Synthesis, crystal structure, and magnetism of a 1-D Cu^{II} chain complex with a mono-bromide bridge

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Synthesis, crystal structure, and magnetism of a 1-D Cu^{II} chain complex with a mono-bromide bridge

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A 1-D Cu^{II} chain, $[Cu(\mu\text{-}Br)(phenmp)_2]_n \cdot (ClO_4)_n$ (phenmp = 2-(4-methyl-pyrazol-1H-yl)-1,10-phenanthroline), was synthesized and its crystal structure was determined by X-ray crystallography. Cu^{II} is located in a distorted square-pyramidal geometry, with the mono-bromide – a bridge linking two adjacent Cu^{II} ions with a separation of 3.788 Å. The result is a uniform 1-D chain that lies along the c axis. Mono-halide-bridged models have not been reported very often. The fitting for the data of the variable-temperature (2.00–330 K) magnetic susceptibilities gave a ferromagnetic interaction of $J = 5.11$ cm^{-1} ($H = -2JS_1S_2$) for adjacent-bridged Cu^{II} ions. Comparing mono-halide bridged Cu^{II} complexes, trigonal-bipyramidal geometry has strong magnetic interactions, whereas square-pyramidal geometry has weak magnetic interactions. In mono-bromide bridged Cu^{II} complexes, the Cu–Br–Cu angle is related to the magnetic coupling signs with small Cu–Br–Cu angle favoring ferromagnetic interaction, while large Cu–Br–Cu angle results in antiferromagnetic interactions.

Keywords: Magnetism; Copper(II) complex; Crystal structure; Bromide

1. Introduction

Molecular magnetism has attracted attention and major advances have been made in both theoretical description and application as a new molecular-based materials [1–8]. There are some magneto-structural correlations that have been obtained by studying the complexes with different bridges and different co-ligands. Such complexes include those with oxalate as bridge and polyamine as co-ligands [9] as well as those with hydroxide [10], alkoxide [10], and azide [11, 12] as bridges. Complexes with halide bridges have been reported,

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especially for chloride bridges, but these mainly deal with bis-halide-bridged complexes [13, 14]. Only a few mono-halide-bridged Cu^{II} complexes have been studied [15–20], with 12 reported to date. The relevant magneto-structural correlations of these mono-halide-bridged Cu^{II} complexes are not understood. 2-(4-Methyl-pyrazol-1H-yl)-1,10-phenanthroline as shown in scheme 1 is one of these tridentate ligands and no complex with this ligand has been reported. Interest in magneto-structural correlations of bromide-bridged complex resulted in the synthesis and the magnetic study of the present 1-D Cu^{II} chain complex, and herein, we report its crystal structure and magnetism.

2. Experimental

2.1. *Materials*

2-(4-Methyl-pyrazol-1H-yl)-1,10-phenanthroline was prepared according to the following method. A flask containing 2-chloro-1,10-phenanthroline (1.07 g, 5 mM), KOH (0.56 g, 10 mM), and 4-methyl-pyrazole (2.05 g, 25 mM) was placed in a microwave oven and irradiated for 30 min at 60 °C. Then, ethanol (50 mL) was added and stirred for a few minutes. Yellowish product (1.0 g, 3.8 mM) was obtained after the insoluble component was separated from the solution and dried in vacuum. ^{1}H NMR (300 MHz, CDCl3, 24 °C, TMS): $\delta = 9.21$ (d, $J = 3$ Hz, 2H), 8.39–8.29 (m, 3H), 7.83-7.65 (m, 3H), 6.36 (s, 1H), 2.43 ppm (s, 3H); HRMS (ESI): m/z calcd for C16H12N4 + H+: 261.1134 [M+H+]; found: 261.1140.

