

Synthesis, Structure and Magnetic Properties of a Diphenoxo-bridged Binuclear Copper(II) Complex

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A mixed-ligand copper(II) complex $[\text{Cu}_2(\text{phen})_2(\text{HL}^1)_2](\text{ClO}_4)_2$ (**1**) was synthesized. X-ray analyses reveal that **1** has a bis(μ_2 -phenoxo)-bridged dicopper(II) structure. 2D hydrogen-bonded network is formed utilizing the N—H, O—H and C—H groups of the $(\text{HL}^1)^+$ ligands ($\text{H}_2\text{L}^1 = N$ -(2-hydroxybenzyl)ethanolamine), the C—H groups of the phenanthrolines and the perchlorate anions. Variable temperature magnetic properties of **1** have shown comparatively weak anti-ferromagnetic interactions with respect to the bridge angles, which have been ascribed to the unfavorable overlaps of the magnetic orbitals for the highly distorted copper coordination polyhedra and the pyramidal distortions at the phenoxo oxygen atoms.

Keywords magnetic properties, hydrogen bond, binuclear copper(II) complex, 2D network

Introduction

Exchange-coupled polynuclear copper(II) complexes are of special interest due to their involvement in biological processes and in inorganic materials.^{1,2} The intimate relationship between the spin coupling and the molecular structure has fostered the emergence of molecular magnetism² as a multidisciplinary field.

The crystal engineering of metal coordination supramolecules is another active research topic of current chemistry due to their potential applications in catalysis, host-guest chemistry and molecular electronics.³⁻⁵ The combination of metal ions with ordered hydrogen-bonding to

build various networks has caused growing interest.^{6,7}

We have reported a 2D hydrogen-bonded coordination network complex $[\text{CuHL}^1]_2$ and a tetranuclear complex with a cubane Cu_4O_4 core structure starting from flexible tridentate ligands *N*-(2-hydroxybenzyl)ethanolamine $(\text{H}_2\text{L}^1)^8$ and *N*-(2-hydroxybenzyl)propanolamine $(\text{H}_2\text{L}^2),^9$ respectively. Herein, a mixed-ligand binuclear complex $[\text{Cu}_2(\text{phen})_2(\text{HL}^1)_2](\text{ClO}_4)_2$ (**1**) is reported. The magnetic exchange coupling between the Cu(II) centers for **1** has been studied.

Experimental

Instruments and reagents

Variable-temperature magnetic studies on **1** have been carried out on a Quantum Design MPMS7 SQUID magnetometer in a magnetic field of 1.0 T. The corrections for the diamagnetism of the complexes were estimated from the Pascal's constants, a value of $60 \times 10^{-6} \text{ cm}^3/\text{mol}$ was used for the temperature independent paramagnetism (TIP) of the Cu(II) ion.

Synthesis

$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.296 g, 0.80 mmol), $\text{H}_2\text{L}^1 \cdot \text{HCl} \cdot 1.5\text{H}_2\text{O}$ (0.178 g, 0.80 mmol), 4.0 mol/L, NaOH (0.40 mL, 1.6 mmol) and phenanthroline $\cdot \text{H}_2\text{O}$ (0.159

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g, 0.80 mmol) were added to 100 mL of methanol. The resulting solution was refluxed for 3 h, and concentrated *in vacuo* to ca. 20 mL. The precipitate was filtered off and the solution was left at room temperature for a few days to afford dark green crystals of **1**. Yield 0.164 g (40.2%); IR (KBr) ν : 3247m (NH), 1593, 1479s, 1455m, 1429s, 1266s (Ar-O), 1244m, 1104s (ClO₄⁻), 1035m, 771s, 724s, 624s (ClO₄⁻) cm⁻¹; Anal. calcd for C₄₂H₄₀Cl₂Cu₂N₆O₁₂: C 49.52, H 3.96, N 8.25; found C 49.81, H 4.12, N 8.18.

Structural determination

A single crystal of **1** was mounted on a glass-fiber. All measurements were made on a Rigaku RAXIS-IV image plate area detector with graphite monochromated Mo-K α radiation. The data were collected at 18 °C and corrected for Lorentz and polarization effects. Correction for secondary extinction was applied. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections [$I > 2.00\sigma(I)$] and variable parameters. All calculations were performed using SHELX-97 software package.¹⁰

Crystal data for **1**: C₄₂H₄₀Cl₂Cu₂N₆O₁₂, $M_r = 1018.79$, triclinic, space group $P\bar{1}$, $a = 0.93281(19)$ nm, $b = 1.1495(2)$ nm, $c = 1.1812(2)$ nm, $\alpha = 113.77(3)^\circ$, $\beta = 104.48(3)^\circ$, $\gamma = 97.80(3)^\circ$, $V = 1.0817(4)$ nm³, $Z = 2$, $T = 291(2)$ K, $\mu(\text{Mo } K_\alpha) = 1.177$ mm⁻¹. Goodness-of-fit on F^2 was 1.087. $R_1[\text{for } I > 2\sigma(I)] = 0.0749$, $wR_2 = 0.1855$.

