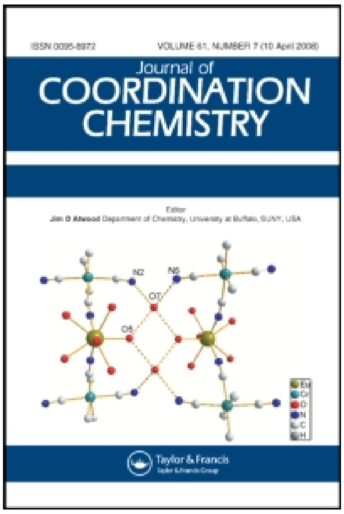

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Synthesis, crystal structure and magnetic susceptibility of a novel binuclear complex: $[Cu_2(phen)_2(4,4'\text{-}dpy)_3(OH)_2]\cdot 2NO_3\cdot 5.5H_2O$

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Synthesis, crystal structure and magnetic susceptibility of a novel binuclear complex: $[Cu_2(phen)_2(4,4'\text{-dpy})_3(OH)_2]\cdot 2NO_3\cdot 5.5H_2O$

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A new binuclear Cu(II) complex: $[Cu_2(phen)_2(4,4'\text{-dpy})_3(OH)_2]\cdot 2NO_3\cdot 5.5H_2O$ (phen = 1,10-phenanthroline and 4,4′-dpy = 4,4′-dipyridine) **1** has been prepared and determined by single X-ray diffraction. The two Cu^{2+} ions are bridged by a 4,4′-dpy ligand. The intramolecular coupling between the two Cu^{II} ($S = 1/2$) ions was found to be weakly antiferromagnetic ($J = -0.38\,cm^{-1}$).

Keywords: Binuclear copper; Crystal structure; Magnetic property; Phenanthroline; 4,4′-Dipyridine

1. Introduction

Planar bidenate diimines such as pyridazine substituted derivatives, pyrazine, 4,4′-dipyridine, *trans*-1,2-bis(4-pyridyl)ethene are useful as bridging ligands for the design and synthesis of discrete multinuclear [1–4] and polymeric [1, 2, 5–13] complexes. These simple ligands for metal complexes are chosen not only as rods to form extended solids with diverse topologies, but also for their capability of mediating strong intramolecular interactions [14]. By selecting the geometry of these ligands and metal ions, the topology of the resultant polymeric network can be tuned. Cu(II)-containing polymers have shown a wide application in topology and crystal engineering [5–13], molecular magnets [14, 15], as well as their potential utility in host–guest chemistry, ion exchange, molecular sieves and catalysis [7, 10]. Although 4,4′-dpy is well known

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as a bridge ligand for transition-metal ions, structurally characterized 4,4′-dpy-bridged binuclear transition metal complexes are still rare [1–4]. In this article, we report the synthesis, crystal structure and magnetic susceptibility of a novel binuclear Cu (II) complex **1**.

2. Experimental

2.1. *Physical measurements*

Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C elemental analyser. The IR spectra were recorded on a VECTOR 22 spectrophotometer with KBr discs, in the 4000–400 cm^{-1} region. The unit cell parameters and data were collected at 293 K on a Bruker Smart Apex CCD diffractometer. Variable-temperature magnetic susceptibilities of ground crystals were measured with a Quantum Design SQUID MPMS-XL magnetometer in the range 2–300 K. Diamagnetic corrections were made with Pascal's constants as -648×10^{-6} emu mol^{-1} for **1**, and the temperature-independent paramagnetism estimated at 60×10^{-6} emu mol^{-1}. Our analyses did not include zero field splitting.

