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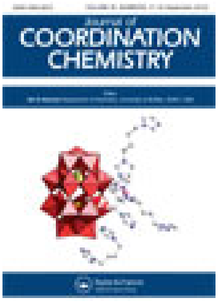

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Synthesis, crystal structure, and magnetism of a two-dimensional copper(II) complex with single end-to-end and double end-on azide bridges

Li-Fang Zhang [a b] , Yun Zhao [a] , Zhong-Hai Ni [a b] , Ming-Ming Yu [b] & Hui-Zhong Kou [b]

[a] School of Chemical Engineering and Technology, China University of Mining and Technology , Xuzhou 221116, Jiangsu Province , P.R. China

[b] Department of Chemistry , Tsinghua University , Beijing 100084 , P.R. China

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Synthesis, crystal structure, and magnetism of a two-dimensional copper(II) complex with single end-to-end and double end-on azide bridges

LI-FANG ZHANG†‡, YUN ZHAO†, ZHONG-HAI NI*†‡,
MING-MING YU‡ and HUI-ZHONG KOU‡

†School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu Province, P.R. China
‡Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China

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A new azido-bridged copper(II) complex, $[Cu(dmp)(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3)]_n$ (**1**) (dmp = 3,5-dimethylpyrazole), has been structurally and magnetically characterized. X-ray diffraction analysis indicates that the compound consists of double end-on (EO) azido-bridged Cu^{II}_2 dimers which are linked by single end-to-end (EE) azide bridges to form a 2-D layer-like structure. Magnetic investigation demonstrates an overall ferromagnetic interaction in **1** and both azide bridges (EE and EO) transmit ferromagnetic coupling. At low temperature ($T < 2.5\,K$), the compound exhibits some metamagnetic behavior.

Keywords: Copper(II) complex; Azido-bridged; Magnetic property; Crystal structure

1. Introduction

The design, assembly, and magnetism of metal complexes have impact in chemistry, materials science, and physics [1–3]. Azido-bridged metal complexes have been obtained to develop effective synthetic strategy, elucidate the nature of magnetic coupling, establish magneto-structural correlation and develop magnetic materials with potential applications [4–7]. In azido-bridged complex systems, the azide group (N_3^-) exhibits flexible and diverse coordination modes, and relative strong ability to transmit magnetic coupling. Magnetic interactions mediated by the azide bridge usually result from the various molecular topologies [8, 9].

Azido-bridged copper(II) complexes offer suitable model systems for the research of magnetic properties because there is only one unpaired electron in copper(II). Some reasonable empirical conclusions for magneto-structural correlation have been proposed for special Cu-azide systems [10, 11]. However, due to the single unpaired

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*Corresponding author. Email: nizhonghai@cumt.edu.cn

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electron from Cu(II), it is difficult to obtain azido-bridged molecular magnetic materials with phase transition compared to metal ions such as Ni(II) and Mn(II) [6c, 12, 13]. Although many Cu(II)-azide complexes have been prepared with various topological structures and azide linking modes [14–17], 2-D Cu(II)-azide examples [18, 19] are limited. Monodentate ancillary ligand should facilitate formation of high-dimensional (2-D and 3-D) metal complexes [20]. Herein, we report the synthesis, molecular structure and magnetic properties of a new 2-D copper(II) complex, $[Cu(dmp)(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3)]_n$ (**1**), with single end-to-end (EE) and double end-on (EO) azide bridges.

2. Experimental

2.1. *Materials and physical measurements*

Starting chemicals were analytically pure and used without purification. IR spectra (4000–400 cm^{-1}) were recorded from KBr pellets on a Nicolet 750 FT-IR spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an EAI CE-440 analyzer. Magnetic measurements on single crystal powder samples were carried out with a Quantum Design MPMS SQUID magnetometer equipped with a helium continuous-flow cryostat. Diamagnetic corrections were estimated from Pascal constants.

2.2. *Synthesis*

Caution! Perchlorate as well as azide salts were used in small quantities and handled with care since explosions may occur.

