided by one chloride ion, two nitrogen atoms from the 2,2'-bipyridine molecule and one oxygen from the nitrate group. The apical position corresponds to a chloride ion Cl(1') from a centrosymmetric neighboring moiety. The two symmetry related Cl ions bridge two copper atoms, generating a dimeric unit (Cu(1)-Cl(1) = 2.2726(11) Å, Cu(1)-Cl (1') = 2.7093(13) Å).

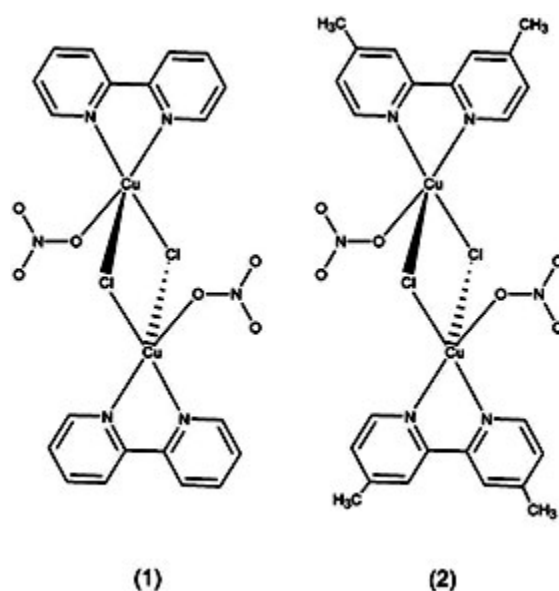
Magnetic susceptibility measurements showed a weak ferromagnetic interaction between dimers.

INTRODUCTION

The compound reported here is part of a research oriented at the synthesis and characterization of transition metal complexes. Our interest in this area has been motivated by a desire to elucidate the relation between structure and magnetic properties in these systems. [1-3]

We report herein the crystal structure and magnetic properties of bis (m_2 -chloro)-(nitrato-*o*)-(2,2'-bipyridine-*N,N'*)copper(II): $[\text{Cu}(2,2'\text{-BP})\text{Cl NO}_3]_2$. A closely related dimer (with the BP group replaced by its bimethylated homologue $[\text{Cu}(2,2'\text{-dmBP})\text{Cl NO}_3]_2$, (dmBP:4,4'-dimethyl-2,2'-bipyridine)) (**2**) had already been reported in the literature.^[1] In spite of both dimeric cores being quite similar, the presence of the bulky methyl groups substantially modifies their packing properties.

Diagrams



EXPERIMENTAL

Synthesis of $[\text{Cu}(2,2'\text{-BP})\text{Cl NO}_3]_2$

A methanol solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was refluxed with CuO for 30 min, and a stoichiometric amount of 2,2'-bipyridine was added while still hot. The pH of the solution was adjusted to 5 by addition of HCl. The resultant mixture was refluxed for 3 h, and filtered to remove excess CuO. After cooling down the solution to room temperature and keeping it undisturbed for several days, green crystals of (1) suitable for X-ray diffraction appeared.

X-ray structure determination:

A highly redundant diffractometer data set was collected up to a 2θ max of ca. 58° using monochromatic Mo K α radiation, $\lambda = 0.7107 \text{ \AA}$, $T = 295 \text{ K}$ on a Bruker Smart diffractometer driven by the SMART-NT^[4] software. Data reduction and absorption corrections were performed using SAINT-NT.^[5] The structure resolution was achieved routinely by direct methods and difference Fourier. The model was refined by least squares on F^2 , with anisotropic displacement parameters for non-H atoms. All the hydrogen atoms in the structure (C-H's) were unambiguously defined by the stereochemistry and were accordingly placed at

their calculated positions and allowed to ride onto their host carbons both in coordinates as well as in thermal parameters.

Data collection calculations to solve and refine the structures and to obtain derived results were carried out with the SHELXS97/SHELXL97, [6] SHELXTL/PC computer programs.[7] Full use of the CCDC package was also made for searching in the CSD Database.[8]

Magnetic Measurements

The magnetic susceptibility of $[\text{Cu}(2, 2'\text{-BP})\text{NO}_3\text{Cl}]_2$ was determined over the temperature range 10-300 K using a SQUID magnetometer (Quantum Design model MPMS-XL5) with a field of 0.1 T. The data were corrected to compensate for the diamagnetism of the constituent atoms using Pascal's constant and for the temperature independent paramagnetism of copper (II).