2.2. *Synthesis of complex 1*

All chemicals were purchased from commercial sources and used as received. 1,10-phenanthroline (0.396 g, 2 mmol) in 15 mL of methanol was added dropwise to a stirred solution of Cu(II) nitrate trihydrate (0.483 g, 2 mmol) in 5 mL of water (pH = 8). To this solution, a solution of 4,4′-dipyridine (0.469 g, 3 mmol) in 10 mL of methanol was added slowly, and the resulting blue precipitates were filtered, redissolved in DMF solvent and allowed to stand for several weeks. Blue block single crystals of **1** suitable for X-ray crystallographic analysis were obtained (yield *c.* 75%). Anal. Calcd for $C_{54}H_{42}N_{12}O_8Cu_2$ (%): C, 58.22; H, 3.77; N, 15.09. Found: C, 58.01; H, 3.89; N, 15.37. IR (cm^{-1}): 3446s, 3040m, 1958w, 1598s, 1516s, 1492s, 1432s, 1384s, 1223s, 1103s, 994s, 849s, 810s, 782m, 722s, 646s.

2.3. *Crystal structure determination and refinement*

A single crystal of complex **1** was carefully selected and glued to a thin glass fibre with adhesive. The unit cell parameters and data were collected at 293 K on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using the ω–2θ scan mode. The data were corrected for Lorenz and polarization effects.

The structure was solved by Patterson methods and refined on F^2 by full-matrix least-squares methods using SHELXTL-2000. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as riding on their attached positions. All computations were carried out on a computer using the SHELXTL-2000 program package [16]. Crystallographic data for complex **1** are summarized in table 1.

CCDC-243799 for **1** contains the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Table 1. Crystal data and structure refinement for compound **1**.

Complex	$[Cu_2(phen)_2(4,4'\text{-dpy})_3(OH)_2]\cdot 2NO_3\cdot 5.5H_2O$
Formula	$C_{54}H_{53}Cu_2N_{12}O_{13.5}$
Formula weight	1213.16
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	19.594(4)
b (Å)	44.022(9)
c (Å)	7.4039(15)
V (Å^3), Z	6137(2), 4
β (°)	106.075(4)
D_{calc} (g cm^{-3})	1.313
$F(000)$	2508
Crystal size (mm)	0.20 × 0.20 × 0.30
μ (Mo Kα) (mm^{-1})	0.762
λ (Å)	0.71073
θ (°)	1.8–26.0
Reflections collected	16 562
Independent reflections	6011 [$R_{int} = 0.054$]
Reflections observed [$I > 2.0\sigma(I)$]	4327
Parameters	397
Goodness of fit	1.01
R_1, wR_2	0.0619, 0.1495
Largest difference peak and hole (e Å^{-3})	0.31, −0.69

Note: $w = [\sigma^2(F_o^2) + (0.0800P)^2 + 1.8800P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

Fax: +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk). Structure factor data are available from the authors upon request.

3. Results and discussion

3.1. *Crystal structure of complex 1*

The structure of the binuclear Cu(II) complex is shown in figure 1 as a perspective view of the dicopper entity with the atomic numbering scheme. Its packing diagram is shown in figure 2. The selected bond distances, angles and torsion angles for complex **1** are presented in table 2. Two Cu^{2+} ions are bridged by one 4,4′-dpy ligand to form a Cu(II) dimer. Each Cu(II) has a distorted octahedral geometry, coordinated to N1 and N2 from the phen ligand, N5 from the bridged 4,4′-dpy ligand, N3 from the terminal 4,4′-dpy ligand and O4 and O1 from the OH^- and NO_3^- anions, respectively. The four nitrogen atoms (N1, N2, N3, N5) were almost in the basal plane, whereas the O4 and O1 were in axial positions. The average Cu1–N (2.011 Å) and Cu1–O4 (2.316(3) Å) distances are in accordance with reported values [1, 14, 15]. The Cu1–O1 (2.764(3) Å) bond length is longer because NO_3^- is axial. The Cu1–Cu1A distance is 11.034 Å, slightly smaller than the reported average Cu–Cu distances (11.177 Å) [1, 14, 15]. The dihedral angle between two pyridyl planes in the bridged 4,4′-dpy ligand is 36.5°, and 18.8° in the terminal 4,4′-dpy ligand.

Through intermolecular hydrogen bonding [O4 ··· N4 (from terminal 4,4′-dpy) (2.844 Å)], a one-dimensional zigzag chain structure was formed along the *a* axis, each terminal 4,4′-dpy is almost parallel to the other (the distance between the adjacent two pyridine is about 4.00 Å), and weak π–π interactions exist between the adjacent pyridine rings.