$[Cu(dmp)(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3)]_n$ (**1**). With stirring, copper(II) perchlorate hexahydrate (74.0 mg, 0.2 mmol) was added to a solution of dmp (48.0 mg, 0.5 mmol) and sodium azide (39.0 mg, 0.6 mmol) in methanol (15.0 mL). The resulting solution grew dark brown immediately and was stirred for an additional 10 min, then filtered. The filtrate stood at room temperature and black rhombic flakes were obtained after two days in *ca* 60% yield. $C_{10}H_{16}Cu_2N_{16}$: Calcd C 24.64, H 3.31, N 45.98; found: C 24.38, H 3.25, N 45.61. IR (KBr): $\nu(N_3^-)$ 2054, 2081 cm^{-1}.

2.3. *Crystallographic data collection and refinement*

The X-ray single crystal data for **1** were collected on a Rigaku R-AXIS RAPID IP diffractometer. Crystallographic data, the conditions for the intensity data collection and some features of the structure refinements are listed in table 1. Graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and the oscillation scans technique for **1** were used to collect the data sets. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on calculated positions by use of the HFIX utility of the SHELXL-97 program.

Table 1. Crystal data and structure-refinement parameters for **1**.

Empirical formula	$C_5H_8CuN_8$
Formula weight	243.73
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	11.903(2)
b	10.225(2)
c	8.4420(17)
β	106.98(3)
Volume (Å^3), *Z*	982.7(3), 4
Calculated density (g m^{-3})	1.647
Absorption coefficient (mm^{-1})	2.198
F(000)	492
θ range for data collection (°)	3.21–27.48
Reflections collected	9349
Independent reflection	2249 [*R*(int) = 0.0238]
Final *R* indices [$I > 2\sigma(I)$]	1962
R_1 [$I > 2\sigma(I)$]	0.0257
wR_2 (all data)	0.0677
Goodness-of-fit on F^2	1.055
Largest difference peak and hole (e Å^{-3})	0.272 and −0.294

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)–N(1)	1.9909(16)	N(1)–N(2)	1.198(3)
Cu(1)–N(4)	1.9586(18)	N(2)–N(3)	1.123(3)
Cu(1)–N(7)	1.9862(16)	N(4)–N(5)	1.174(2)
Cu(1)–N(1A)	2.0084(17)	N(5)–N(6)	1.152(2)
Cu(1)–N(6B)	2.3455(19)	Cu(1)–Cu(1A)	3.111(2)
Cu(1)–Cu(1B)	5.610(2)		
Cu(1)–N(1)–Cu(1A)	102.16(8)	N(1)–Cu(1)–N(1A)	77.84(8)
N(5)–N(4)–Cu(1)	121.67(15)	N(4)–Cu(1)–N(1)	91.73(8)
N(5)–N(6)–Cu(1C)	126.29(16)	N(4)–Cu(1)–N(1A)	162.58(9)
N(8)–N(7)–Cu(1)	122.80(12)	N(7)–Cu(1)–N(1)	170.17(7)
N(2)–N(1)–Cu(1)	126.81(15)	N(7)–Cu(1)–N(1A)	94.28(7)
N(2)–N(1)–Cu(1A)	127.00(15)	N(4)–Cu(1)–N(7)	94.42(8)
N(3)–N(2)–N(1)	179.2(3)	N(6)–N(5)–N(4)	176.7(2)

Symmetry codes: A: $-x+2$, $-y$, $-z$; B: x, $-y+1/2$, $z-1/2$; C: x, $-y+1/2$, $z+1/2$.

3. Results and discussion

3.1. *Descriptions of crystal structure*

X-ray diffraction analysis shows that **1** has a neutral 2-D layer-like structure. Two identical copper(II) ions are bridged by symmetrical double EO azide bridges and these binuclear copper(II) units are connected by single asymmetrical EE azide linkages to form the 2-D network structure. Selected bond distances and angles are listed in table 2. The crystal structure is shown in figures 1 and 2. The molecular structure is similar to that of $[Cu(L)(N_3)_2)]_n$ (L = benzylamine) [18e].

Each copper(II) in **1** is five-coordinate by five nitrogen atoms from two $\mu_{1,1}$-N_3, two $\mu_{1,3}$-N_3 bridges and one ancillary bmp, yielding a slightly distorted square pyramid.

