

Crystal Structure and Magnetic Properties of (2,2'-Dipyridyl)-(2-acetylphenolato)copper(II) Perchlorate

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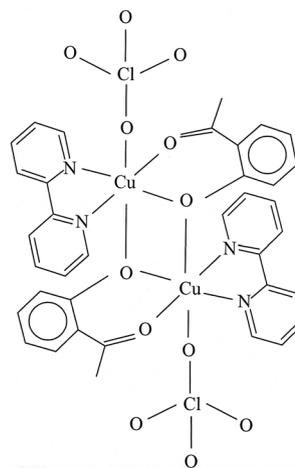
Mixed-Ligand Binuclear Copper(II) Complex, Crystal Structure, Antiferromagnetic Interaction

The mixed-ligand dinuclear complex (2,2'-dipyridyl)-(2-acetylphenolato)copper(II) perchlorate was synthesized and its crystal structures determined. The structure consists of a dimeric unit involving a planar Cu_2O_2 group. The coordination sphere of the Cu atom can be described as an elongated octahedron where the basal plane is formed by the two N atoms of the 2,2'-dipyridyl molecule and the two O atoms of the acetophenon molecule. Two apical Cu - O contacts complete the 4+2 coordination of the Cu atoms. They correspond to one of the O atoms of the perchlorate anion and to the O atom of the second unit. Magnetic susceptibility data obey the Curie-Weiss law with $\Theta = -8.1(2)$ K. The decreasing of the effective magnetic moment from $1.94(8) \mu_{\text{B}}$ at 300 K to $1.86(8) \mu_{\text{B}}$ at 70 K and the negative Weiss constant indicate weak antiferromagnetic interactions between the two copper atoms in the dimeric units.

Introduction

The five-coordination copper(II) complexes usually show a stereochemistry ranging from slightly distorted trigonal-bipyramidal to distorted square-pyramidal arrangement [1, 2]. Di-2-pyridylamine and similar ligands (rigid or semi-rigid) are well known for their stabilizing effect on the five-coordination state of copper(II) [3]. The complexation by 2,2'-dipyridyl (dp) or dp-related ligands gives rise to a wide variety of complexes depending on the oxidation state of the Cu ion and the nature of the other coordinating ligands. The inherent flexibility of the copper(II) coordination sphere and the dp along with 2'-hydroxyacetophenon led to our interest in these complexes.

Very recently, we studied the crystal structures and magnetic properties of the mixed-ligand dinuclear complexes (2,2'-dipyridyl)-(3-methoxysalicylaldiminato)copper(II) perchlorate and (2,2'-dipyridyl)-(4-methoxysalicylaldiminato)copper(II) perchlorate [4]. In order to extend further the study of such complexes, we synthesized (2,2'-dipyridyl)-(2-acetylphenolato)copper(II) perchlorate and determined its crystal structure and magnetic properties.



Scheme 1. Chemical diagram of the title compound.

Experimental Section

Preparation

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Even small amounts of material should be handled with caution.

For the preparation of the title compound, solutions of 0.1 mmol of 2'-hydroxyacetophenon in methanol (10 ml) and of 0.1 mmol of 2,2'-dipyridyl (20 ml) in methanol

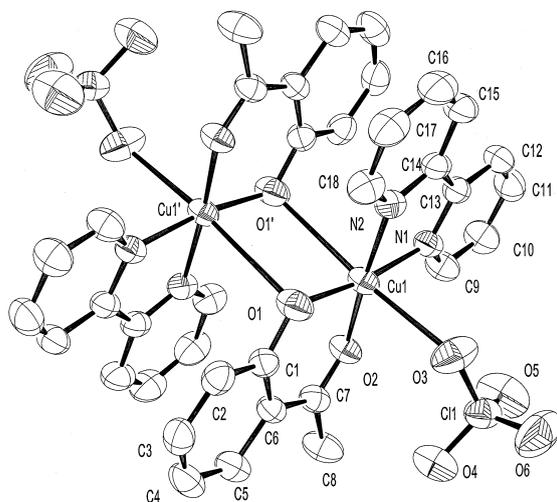


Fig. 1. View of the dimeric unit of the title compound (symmetric code: (') $-x, -y, -z$). Displacement ellipsoids are plotted at the 50% probability level [10]. H atoms have been omitted for clarity.

were added to a solution of 0.1 mmol of copper(II) perchlorate hexahydrate in methanol (25 ml). Ammonia (10 ml) was added into the solution. The mixture was stirred and prism dark green crystals were collected and washed with methanol.