EPR spectra were recorded at room temperature with a Bruker ECS 106 Spectrometer at 9.85 GHz in a rectangular cavity with 50 kHz field modulation.

RESULTS AND DISCUSSION

Crystal structure:

[Fig. 1](#) shows a molecular view of $[\text{Cu}(2,2'\text{-BP})\text{NO}_3\text{Cl}]_2$, while relevant experimental data are presented in [Tables 1](#) and [2](#), and a selection of coordination bond lengths and angles are given in [Table 3](#).

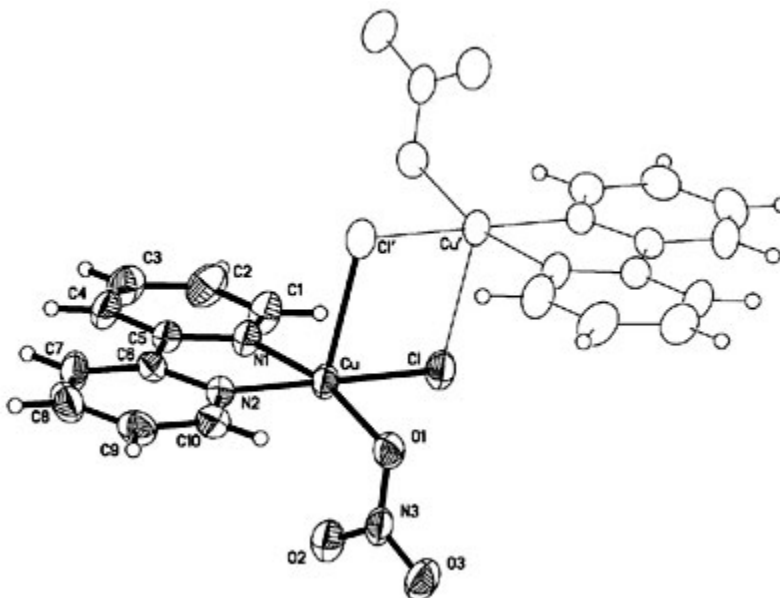


Fig. 1: Molecular plot showing the dimeric unit in **(1)**. Only the independent part is highlighted. Displacement ellipsoids represented at a 40% level.

Symmetry codes.1-x, 1-y, 1-z.

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

Empirical formula	C ₁₀ H ₈ Cl Cu N ₃ O ₃
Formula weight	318.19
Temperature	297(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1 (No. 2)
Unit cell dimensions	a = 7.5152(12) Å a = 112.181(2)°. b = 9.2531(14) Å b = 102.155(2)°. c = 10.2834(16) Å g = 105.617(2)°.
Volume	597.38(16) Å ³
Z	2
Density (calculated)	1.769 Mg/m ³
Absorption coefficient	2.054 mm ⁻¹
F(000)	320
Crystal size	0.210 x 0.096 x 0.034 mm ³
Theta range for data collection	2.28 to 28.00°.
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 12, -12 ≤ l ≤ 13
Reflections collected	5017
Independent reflections	2568 [R(int) = 0.0332]
Completeness to theta = 28.00°	89.2 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2568 / 0 / 164
Goodness-of-fit on F ²	0.985
Final R indices [I > 2σ(I)]	R1 = 0.0467, wR2 = 0.0996
R indices (all data)	R1 = 0.0780, wR2 = 0.1108
Largest diff. peak and hole	0.417 and -0.355 e.Å ⁻³

The structural unit is a dimeric copper(II) complex built around a symmetry center. The coordination geometry of the copper atoms can be described as a square pyramid, the basal bonds being provided by two N atoms from the 2,2'-bipyridine molecule [Cu(1)-N(1) = 1.993(3), Cu(1)-N(2) = 1.994(3) Å], one oxygen atom from the nitrate group [Cu(1)-O(1) = 2.003 Å] and one chloride ion [Cu(1)-Cl(1) = 2.2726(11) Å]. The resulting equatorial plane is rather ill-defined, with the Cu(II) ion showing no significant departure in terms of the individual deviations of the atoms defining the plane (viz., 0.1067, -0.0984, 0.0842, -0.0925 and 0.1218 Å for N(1), N(2) Cl(1), O(1) and Cu(1), respectively).