2.2. *Synthesis of [Cu(μ-Br)(phenmp)]$_n$·(ClO$_4$)$_n$*

Water solution of NaBr (5 mL) (0.0228 g, 0.222 mM) was added slowly into a 15 mL methanol solution containing 2-(4-methyl-pyrazol-1H-yl)-1,10-phenanthroline (0.0350 g, 0.134 mM) and Cu(ClO$_4$)$_2$·6H$_2$O (0.0769 g, 0.208 mM). The mixed solution was then stirred for a few minutes and green single crystals were obtained after the filtrate was allowed to stand at room temperature for one week. Anal. Calcd for C$_{16}$H$_{12}$BrClCuN$_4$O$_4$ (Fw: 503.20): C, 38.19; H, 2.40; N, 11.13; Cu, 12.63%. Found: C, 38.39; H, 2.12; N, 11.44; Cu, 13.01%.
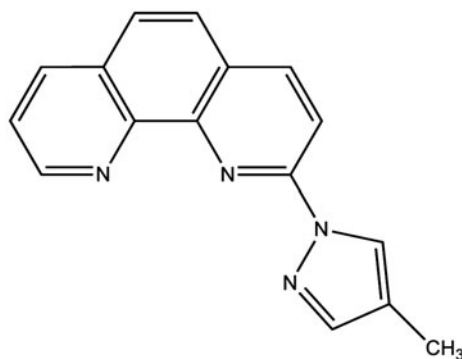
Scheme 1.   Molecular structure of 2-(4-methyl-pyrazol-1H-yl)-1,10-phenanthroline.

2.3. *Physical measurements*

C, H, and N elemental analysis were carried out on a Perkin–Elmer 240 instrument and Cu content was measured on an atomic spectrophotometer model Z-8000. Variable-temperature magnetic susceptibilities of microcrystalline powder samples were measured in a magnetic field of 1 kOe from 2.00 to 330 K on a MPMS-7SQUID magnetometer. The data were corrected for the magnetization of the sample holder and for the diamagnetic contributions which were estimated from Pascal's constants.

2.4. *X-ray crystallography*

A yellow single crystal ($0.13 \times 0.05 \times 0.03$ mm) was selected and glued on the tip of a glass fiber. The crystal structure determination was carried out at 25 °C on a X-ray diffractometer, Bruker Smart-1000 CCD, using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) in the range $4.76 < 2\theta < 51.36°$. A total of 4539 reflections were collected, of which 2389 were independent ($R_{int} = 0.044$) and 1663 observed reflections with $I > 2\sigma(I)$ were used in the structure analysis. Corrections for Lp factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens were placed in the calculated positions and refined as riding. The programs for structure solution and refinement were SHELXS-97 and SHELXTL (Bruker, 2001). The pertinent crystallographic data and structural refinement parameters are summarized in table 1.

3. Results and discussion

3.1. *Synthesis*

Addition of hydrated copper perchlorate is one of the key factors for obtaining the mono-bromide-bridged Cu^{II} complex. If the hydrated copper perchlorate is replaced with copper(II) bromide, the product is not a mono-bromide-bridged Cu^{II} complex. Using methanol as a solvent, rather than ethanol, produces superior single crystals. H_2O was used as a solvent to dissolve NaBr, resulting in more defined single crystals (the high polarity and slow evaporation rate of H_2O may contribute to this result). The mole ratio of phenmp:

Table 1. Crystal data and structural refinements for the complex.

Empirical formula	$C_{16}H_{12}BrClCuN_4O_4$
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions (Å, °)	
a	10.658(5)
b	25.615(12)
c	7.541(4)
β	121.702(6)
Volume (Å³), Z	1751.5(14), 4
Calculated density (g cm⁻³)	1.908
Absorption coefficient (mm⁻¹)	3.713
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0482$, $wR_2 = 0.0937$
Goodness-of-fit on F^2	0.926
Largest difference peak and hole (e Å⁻³)	0.705 and −0.491

Cu^{II}:Br in the reactants is $1:1.55:1.66$; the excess molar quantities of the Cu^{II} and bromide play a minor role in obtaining the desired complex.