Physical measurements

The EPR spectra were obtained in X-band using a Bruker ER 200D-SRC. Magnetic susceptibility measurements of powdered sample were performed on a Faraday-type magnetometer consisting of a CAHN D-200 microbalance, a Leybold Heraeus VNK 300 helium flux crystal and a Bruker BE 25 magnet connected with a Bruker B-Mn 200/60 power supply in the temperature range 70 - 300 K. Details of the apparatus have already been described [5]. Diamagnetic corrections of the molar magnetic susceptibility of the compound were applied using Pascal's constants [6]. The applied field was ≈ 1.2 T. Magnetic moments were obtained from the relation $\mu_{\text{eff}} = 2.828 (\chi T)^{1/2}$.

X-ray structure determination

X-ray data collections were carried out on an Enraf-Nonius CAD-4 diffractometer using a single crystal with dimensions $0.30 \times 0.30 \times 0.10$ mm³ with graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å). Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [7]. The structures were solved

Table 1. Crystallographic data for the title compound.

Formula	C ₁₈ H ₁₅ ClCuN ₂ O ₆
f_w (g·mol ⁻¹)	454.31
Space group	<i>P2₁/c</i> (No. 14)
	$a = 9.6999(9)$ Å
	$b = 10.496(2)$ Å
	$c = 17.670(3)$ Å
	$\beta = 96.560(10)^\circ$
Vol [Å ³]	1787.2(5)
Z	4
D_{calc} (g·cm ⁻³)	1.688
μ [cm ⁻¹]	1.412
$F(000)$	924
Index ranges	$-11 \leq h \leq 5$ $-12 \leq k \leq 0$ $-21 \leq l \leq 21$
Reflections collected	5549
Independent reflections	3492 [$R(\text{int}) = 0.023$]
Data / restraints / parameters	3492 / 0 / 254
Goodness-of-fit on F^2	0.88
R indices for all data	$R = 0.052$, $wR = 0.095$
Final R indices [$I > 2\sigma(I)$]	$R = 0.028$, $wR = 0.082$
Largest diff. peak and hole	0.32 and -0.30 e·Å ⁻³

by SHELXS-97 [8] and refined with SHELXL-97 [9]. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å), and refined using a riding model, and H atom displacement parameters were restricted to be 1.2 U_{eq} of the parent atom. The crystal structure of the title compound is illustrated in Fig. 1 [10] and experimental conditions are summarized in Table 1. Selected bond distances and bond angles are listed in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-182898 [11].

Results and Discussion

As shown in Fig. 1, the crystal structure of the title compound can be described as consisting of dimeric units: Cu-O1 bond of 3.019(2) Å links the two monomeric units to form the binuclear complex. This related distance in the similar dimeric Cu(II) complex [(Cu(dp)(sal))ClO₄; sal: salicylaldehyde and dp: di-2-pyridyl] is 2.690(3) Å [12]. The Cu...Cu separations are 3.446(1) Å. The coordination sphere of the Cu atom can be described as an elongated octahedron because of Jahn-Teller effect [13], the basal plane being formed by the two N atoms of the 2,2'-dipyridyl molecule and by the two O atoms of the acetophenon ligand. The copper atom is located in this equatorial plane of the octahedron. The axial

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

Atom	x	y	z	$U(\text{eq})$
C1	-0.0870(3)	-0.0609(2)	-0.1456(1)	0.0400(5)
C2	-0.0119(3)	-0.1289(3)	-0.1960(2)	0.0475(6)
C3	-0.0747(3)	-0.2202(3)	-0.2437(2)	0.0531(7)
C4	-0.2153(4)	-0.2461(3)	-0.2447(2)	0.0568(7)
C5	-0.2923(3)	-0.1774(3)	-0.1998(1)	0.0490(6)
C6	-0.2313(3)	-0.0832(2)	-0.1488(1)	0.0374(5)
C7	-0.3182(3)	-0.0159(2)	-0.1010(1)	0.0400(5)
C8	-0.4712(3)	-0.0356(3)	-0.1092(2)	0.0600(8)
C9	-0.2696(3)	-0.2755(3)	-0.0635(2)	0.0492(6)
C10	-0.2964(3)	-0.3611(3)	-0.1185(2)	0.0559(7)
C11	-0.1938(3)	-0.4435(3)	-0.1468(2)	0.0576(7)
C12	-0.0669(3)	-0.4391(3)	-0.1191(2)	0.0493(6)
C13	-0.0453(3)	-0.3490(2)	-0.0643(1)	0.0387(5)
C14	-0.0873(2)	-0.3304(2)	-0.0320(1)	0.0402(6)
C15	-0.2045(3)	-0.4033(3)	-0.0515(2)	0.0545(7)
C16	-0.3214(3)	-0.3783(3)	-0.0163(2)	0.0625(9)
C17	-0.3197(3)	-0.2825(3)	-0.0356(2)	0.0593(8)
C18	-0.2002(3)	-0.2110(3)	-0.0521(2)	0.0501(7)
N1	-0.1458(2)	-0.2681(2)	-0.0371(1)	0.0382(4)
N2	-0.0860(2)	-0.2354(2)	-0.0190(1)	0.0387(5)
O1	-0.0166(2)	-0.0189(2)	0.0983(1)	0.0527(5)
O2	-0.2724(2)	-0.0613(2)	0.0501(1)	0.0433(4)
O3	-0.1855(2)	-0.2927(3)	0.1435(1)	0.0715(7)
O4	-0.3857(3)	-0.2083(3)	0.2127(2)	0.0946(9)
O5	-0.4021(3)	-0.3527(3)	0.1160(2)	0.0946(9)
O6	-0.3207(3)	-0.4184(3)	0.2282(2)	0.0997(1)
Cu1	-0.09216(3)	-0.14100(3)	0.03750(2)	0.0389(1)
C11	-0.32547(7)	-0.31798(7)	0.17619(4)	0.0513(2)