The apical position corresponds to a chloride ion, Cl(1'), from a neighboring, symmetry related unit, at a larger distance Cu(1)-Cl(1') = 2.7093(13) Å than the basal one. As shown in [Fig.1](#), the copper-chloride interaction around the inversion center determines a closed loop giving rise to the dimeric unit. This loop is characterized by a Cu(1)-Cu(1') distance of 3.488 Å, and a Cu(1)-Cl(1)-Cu(1') angle of 88.40(4)°.

Table 2. Atomic coordinates ($\times 10^4$ and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **(1)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	2946(1)	4666(1)	8592(1)	37(1)
Cl(1)	3100(2)	4389(1)	10712(1)	44(1)
C(1)	2712(6)	3883(5)	5453(5)	44(1)
C(2)	2530(6)	4191(6)	4231(5)	48(1)
C(3)	2400(6)	5695(6)	4370(5)	54(1)
C(4)	2443(6)	6828(6)	5698(5)	48(1)
C(5)	2616(5)	6459(5)	6902(4)	38(1)
C(6)	2632(5)	7566(5)	8378(4)	37(1)
C(7)	2476(6)	9115(5)	8749(5)	50(1)
C(8)	2453(7)	10019(6)	10130(6)	54(1)
C(9)	2646(7)	9407(5)	11157(5)	56(1)
C(10)	2810(7)	7861(5)	10730(5)	50(1)
N(1)	2747(4)	4990(4)	6765(3)	35(1)
N(2)	2794(5)	6939(4)	9364(4)	38(1)
N(3)	558(6)	1426(4)	6944(4)	43(1)
O(1)	2441(4)	2210(3)	7478(3)	45(1)
O(2)	-484(5)	2254(4)	7017(3)	55(1)
O(3)	-92(5)	-120(4)	6406(4)	63(1)

The nitrate group clearly reflects in its geometry the oxygen involvement in coordination, O(1) being unique in that N(1)-O(1) is some 5% longer than the other two bonds which involve the non-coordinated O(2) and O(3), at the same time that the angles in which it is involved are about 5% smaller ([Table 3](#)).

Table 3. Selected bond lengths [Å] and angles [°] for **(1)**^(this work) and **(2)**^[1]

	(1)	(2)
Cu(1)-N(1)	1.993(3)	2.004
Cu(1)-N(2)	1.994(3)	2.008
Cu(1)-O(1)	2.003(3)	1.990
Cu(1)-Cl(1)	2.2726(11)	2.276
Cu(1)-Cl(1)#1	2.7093(13)	2.650
N(3)-O(3)	1.226(4)	1.229
N(3)-O(2)	1.229(4)	1.228
N(3)-O(1)	1.284(4)	1.291
N(1)-Cu(1)-N(2)	80.86(13)	80.7
N(1)-Cu(1)-O(1)	166.16(12)	169.9
N(2)-Cu(1)-O(1)	92.90(12)	91.2
N(1)-Cu(1)-Cl(1)	96.56(10)	95.3
N(2)-Cu(1)-Cl(1)	177.19(10)	172.4

O(1)-Cu(1)-Cl(1)	89.37(8)	91.9
N(1)-Cu(1)-Cl(1)#1	99.55(10)	95.8
N(2)-Cu(1)-Cl(1)#1	89.93(9)	94.5
O(1)-Cu(1)-Cl(1)#1	92.75(9)	90.9
Cl(1)-Cu(1)-Cl(1)#1	91.60(4)	92.3
O(2)-N(3)-O(1)	118.9(3)	119.1
O(3)-N(3)-O(1)	117.3(4)	117.7
O(3)-N(3)-O(2)	123.8(4)	123.2

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

The BP group does not present any unusual feature: it binds in a quite even fashion with indistinguishable Cu-N bond lengths, and the perfect molecular plane (mean deviation 0.015 Å) coincides with the coordination plane (the C(5)-N(1)-Cu-N(2)-C(6) loop) within 0.5°.