3.2. Crystal structure

Figure 1 shows the coordination diagram with the atom numbering scheme. The data in table 2 show that the coordination bond lengths of Cu1 are 1.945(7)–2.6849(19) Å and the associated angles change from 76.8(3)° to 159.8(3)°. Cu1 is a distorted square-pyramidal geometry due to its Addison parameter $\tau = (\alpha - \beta)/60 = 0.068$ [21]. 2-(4-Methyl-pyrazol-1H-yl)-1,10-phenanthroline is a tridentate, coordinating to Cu^{II} with N1, N2, and N4. Br1 functions as an equatorial–axial bridge, resulting in the formation of a 1-D chain along the c axis as shown in figure 2. The φ angle of Cu1–Br–Cu1A is 97.21(6). In the chain, all 2-(4-methyl-pyrazol-1H-yl)-1,10-phenanthroline ligands are on the same side of the complex, while bromides are located on the other side. In contrast, terminal tridentate ligands alternate on both sides of the chain in a 1-D Cu complex [17]. In the chain, there is a pair of nonbonded atoms with interatomic distances less than those of the sum of the default contact radii [22], C2$\cdots$C15^i 3.360(17) Å (symmetry code i: x, $2-y$, $-1/2+z$), which deals with the adjacent 1,10-phenanthroline rings. Besides intra-chain molecular forces, there are inter-chain molecular forces, particularly, between H10$\cdots$Br1^{ii} at 3.01 Å (symmetry code ii: $-1+x$, $2-y$, $-1/2+z$). There are also intermolecular forces among perchlorate counter anion and adjacent complexes, specifically O1$\cdots$H11^{iii} 2.41, O2$\cdots$H3^{iv} 2.38, O2$\cdots$H16B^v 2.62, and O4$\cdots$H1^{vi} 2.62 Å (symmetry codes: iii: $1+x$, y, $1+z$; iv: $1/2+x$, $-1/2+y$, $1+z$; v: x, y, $1+z$; vi: x, $2-y$, $1/2+z$). All these intermolecular forces solidify the crystal forming a supramolecular 3-D structure.

3.3. Magnetic study

The experimental data of variable-temperature (2.00–330 K) magnetic susceptibilities are shown in figure 3, where χ_M is the molar magnetic susceptibility per binuclear Cu^{II} unit and μ_{eff} is the magnetic per binuclear Cu^{II} ion. The μ_{eff} value at 300 K is 2.70 B. M slightly larger than that of uncoupled binuclear Cu^{II} ion (2.45 B.M. for $g_{av} = 2$) at room temperature. The μ_{eff} values are nearly constant as the temperature drops to 50.0 K. Below 50.0 K, the values increase sharply as the temperature decreases reaching a maximum value of 3.95 B.M. at 2.00 K. These data indicate a ferromagnetic interaction between
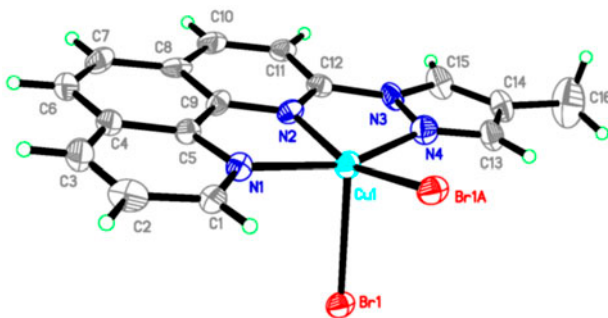

Figure 1. Representation of the molecular structure of the complex with the atom numbering scheme.

Table 2. Selected bond lengths (Å) and angles (°).

Cu1–N2	1.945(7)	Cu1–N4	2.067(7)	Cu1–N1	2.083(7)
Cu1–Br1A	2.3555(15)	Cu1–Br1	2.6849(19)		
N2–Cu1–N4	76.8(3)	N1–Cu1–Br1A	100.1(2)	N1–Cu1–Br1	95.0(2)
N2–Cu1–N1	79.8(3)	N2–Cu1–Br1	103.4(3)	Br1A–Cu1–Br1	96.75(6)
N4–Cu1–N1	155.7(4)	N4–Cu1–Br1	96.6(3)	N4–Cu1–Br1A	99.7(3)
N2–Cu1–Br1A	159.8(3)	Cu1–Br1–Cu1A	97.21(6)		