positions of the elongated octahedron are occupied by the oxygen atoms from a perchlorate anion and a phenoxo group. The larger axial Cu-O3 distance is 2.544(2) Å.

The two planar parts (acetophenone and 2,2'-dipyridyl) of the title complex in the basal plane are inclined at an angle of 9.01(9)°. Other relevant planes can be defined among them the chelate ring formed by (N1, C13, C14, N2 and Cu1), and that formed by acetophenon moiety (O1, C1, C7, O2 and Cu1). Both are only slightly distorted (r.m.s. deviations to the fitted atoms are 0.011 and 0.101 Å). Being six-membered, the acetophenon-copper ring is expected to have a greater distortion but, when the sixth member in this ring is included (O1, C1, C6, C7, O2 and Cu1), the r.m.s. deviation remains almost the same, at 0.109 Å. This can be ascribed to ring aromaticity.

Table 3. Selected bond lengths [Å] and angles [°] for the title compound (symmetry code: (') $-x, -y, -z$).

N1-Cu1	1.986(2)	N2-Cu1	1.987(2)
O1-Cu1	1.875(2)	O2-Cu1	1.928(2)
O3-Cu1	2.544(2)	O1'-Cu1	3.019(2)
O1-Cu1-O2	192.63(8)	O1-Cu1-N1	171.46(8)
O2-Cu1-N1	193.73(8)	O1-Cu1-N2	192.63(8)
O2-Cu1-N2	174.74(8)	N1-Cu1-N2	181.06(9)
O1'-Cu1-O1	187.24(8)	Cu1'-O1-Cu1	192.76(4)
O1'-Cu1-O2	194.60(8)	O1'-Cu1-N1	185.86(9)
O1'-Cu1-N2	185.87(9)		

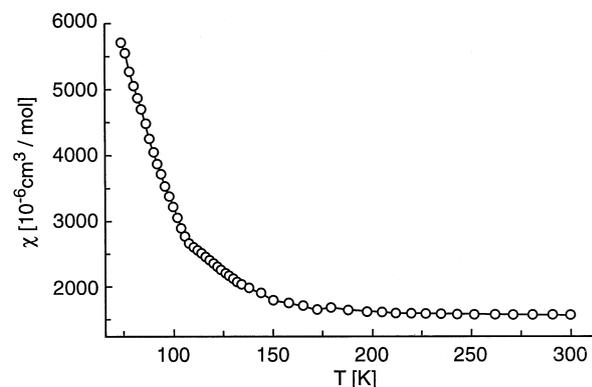


Fig. 2. Molar susceptibility per copper(II) vs. temperature curve for the investigated complex.

Bond distances and angles within the 2,2'-dipyridyl and acetophenon ligands are normal.

Magnetic susceptibility data of poly-crystalline samples of the title compound between 70 and 300 K obey the Curie-Weiss law $\chi = C/(T - \Theta)$, with $C = 0.5 \text{ emu K mol}^{-1}$ and $\Theta = -8.1(2) \text{ K}$. The decreasing of the effective magnetic moment from 1.94(8) μ_B at 300 K to 1.86(8) μ_B at 70 K and the negative Weiss constant indicate weak antiferromagnetic interactions between the two copper atoms in the dimeric unit. Similar behavior has been found in other dimeric copper(II) complexes [14 - 16].

The EPR spectrum obtained for polycrystalline samples at room temperature show axial symmetry with $g_{\perp} = 2.04$, $g_{\parallel} = 2.22$. The values of $2.0 \leq g_{\perp} \leq g_{\parallel}$ suggested that the ground state of the dimer was $d_{x^2-y^2}$ and the coordination geometry was octahedral or square pyramidal [17]. The forbidden transition $\Delta m_s = \pm 2$ was also observed in the $g = 4$ region, which indicated that the complex was dimeric.

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