The presence of the nitrate and chloride ions (eager acceptors for H-bonding) seems to counterbalance the lack of efficient donors of similar quality, and as a result a few medium strength but nonetheless important C-HO and C-HCl bonds build up. Thus, O(3) receives two H-bonds while Cl(1), O(2), O(1) just one H-bond each (Table 4 and Fig. 2, single dotted lines). These interactions, which determine a highly stable 2D network evolving parallel to the (-101) plane, are in turn Reinforced by a p-p contact between centrosymmetrically related N(2),C(6)-C(10) pyridyl cycles in two neighboring BP units (Fig. 2, double dotted lines). Due to the symmetry relationship, the two planar groups are exactly parallel to each other, with a graphitic interplanar distance of ca. 3.40 Å, a distance between centroids of 3.60 Å, and a slippage angle (the one between the normal to the plane and the vector joining centroids) of 19.5° (for details and nomenclature see Ref [9]).

Table 4. Hydrogen bonds for **(1)** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4)-H(4)...O(3)#2	0.93	2.43	3.191(5)	138.6
C(10)-H(10)...O(3)#3	0.93	2.46	3.046(5)	121.4
C(3)-H(3A)...Cl(1)#2	0.93	2.86	3.732(4)	157.5
C(8)-H(8)...O(2)#4	0.93	2.58	3.220(5)	126.7
C(10)-H(10)...O(1)	0.93	2.52	3.037(5)	115.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 x,y-1,z #3 -x+2,-y+2,-z+2

#4 -x+2,-y+1,-z+2

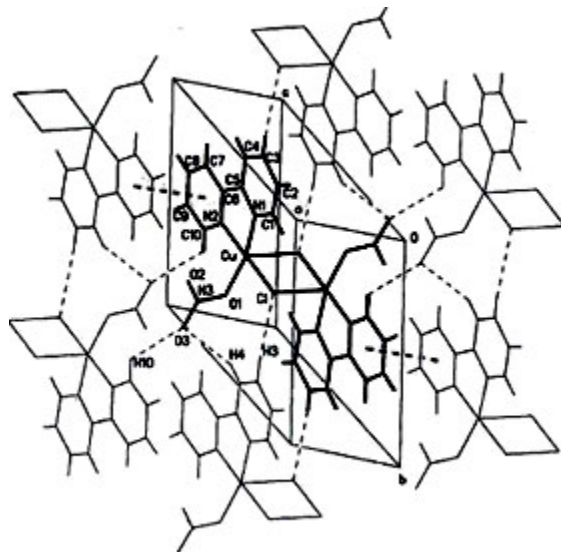


Fig. 2: Packing diagram of **(1)** showing the way in which the 2D structures are formed. The reference dimer has been highlighted at the centre of the field. For clarity, only the most relevant H-bonds to this reference dimer have been represented with simple dashed lines; double dashed lines, π - π contacts linking symmetry-related pyridyl cycles.

No definite H-bonding or p-p interactions connecting planes seem to be present, and therefore the corresponding stabilizing forces must be found in diffuse, much weaker van der Waals interactions.

Structure **(2)**^[1] bears almost the same structural motif as **(1)** (with dmBP instead of BP, see diagrams), and comparison of the values presented in [Table 3](#) shows that they share a very similar cation coordination sphere. However, while structure **(1)** organizes as strongly linked planes, the dimers in **(2)** aggregate in the form of chains. The rotation of the nitrate group around the N(3)-O(1) bond changes the H-bonding targets for O(3), the main intermolecular H-bond acceptor in both structures.

While in structure **(1)** it receives two strong, widely open H-bonds (HO(3)H ca. 110°) from two different dimers, in structure **(2)** it receives just one, obviously from a single, unique molecular group. This is the reason why the 2D character of the self assembly in **(1)** is lost into a set of strongly coupled but weakly connected chains in **(2)**.