Notes: Symmetry codes: (Br1A) x, $-y+2$, $z-1/2$; (Cu1A) x, $-y+2$, $z+1/2$.
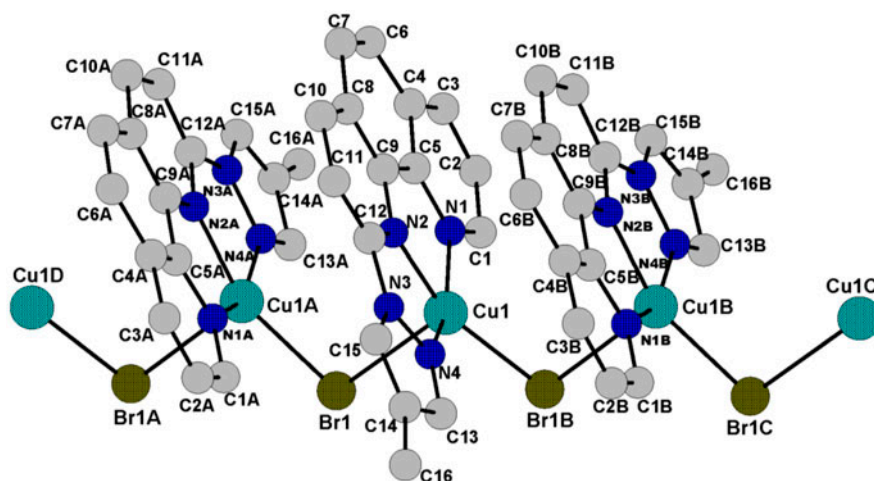

Figure 2. Uniform 1-D chain of the mono-bromide-bridged Cu^{II} complex. Hydrogens have been omitted for clarity (symmetry codes: A: x, $2-y$, $0.5+z$; B: x, $2-y$, $-0.5+z$; C: x, y, $-1+z$; D: x, y, $1+z$).
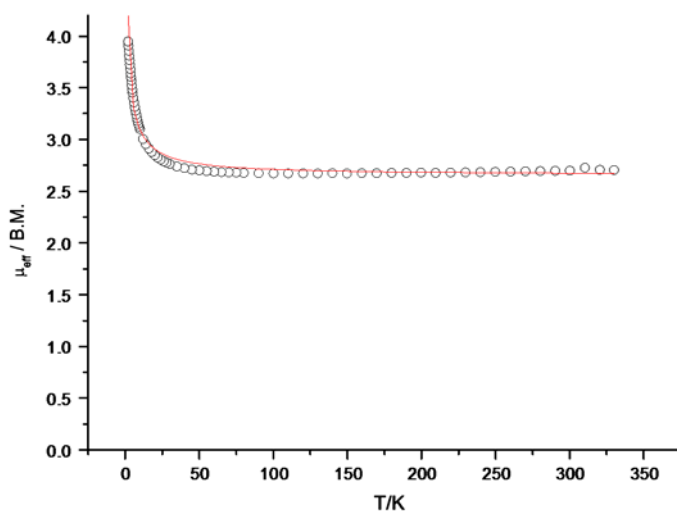

Figure 3. Plot of μ_{eff} (the open circle for the experimental data and the red curve for the fitting value) *vs* T for the Cu^{II} complex.

bridged Cu^{II} ions. The uniform 1-D Cu^{II} chain formulas [23] were first used to fit the experimental data of the variable-temperature magnetic susceptibilities, but this approach did not prove useful. Based on the isotropic Hamiltonian (1) and the modified Bleaney–Bowers equation (2) [24] for exchange-coupled binuclear Cu^{II} gave a good fit to the experimental data as shown in figure 3, where J is the Heisenberg exchange constant between the mono-bromide-bridged adjacent copper(II) ions, S_1 and S_2 are the spin operators corresponding to Cu^{II}, zJ' is the inter-binuclear-unit interaction and the temperature-independent paramagnetism (TIP) equals 1.2×10^{-6}.

$$H = -2JS_1S_2 \tag{1}$$

$$\chi = [(2Ng^2\beta^2)/(\kappa T)]\{3 + \exp[(-2J)/(\kappa T)]\}^{-1} + \text{TIP}$$

$$\chi_m/[1 - (zJ'\chi)/(Ng^2\beta^2)] \tag{2}$$

The relevant fitting parameters are: $g = 2.17$, $J = 5.11\,\text{cm}^{-1}$, $zJ' = 0.97\,\text{cm}^{-1}$, and agreement factor $R = \Sigma(\chi_{\text{Obsd}} - \chi_{\text{Calcd}})^2/(\chi_{\text{Obsd}})^2 = 4.38 \times 10^{-3}$. The values of $J = 5.11\,\text{cm}^{-1}$ and $zJ' = 0.97\,\text{cm}^{-1}$ indicate that there is a weak ferromagnetic interaction between the mono-bromide-bridged Cu^{II} ions. Table 3 shows the magneto-structural data of known mono-halide-bridged Cu^{II} complexes. Complexes [19, 20] with trigonal-bipyramidal coordination display strong antiferromagnetic interactions, whereas the complexes [15–18] with the square-pyramidal coordination show weak magnetic interactions. The magnetic coupling strength of the mono-halide-bridged Cu^{II} ions is strongly correlated to the coordination geometry. Table 3 also indicates for the four mono-bromide-bridged Cu^{II} complexes, the φ angle is related to the magnetic coupling sign with small φ favoring ferromagnetic interactions (**7** and **8**), while large φ favors antiferromagnetic interactions (**6** and **11**). Since the