Results and discussion

Crystal structure

Selected bond lengths and angles for **1** are listed in Table 1. Each copper(II) atom is coordinated to one phenanthroline and one (H₂L¹)⁻ ligand, where (H₂L¹)⁻ acts in a bidentate mode, with the amino N and the phenoxo O atoms coordinated, and the alkoxy O atom is left uncoordinated, in contrast to the tridentate mode in [CuHL¹]₂.⁸ Two copper atoms are bridged by the phenoxo groups giving a diphenoxo-bridged binuclear structure (Fig. 1), containing an exactly planar Cu₂O₂ moiety owing to crystallographic inversion symmetry. The copper(II) centers are separated by 0.3147(3) nm. The Cu-O-Cu bridging angles of 100.42(13)° fall in the normal range for diphenoxo-bridged copper(II) complexes.¹¹⁻¹³ The coordination polyhedron around Cu(1) may be described as highly distorted trigonal bipyramidal (tbp). N(1), N(3) and O(1) # 1 lie in the equatorial plane, with the axial positions occupied by N(2) and O(1) atoms. Cu(1) is displaced 0.0002 nm from the equatorial plane towards O(1). The N(2)-Cu(1)-O(1) angle is 171.42(14)°, and the bond angles in the equatorial plane are 110.7(1)°, 112.9(1)° and 136.4(1)°, respectively, indicating a significant distortion towards square pyramidal (sp). The Reedijk distortion index τ ¹⁴ ($\tau = 0$ for a sp, and $\tau = 1$ for a tbp) is 0.58. The shortest and the longest coordination bond lengths around Cu(1) are 0.1930(3) nm and 0.2161(3) nm for the bridging phenoxo oxygen atoms O(1) and O(1) # 1, respectively. There are no unusual bond lengths and angles for phen. The sum of the angles at the phenoxo oxy-

Table 1 Selected bond lengths (nm) and angles (°) for **1**^a

Cu(1)—O(1)	0.1930(3)	Cu(1)—N(2)	0.2020(3)
Cu(1)—N(3)	0.2057(4)	Cu(1)—N(1)	0.2071(3)
Cu(1)—O(1A)	0.2161(3)		
N(2)-Cu(1)-O(1)	171.42(14)	O(1)-Cu(1)-N(3)	94.61(12)
N(2)-Cu(1)-N(3)	93.96(13)	O(1)-Cu(1)-N(1)	93.24(12)
N(2)-Cu(1)-N(1)	80.79(13)	N(3)-Cu(1)-N(1)	136.38(14)
O(1)-Cu(1)-O(1A)	79.58(12)	N(2)-Cu(1)-O(1A)	97.00(13)
N(3)-Cu(1)-O(1A)	110.67(13)	N(1)-Cu(1)-O(1A)	112.95(13)
Cu(1)-O(1)-Cu(1A)	100.42(13)		

^aSymmetry operation: A, $-x+2, -y+1, -z+1$.

gen is 348.1° , which is quite different from 360° , indicating a significant pyramidal distortion.

Approximately along the *bc* plane, each complex molecule is connected with four surrounding molecules by multiple hydrogen bonds¹⁵ between N—H, O—H, C—H groups of the (HL)¹⁻ ligands, C—H groups of the phen molecules and the perchlorate anions, leading to a 2D network (Fig. 2, Table 2).

Magnetic properties

A gradual decrease in $\chi_m T$ is observed as the temperature is decreased (Fig. 3), indicating an antiferromagnetic interaction between the binuclear copper(II) centers. The data were fitted to the following binuclear equation:¹²

$$\chi_m = (1 - \rho) \frac{N_A g^2 \mu_B^2}{kT} \cdot \frac{1}{3 + e^{-2J/kT}} + \rho \cdot \frac{N_A \beta^2 g^2}{4kT} + \chi_{TiP} \quad (1)$$

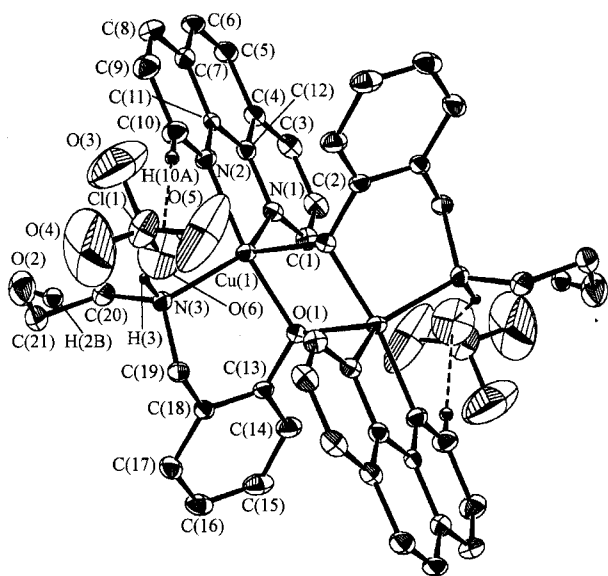


Fig. 1 View of complex 1 showing the numbering scheme at the 30% probability level with H atoms omitted for clarity.