Magnetic properties and EPR spectra:

The polycrystalline powder EPR spectra of complex **(1)** at room temperature exhibit a structure typical of isolated copper(II) with $g_{\parallel} = 2.09$

Magnetic susceptibility data for a polycrystalline sample of $[\text{Cu}(2,2'\text{-BP})\text{NO}_3 \text{Cl}]_2$ were collected in a 0.1 T field over the temperature range of 10-300 K. Plots of the inverse of the magnetic susceptibility (χ^{-1}) and effective magnetic moment as a function of temperature are shown in [Figure 3](#).

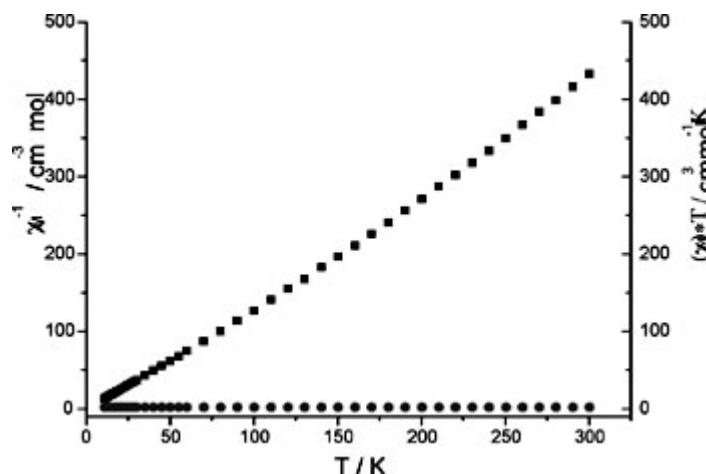


Fig. 3: The inverse of the magnetic susceptibility (χ^{-1}) and the effective magnetic moment (χ^*T) plotted as a function of temperature for complex **(1)**.

The data obey the Curie-Weiss law, and a least-squares calculation of C and θ (the Curie-Weiss constant) using measurements over the whole temperature range resulted in $C = 0.8121 \text{ cm}^3 \text{ mol}^{-1}$ and $\theta = 0.804 \text{ K}$. The low positive value of θ is indicative of a weak ferromagnetic interaction between dimeric units.

The model of an isolated Heisenberg dimer of $S=1/2$ ion with Hamiltonian interaction $H = -2J S_1 S_2$ has been used to analyze the magnetic data. The susceptibility of this model is described by the Bleaney-Bowers equation, which contains a term corresponding to the presence of a small amount of paramagnetic species.

$$\chi_M = \frac{Ng^2 \beta^2}{3k} \left[\frac{1}{1 + \frac{1}{3} \exp(2J/kT)} \right]$$

Least-squares fitting of χ_M vs. T yielded $g = 2.02$ and $2J = -0.023 \text{ cm}^{-1}$, with an agreement factor $F = 6.3 \times 10^{-4}$ ($F = \sum[(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calc}}]^2 / \sum[(\chi_M)_{\text{obs}}]^2$). The g value obtained from the magnetic susceptibility data agrees reasonably with the g value of 2.09 obtained from EPR spectra.

Hodgson et al. [10] have suggested that for bis-chloro-bridged Cu(II) dimers where the copper centers adopt a square-pyramidal or trigonal-bipyramidal geometry, an empirical correlation exists between the exchange energy J and the ϕ/R ratio, where ϕ is the Cu-Cl-Cu bridging angle and R is the longest copper-chloride distance in the bridge.

There are, however, a number of cases in the literature where Hodgson's semiempirical rule does not seem to apply: as an example, for $\text{Cu}(\text{dmgH})\text{Cl}_2$ (dmgH: dimethylglyoxime)[11] with $\phi/R = 32.6$, Hodgson's rule calculates an exchange energy $J = +6.3 \text{ cm}^{-1}$, far in excess of the experimental value $J = +0.31 \text{ cm}^{-1}$.

The present case of structure **(1)** is in this respect very similar: it has a Cu-Cl-Cu bridging

angle of 88.4° and a Cu-Cl distance $R = 2.7093 \text{ \AA}$ which determine a f/R ratio of 32.6 (identical to that in Reference [11]) and an experimental $J = -0.012$ ($2J = -0.023$) cm^{-1} , far below Hodgson's forecast.

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SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC N 241397. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, (Fax +44 1223 336033), e-mail: linstead@ccdc.cam.ac.uk; or deposit@ccdc.cam.ac.uk.

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