Table 3. Known magneto-structural data for mono-halide-bridged Cu^{II} complexes.

Complex	Geometry	φ (°)	Cu–Xe[*1]	Cu–Xa[*2]	J (cm^{-1})	Refs.
(**1**) [Cu(μ-Cl)(L1)Cl]$_n$	SP	145	2.290(2)	2.702(2)	−6.1	[9, 10]
(**2**) [Cu(μ-Cl)L2]$_n$·(PF$_6$)$_n$	SP	137	2.265(7); 2.276(7)	2.797(8); 2.830(8)	−1.39	[11]
(**3**) [Cu(μ-Cl)L3Cl]$_n$	SP	114	2.300(2)	2.785(2)	1.58	[9]
(**4**) [Cu(μ-Cl)L4Cl]$_n$	SP	117	2.365(4)	2.751(6)	−2.1	[9]
(**5**) [Cu(μ-Cl)L5Cl]$_n$	SP	128	2.319(2)	2.788(2)	0.48	[9]
(**6**) [Cu(μ-Br)L1Br]$_n$	SP	136	2.451(4)	2.777(4)	−7.9	[9, 12]
(**7**) [Cu(μ-Br)L2]$_n$·(PF$_6$)$_n$	SP	134	2.265(7); 2.276(7)	2.856(3); 2.866(3)	0.70	[11]
(**8**) [Cu(μ-Br)(phenP)]$_n$·(ClO$_4$)$_n$	SP	97	2.3555(15)	2.6849(19)	5.11	This work
(**9**) [Cu$_2$(μ–F)(μ-L6)$_2$](ClO$_4$)$_3$	TP	180	2.20227(2)	2.20227(2)	−340	[13]
(**10**) [Cu$_2$(μ-Cl)(μ-L6)$_2$](ClO$_4$)$_3$	TP	180	2.3308(4)	2.3308(4)	−720	[13]
(**11**) [Cu$_2$(μ-Br)(μ-L6)$_2$](ClO$_4$)$_3$	TP	180	2.4733(3)	2.4733(3)	−945	[13]
(**12**) [Cu$_2$(μ–F)(μ-L6)$_2$](BF$_4$)$_3$	TP	180	2.0631(8)	2.0631(8)	−322	[14]

Notes: L1: dimethyl sulfoxide; L2: N-(2-pyridyl)pyridine-2-carbaldimine; L3: 2-(2′-methylaminoethyl)pyridine; L4: imidazole; L5: caffeine; L6: m-bis[bis(3,5-dimethyl-1-pyrazolyl)methyl]benzene; [*1]: equatorial bond; [*2]: axial bond.

number of mono-bromide-bridged Cu^{II} complexes are very limited, further synthesis of mono-bromide-bridged Cu^{II} complexes is necessary to verify this working hypothesis.

4. Conclusion

A uniform 1-D Cu^{II} complex with mono-bromide bridge has been synthesized and displays a weak ferromagnetic interaction between the bridged Cu^{II} ions. For the mono-halide-bridged Cu^{II} complexes, magneto-structural data reveal coordination geometry – a major factor affecting the magnetic coupling strength; complexes with trigonal-bipyramidal geometry exhibit strong magnetic interactions, whereas complexes with square-pyramidal geometry display weak magnetic interactions. For the mono-bromide-bridged Cu^{II} complexes, the Cu–Br–Cu angle is related to the magnetic coupling signs with large angle favoring antiferromagnetic interactions, while small angle favoring ferromagnetic interactions.

Supplementary materials

The ^{1}H NMR spectrum of 2-(4-methyl-pyrazol-1H-yl)-1,10-phenanthroline has been provided. CCDC 928789 contains detailed information of the crystallographic data for this article and these data can be obtained free of charge from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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