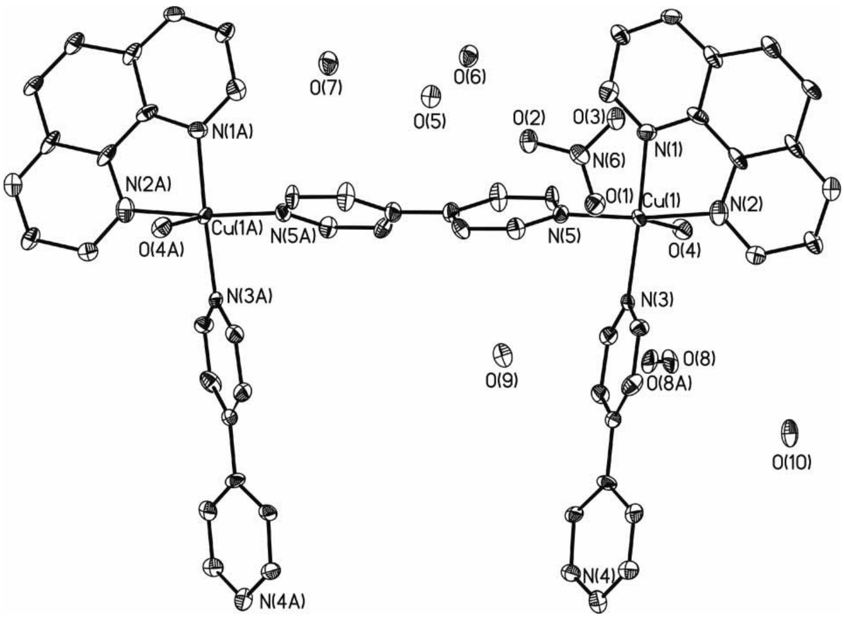

Figure 1. Perspective view of complex **1** (hydrogen atoms are omitted for clarity). Thermal ellipsoids are plotted at the 30% probability level.

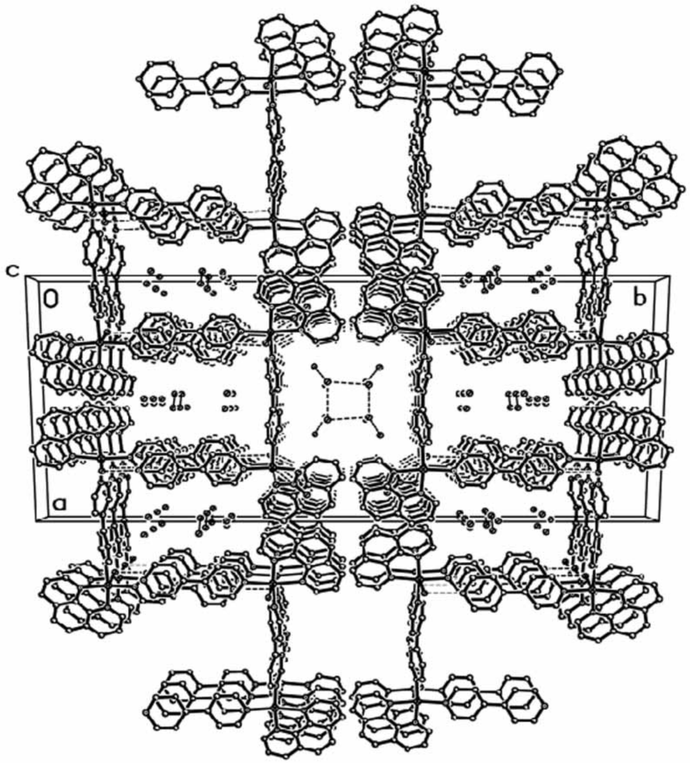

Figure 2. Perspective view of the unit cell packing down the *c* axis for complex **1**.

Table 2. Selected bond distances and angles for complex **1**.

