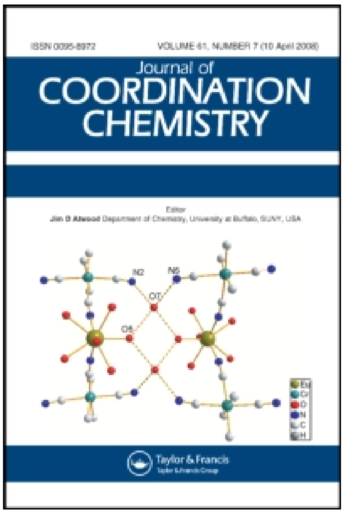

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Synthesis, Crystal Structures and Magnetic Properties of Two Methoxo-Bridged Dimeric Copper(II) Complexes [Cu $_2$(APMD)$_4$(μ$_2$-OMe) 2]X_2(APMD = 2-aminopyrimidine; X = BF$_4$ or ClO$_4$)

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SYNTHESIS, CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES OF TWO METHOXO-BRIDGED DIMERIC COPPER(II) COMPLEXES $[Cu_2(APMD)_4(\mu_2\text{-}OMe)_2]X_2$ (APMD = 2-AMINOPYRIMIDINE; $X = BF_4^-$ or ClO_4^-)

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Two bis-methoxo-bridged dimeric copper(II) complexes, $[Cu_2(OMe)_2(APMD)_4](BF_4)_2$ **1** and $[Cu_2(OMe)_2(APMD)_4](ClO_4)_2$ **2**, were prepared and characterized by x-ray single-crystal structure analysis and magnetic susceptibility. Complexes **1** and **2** are isomorphous, being composed of discrete $[Cu_2(\mu_2\text{-}OMe)_2(APMD)_4]^{2+}$ cations and anions with each Cu(II) atom ligated by two pyrimidine nitrogen atoms (Cu–N $\approx$ 2.01 Å) from two APMD ligands and two oxygen atoms (Cu–O $\approx$ 1.92 Å) from the μ_2-methoxo groups in a distorted square-planar geometry. The intramolecular metal–metal separations in the two complexes are *ca.* 2.95 Å. The intermediate antiferromagnetic exchanges ($J \approx -270\,\text{cm}^{-1}$) for the two complexes indicate a good overlap between the electronic orbitals of the square-planar copper(II) center *via* bridging oxygen atoms.

Keywords: Copper(II) complexes; 2-aminopyrimidine; Crystal structure; Magnetic susceptibility

INTRODUCTION

Polynuclear metal clusters are of current interest in the field of molecular magnetism and inorganic materials. Many homonuclear and heteronuclear clusters have been documented recently [1–20]. Particularly, a number of alkoxo-bridged di-, tetra-, or poly-nuclear copper(II) complexes [5–20] have been synthesized, the magnetism of some has been investigated. Most of these compounds are tetra- or poly-nuclear with only a few simple dinuclear complexes [10,11]. On the other hand, a good understanding of the intramolecular magnetic interactions within the complicated clusters requires a good understanding of simpler dinuclear cases [2,4]. We now report the preparation

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and crystal structures of two new dimeric complexes, $[Cu_2(\mu_2\text{-}OMe)_2(APMD)_4](BF_4)_2$ (**1**) $[Cu_2(\mu_2\text{-}OMe)_2(APMD)_4](ClO_4)_2$ (**2**), where APMD is 2-aminopyrimidine. The results show that the μ_2-methoxo-bridged Cu_2O_2 core is coplanar, with an antiferromagnetic interaction ($J \approx -270\,cm^{-1}$) within the dimer.

EXPERIMENTAL

Materials and Measurements

Solvents and reagents were used as obtained without further purification. C, H and N elemental analyses were performed on a Perkin-Elmer elemental analyzer. The variable temperature magnetic susceptibility data were obtained on polycrystalline samples of complex **1** (0.0428 g) and **2** (0.0553 g) from 4 to 280 K in a magnetic field of 0.5 T using a SQUID magnetometer. Diamagnetic corrections were estimated from the Pascal's constants [21].