where ρ is the molar ratio of the paramagnetic impurities, N_A is Avogadro constant, g is the Lande factor, and β is Bohr magneton. The best fit gave $2J = -226.8 \text{ cm}^{-1}$, $g = 2.144$, $\rho = 0.0169$, and $R = 1.1 \times 10^{-5}$. The $-2J$ value is much smaller than those of the complexes^{11,12} with similar bridge angles and the value expected from the empirical linear relationship¹³ of Thompson: $-2J = 31.95\phi - 2462 = 746.4 \text{ cm}^{-1}$. The comparatively weak antiferromagnetic interactions for complex 1 may be ascribed to the unfavorable overlaps of the magnetic orbitals for the highly distorted trigonal bipyramidal copper ions ($\tau = 0.58$), as compared to the distorted square pyramidal copper complexes ($\tau \leq 0.41$) reported by Thompson.¹³ Furthermore, the pyramidal distortions at the phenoxo oxygen atoms as shown by the crystal structure, also weaken the magnetic interactions between the copper atoms.^{16,17}

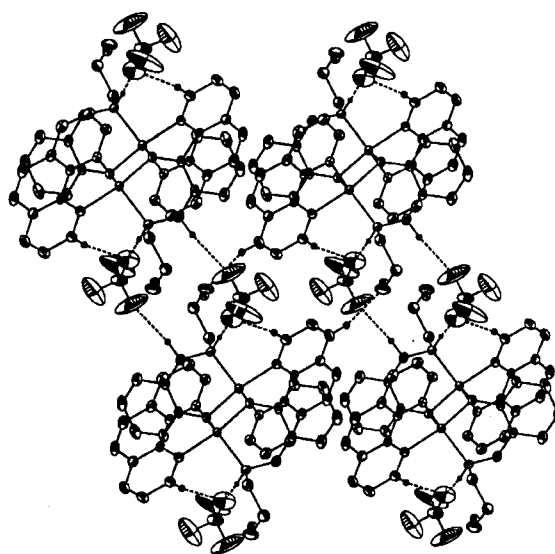


Fig. 2 2D network of complex 1 approximately along the *bc* plane.

Table 2 Hydrogen bonds for 1 (nm and $^\circ$)

D—H	<i>d</i> (H...A)	\angle DHA	<i>d</i> (D...A)	A (symmetry operations)
N(3)—H(3)	0.2421	137.62	0.3070	O(6)
C(10)—H(10A)	0.2463	164.99	0.3370	O(6)
C(8)—H(8A)	0.2461	138.87	0.3220	O(2) [$-x + 2, -y, -z$]
C(19)—H(19A)	0.2411	161.28	0.3344	O(4) [$-x + 2, 1 - y, -z$]

In conclusion, the flexible tridentate ligand H_2L^1 has been shown to form a mixed-ligand complex of $(HL^1)^-$ and phen with copper, with a bis(μ_2 -phenoxo)-bridged binuclear structure. Furthermore, **1** forms a 2D network approximately along the *bc* plane. The comparatively weak antiferromagnetic interactions with respect to the bridge angles for **1** have been ascribed to the unfavorable overlaps of the magnetic orbitals for the copper atoms with highly distorted coordination polyhedra and the phenoxo oxygen atoms with pyramidal distortions.

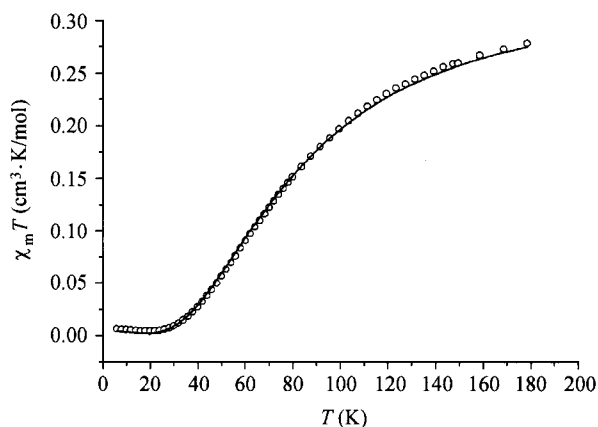


Fig. 3 Plot of the products $\chi_m T$ vs. temperature for **1**. The solid line represents the best calculated fit of the data (see text for the fitted parameters).

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The occurrence of the hydrogen bonds (D—H \cdots A) can be inferred from the atom distances. For all the listed hydrogen bonds in this work, the A \cdots H distances are at least 0.01 nm less than the van der Waals contact distances, and the A \cdots D distances are less than 0.34 nm apart.

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