Cu1–O1	2.764(3)	Cu1–O4	2.316(3)
Cu1–N1	2.010(3)	Cu1–N2	2.012(4)
Cu1–N3	2.014(3)	Cu1–N5	2.008(3)
O4–Cu1–N1	96.53(12)	O4–Cu1–N2	86.44(13)
O4–Cu1–N3	95.45(11)	O4–Cu1–N5	91.83(13)
N1–Cu1–N2	80.97(15)	N1–Cu1–N3	167.62(13)
N1–Cu1–N5	93.11(14)	N2–Cu1–N3	96.70(14)
N2–Cu1–N5	173.60(15)	N3–Cu1–N5	89.60(13)
N1–Cu1–N2–C10	−175.4(4)	N2–Cu1–N3–C13	47.4(3)
N3–Cu1–N2–C10	16.9(4)	N5–Cu1–N3–C13	−133.8(3)
C14–C15–C16–C17	−18.8(6)	C24–C25–C25a–C24a	−143.5(4)
N2–C11–C12–N1	−3.1(5)		

Note: $a = 2 - x$, y, $(3/2) - z$.

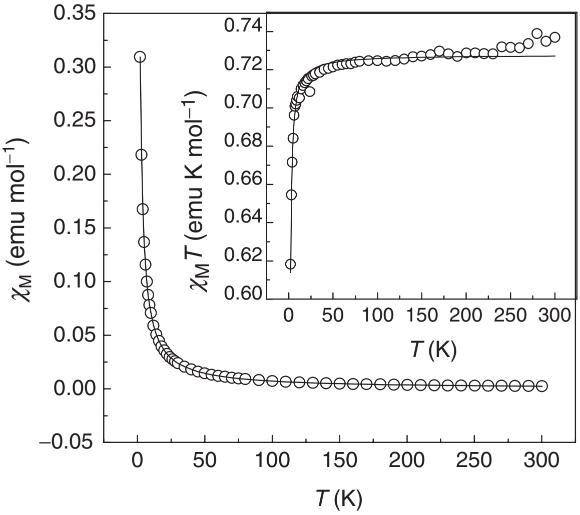

Figure 3. Thermal variation of χ_m for **1**. The solid line corresponds to the best theoretical fit, and the inserts show the thermal dependence of $\chi_m T$.

3.2. *Magnetic properties*

The variable temperature magnetic susceptibility was measured with a Quantum Design SQUID MPMS-XL magnetometer using samples of ground crystals at a field of 2 kOe for **1** in the range 2–300 K.

The magnetic susceptibility χ_m and $\chi_m T$ product of the Cu_2 unit of **1** is shown in figure 3. The χ_m value increased from 0.00245 to 0.30945 emu mol^{-1} when the temperature decreased from 300 to 2 K. At room temperature, the $\chi_m T$ value is 0.73691 (2.43 μ_B) emu mol^{-1} K, which is slightly smaller than the value of 0.75 emu mol^{-1} K (2.45 μ_B) expected for two magnetically isolated copper ions ($S = 1/2$) assuming $g = 2.00$. This value remains almost constant as the temperature decreases from 300 to 24 K; below this temperature, the $\chi_m T$ rapidly decreased, perhaps due to the intermolecular antiferromagnetic interaction.

A dinuclear model of Hamiltonian $\boldsymbol{H} = -2J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$ was used to analyse the experimental data in the range from 300 to 20 K, where J denotes the intramolecular exchange interaction, and $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$ are the spin operators for each Cu(II). The susceptibility equation for dimeric Cu(II) is used according to the Bleaney–Bowers equation [17]. The best fit of the data for **1** with two interacting Cu(II) ions ($S = 1/2$) leads to $g = 2.00$, $J = -0.38\,\mathrm{cm}^{-1}$, and $R = 2 \times 10^{-5}$ ($R = \sum[(\chi_m T)_{\mathrm{obsd}} - (\chi_m T)_{\mathrm{calc}}]^2\}/\sum[(\chi_m T)^2_{\mathrm{obsd}}]$). The crystal structure shows that two copper ions are bridged by one 4,4′-dpy ligand with a Cu(II)–Cu(II) separation of 11.034 Å; the exchange interaction of the two Cu(II) ions through the 4,4′-dpy bridge should be very weak, in agreement with the magnetic result.

Acknowledgements

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