$[Cu_2(OMe)_2(APMD)_4](BF_4)_2$ (1)

An acetonitrile solution (5 mL) of $Cu(BF_4)_2$ (1 mmol, 0.238 g) was added to a methanol solution (5 mL) of 2-aminopyrimidine (APMD) (1 mmol, 0.081 g) with stirring, and then terephthalaldehyde (~0.05 g) was added. Slow diffusion of diethyl ether into the resulting solution for 24 h yielded dark blue prism crystals of complex **1** suitable for x-ray single-crystal determination, which were collected by filtration, washed with acetonitrile and methanol and dried in a vacuum desiccator over silica gel (yield 81%). Anal. calcd. for $C_{18}H_{26}B_2Cu_2F_8N_{12}O_2$ (%): C, 29.1; H, 3.5; N, 22.6. Found: C, 29.3; H, 3.6; N, 22.9.

$[Cu_2(OMe)_2(APMD)_4](ClO_4)_2$ (2)

Complex **2** was prepared by a similar procedure as described for complex **1** with $Cu(BF_4)_2$ (1 mmol, 0.238 g) replaced by $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol, 0.373 g). Yield: 85%. Anal. calcd. for $C_{18}H_{26}Cl_2Cu_2N_{12}O_{10}$ (%); C, 28.1; H, 3.4; N, 21.9. Found: C, 28.3; H, 3.6; N, 22.0.

Caution! Although no problems were encountered in the preparation of the perchlorate salt, care should be taken when handing such potentially hazardous compounds.

X-Ray Crystallography

Diffraction intensities for complexes **1** and **2** were collected at 293(2) K on a Siemens R3m diffractometer using MoKα radiation ($\lambda = 0.71073$ Å). Lorentz-polarized and absorption corrections were applied [22]. The structure solutions and full-matrix least-squares refinements based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packages, respectively [23,24]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically and allowed to ride on their parent carbon and nitrogen atoms. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [25]. The crystallographic data for **1** and **2** are summarized in

Table I. The non-hydrogen atomic coordinates and selected bond lengths and bond angles for the complexes are presented in Tables II and III, respectively. Additional crystallographic data are available as supplementary data.

RESULTS AND DISCUSSION

Preparations

Complexes **1** and **2** were prepared by reacting copper (II) tetrafluoroborate or perchlorate with 2-aminopyrimidine in a mixed methanol–acetonitrile solution in the presence of tere- or iso-phthalaldehyde. Although the aldehydes were added for condensation with the amine, reaction did not occur. This observation may be attributed to the conjugation effect of the amine group with the aromatic pyrimidine ring. Interestingly, we were not able to isolate the products in the absence of the phthalaldehyde, which may influence the solubility of the products. The shiny crystals of these two complexes turn viscous when exposed to air.

Crystal Structures

The crystallographic study reveals that complexes **1** and **2** are isomorphous, composed of discrete $[Cu_2(\mu_2\text{-}OMe)_2(APMD)_4]^{2+}$ cations and uncoordinated anions. The molecular structure of the dimeric cation is shown in Fig. 1. The cation possesses $2/m$ site symmetry, in which each copper(II) atom is ligated by two nitrogen atoms from two APMD ligands (Cu–N = 2.009(3) and 2.014(3) Å for **1** and **2**, respectively) and two oxygen atoms (1.919(2) and 1.928(2) Å for **1** and **2**, respectively) from the μ_2-methoxo groups to furnish a distorted square-planar geometry with the most distorted angle being O(1)–Cu–O(1a) at 79.7(2)° and 80.1(1)° for complexes **1** and **2**, respectively. These angles are compatible with those found in similar μ_2-methoxo-bridged complexes

TABLE I Crystal data and structure refinement parameters for complexes **1** and **2**

	1	2
Formula	$C_{18}H_{26}B_2Cu_2F_8N_{12}O_2$	$C_{18}H_{26}Cl_2Cu_2N_{12}O_{10}$
Formula weight	743.21	768.48
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/m$
a, Å	16.338 (6)	16.466 (5)
b, Å	14.704 (2)	14.969 (5)
c, Å	12.040 (4)	12.003 (4)
β, °	132.34 (1)	132.40 (1)
V (Å^3)	2138 (1)	2185 (1)
Z	2	2
D_{calc}, g cm^{-3}	1.154	1.168
μ (Mo-Kα), cm^{-1}	1.058	1.144
$F(000)$	748	780
Reflections collected	3033	5805
Independent reflections	2938 [$R_{int} = 0.0322$]	3012 [$R_{int} = 0.0471$]
No. of parameters refined	108	109
Goodness-of-fit	1.049	1.071
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0656$; $wR_2 = 0.1930$	$R_1 = 0.0564$; $wR_2 = 0.1752$
R indices (all data)	$R_1 = 0.0918$; $wR_2 = 0.2181$	$R_1 = 0.0833$; $wR_2 = 0.1929$
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, eÅ^{-3}	1.112, −0.611	0.587, −0.593

TABLE II Fractional atomic coordinates and isotropic thermal parameters ($Å^2 \times 10^3$) for complexes **1** and **2**

Atom	x/a	y/b	Z/c	U_{eq}^{a}
$[Cu_2(OMe)_2(APMD)_4](BF_4)_2$ (**1**)				
Cu(1)	0	1002 (1)	0	42 (1)
O(1)	970 (3)	0	1194 (4)	44 (1)
C(5)	2122 (5)	0	2009 (8)	65 (2)
N(1)	1161 (3)	1969 (2)	1243 (4)	51 (1)
N(2)	1489 (4)	1672 (3)	3382 (4)	80 (1)
N(3)	2421 (4)	2854 (3)	3457 (4)	72 (1)
C(1)	1688 (4)	2154 (3)	2687 (5)	56 (1)
C(2)	2643 (5)	3335 (4)	2772 (6)	78 (2)
C(3)	2176 (6)	3167 (4)	1331 (7)	85 (2)
C(4)	1412 (5)	2485 (3)	585 (5)	68 (1)
B(1)	629 (4)	0	−2230 (5)	25 (1)
F(1)	−459 (5)	0	−3604 (6)	99 (2)
F(2)	1388 (6)	0	−2372 (9)	111 (2)
F(3)	768 (3)	785 (2)	−1430 (4)	73(1)
$[Cu_2(OMe)_2(APMD)_4](ClO_4)_2$ (**2**)				
Cu(1)	0	986 (1)	0	45 (1)
O(1)	253 (3)	0	1233 (3)	44 (1)
C(1)	−68 (6)	0	2070 (7)	72 (2)
N(1)	91 (3)	1942 (2)	1260 (3)	54 (1)
N(2)	1056 (3)	2834 (3)	3479 (4)	75 (1)
N(3)	1891 (3)	1657 (3)	3410 (4)	80 (1)
C(2)	993 (3)	2145 (3)	2691 (4)	57 (1)
C(3)	−812 (4)	2451 (3)	603 (5)	71 (1)
C(4)	−832 (4)	3126 (4)	1353 (6)	88 (2)
C(5)	145 (4)	3303 (3)	2810 (5)	82 (2)
Cl(1)	2143 (1)	5000	7802 (2)	58 (1)
O(2)	2793 (3)	4216 (2)	8604 (4)	70 (1)
O(3)	1852 (5)	5000	6370 (6)	92 (2)
O(4)	1221 (4)	5000	7670 (8)	101 (2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Selected bond lengths (Å) and bond angles (°) for complexes **1** and **2**

	1	2
Cu(1)–O(1)	1.917 (2)	1.926 (2)
Cu(1)–N(1)	2.009 (3)	2.013 (3)
Cu(1)···Cu(1a)	2.945 (1)	2.951 (1)
O(1a)–Cu(1)–O(1)	79.7 (2)	80.0 (1)
O(1a)–Cu(1)–N(1)	172.2 (1)	171.9 (1)
O(1)–Cu(1)–N(1)	95.6 (1)	95.7 (1)
O(1)–Cu(1)–N(1b)	172.2 (1)	171.9 (1)
N(1)–Cu(1)–N(1b)	89.9 (2)	89.4 (2)
Cu(1)–O(1)–Cu(1a)	100.4 (2)	100.0 (1)

Symmetry codes: (a) $-x, -y, -z$; (b) $-x, y, -z$

such as $[\{CuLn(\mu_2\text{-}OMe)(chp)_2(NO_3)_2(MeOH)_2\}_2]$ (chp = 6-chloro-2-pyridonate) (81.4 ~ 82.7°) [6] $[Ln_2Cu_2(\mu_2\text{-}OMe)_2(mhp)_4(NO_3)_4(Hmhp)_2(MeOH)_2]$ (Hmhp = 6-methyl-2-pyridone) (81.1 ~ 82.4°) [7], $[\{Cu_4(\mu_2\text{-}OMe)_4(fhp)_4\}_n]$ (fhp = 6-fluoro-2-pyridonate) (75.3°) [8] and $[Cu_2(tbz)_2(\mu_2\text{-}OMe)](ClO_4)_2(MeOH)_2$ (tbz = bis(2-benzimidazolyl)propane) (77.1°) [9]. A pair of Cu (II) atoms are bridged by a pair of μ_2-methoxo groups into a dimeric structure with the metal–metal separations of 2.954(1) and 2.951(1) Å for complexes **1** and **2**, respectively, which are also comparable to those reported in the literature [9,10]. The Cu–O(OMe) bond lengths for complexes **1** and **2**

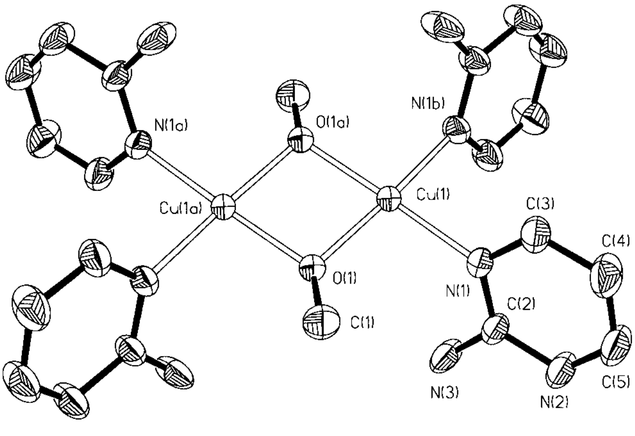

FIGURE 1 An Ortep view of the dimeric cation in complex **1**.

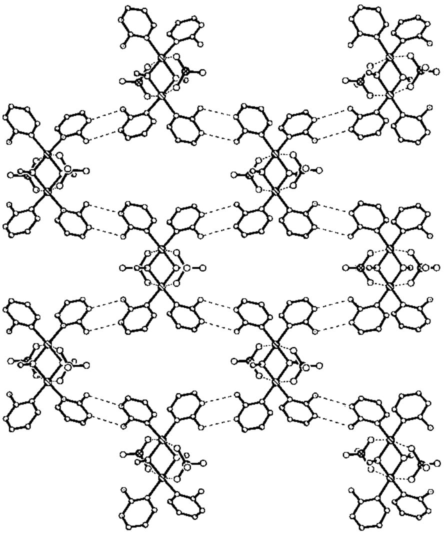

FIGURE 2 A perspective view of the two-dimensional network of complex **1** showing the weak interactions.

are comparable to those found in [{($C_{10}H_{14}N_2$)CuBr(μ-OMe)}$_4$(MeOH)] (Cu–O ≈1.912 Å) [10]. Due to the imposed molecular symmetry, the Cu_2O_2 rhomb is coplanar with the Cu–O–Cu angle of *ca.* 100° for both complexes **1** and **2**, being in the normal range for similar bis-methoxo-bridged di-copper(II) complexes [9,10].

Weak interactions play an important role in the crystal structures of complexes **1** and **2**. As shown in Fig. 2, each anion has two Cu···F (2.748 (2) Å) or Cu···O (2.809 (2) Å) contacts at the axial positions of the metal atoms, respectively, indicating a weak interaction. More interesting is the fact that each APMD ligand forms one donor (the amino group) and one acceptor (the uncoordinated pyrimidine nitrogen atom) hydrogen bond with (N···N = 3.002 Å for **1** and 2.988 Å for **2**) an adjacent molecule, thus generating a two-dimensional brickwall network in the solid state (Fig. 2).

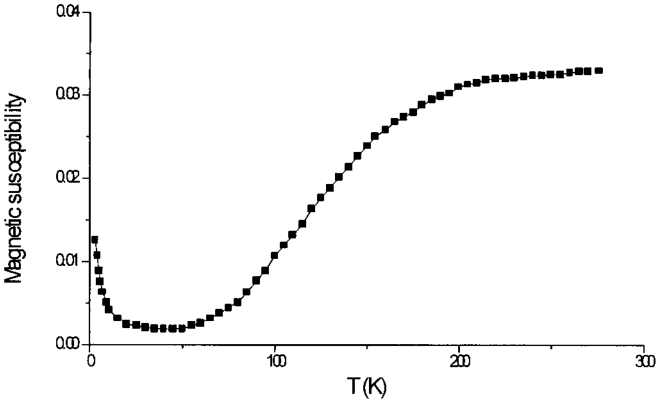

FIGURE 3 Temperature-dependent molar magnetic susceptibility of a powdered sample of complex **1**.

Magnetic Susceptibility

Complexes **1** and **2** have very similar magnetic behavior. The magnetic data of complex **1** are shown in Fig. 3. The molar susceptibility is increased with increasing temperature and reaches a maximum above room temperature, which is characteristic of an antiferromagnetic exchange coupled system. The abrupt rise in susceptibility at low temperature is attributed to a small amount of paramagnetic impurity. The magnetic susceptibility data for the two complexes were fitted with the Bleaney–Bowers equation (Eq. 1) [26] using the isotropic (Heisenberg) exchange Hamiltonian ($H = -2JS_1 \cdot S_2$) for two interacting $S = 1/2$ centers (χ_m is expressed per mole of copper atoms, $N\alpha$ is the temperature-independent paramagnetism, ρ is the fraction of monomeric impurity, and θ is a corrective, Weiss-like term to account for possible intermolecular magnetic associations [27, 28].

$$\chi_m = [(Ng^2\beta^2)/3k(T-\theta)][1+\{\exp(-2J/kT)\}/3]^{-1}(1-\rho) + (Ng^2\beta^2)\rho/4kT + N\alpha \qquad (1)$$

A good fit of the nonlinear regression analysis for the data for complex **1**, as indicated by the solid curve in Fig. 3, was achieved with $g = 2.055$, $J = -275\,\mathrm{cm}^{-1}$, $\rho = 0.0010$, $N\alpha = 61 \times 10^{-6}$ cgsu, $\theta = 0.2$ K and $R = 0.0098$ ($R = [\sum(\chi_{\mathrm{obs}} - \chi_{\mathrm{calc}})^2/\sum(\chi_{\mathrm{obs}})^2]^{1/2}$). A similar fitting for complex **2** shows a similar antiferromagnetic exchange with $g = 2.055$, $J = -268\,\mathrm{cm}^{-1}$, $\rho = 0.0030$, $N\alpha = 60 \times 10^{-6}$ cgsu, $\theta = 0.2$ K and $R = 0.0096$). The intermediate antiferromagnetic exchanges for the two complexes are expected [25] for an alkoxo-bridged complex with a Cu–O–Cu angle of *ca.* 100°, indicating good overlap between the electronic orbitals of the square-planar copper(II) center *via* bridging oxygen atoms.

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Supplementary Material

Tables of x-ray crystallographic data in CIF format for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 146000 and 146001. Copies of the available material can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (E-mail: deposit@ccdc.cam.ac.uk).

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