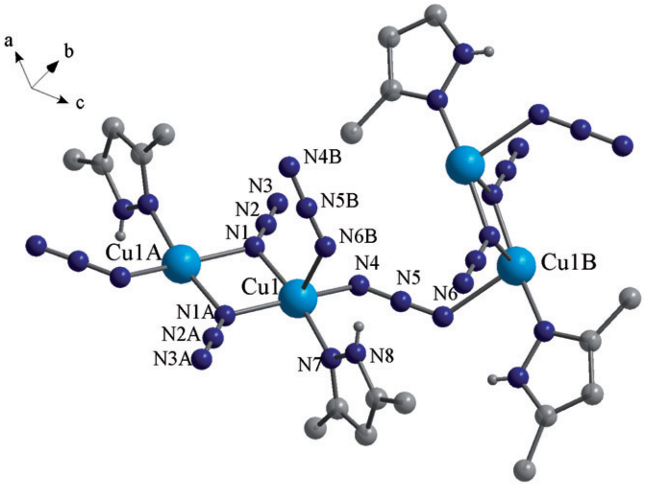


Figure 1. The molecular structure of **1** [symmetry codes: A: $-x+2$, $-y$, $-z$; B: x, $-y+1/2$, $z-1/2$].

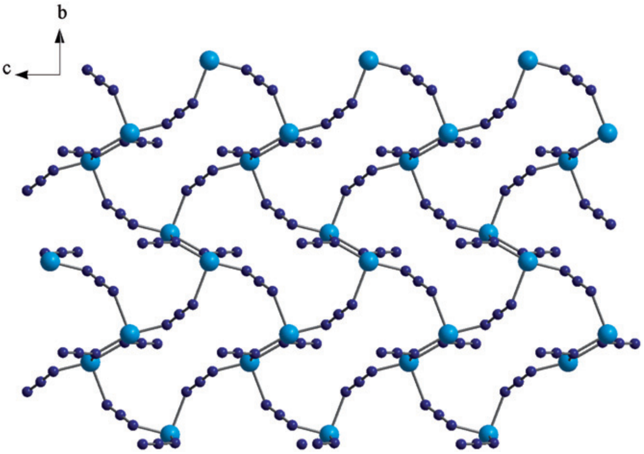


Figure 2. Arrangement of 2-D layer-like structure of **1** in the *bc* plane (dmp has been omitted for clarity).

The apical position is occupied by N(6B) [x, $-y+1/2$, $z-1/2$] from the EE azide bridge with bond length of 2.3455(19) Å, the longest distance of the five Cu–N bonds. The square base is formed by nitrogen from dmp (N(7)), two EO azido bridges (N(1) and N(1 A)) and a second EE azido bridge (N(4)). The Cu–N bond length in the basal plane is 1.9586(18) to 2.0084(17) Å. The maximum deviation of four nitrogen atoms from the least squares plane of N(7)–N(1)–N(1 A)–N(4) is 0.0742 Å (N(1)) and Cu lies 0.185 Å above this plane. The trigonality index $\tau = 0.130$ confirms the square pyramidal character. Two EO azide bridges link above two metal centers into a symmetrical planar entity (Cu(1)–N(1)–Cu(1A)–N(1A) [$-x+2$, $-y$, $-z$]). The two quasi-linear (N(3)–N(2)–N(1) = 179.2(3)°) EO azido bridges slightly deviate (up and down) from the plane. The two Cu(II) ions are related by an inversion center. Each binuclear entity is further

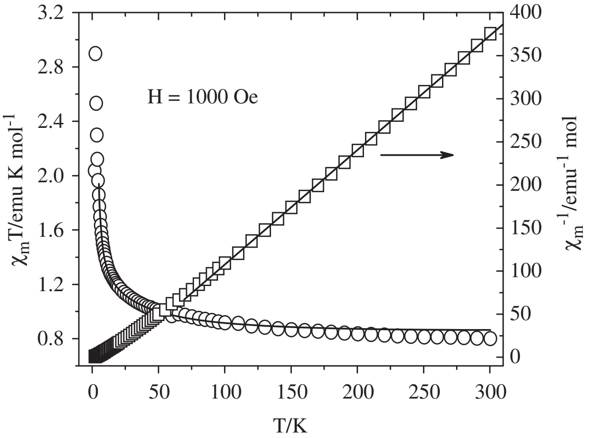


Figure 3. Curves for $\chi_m T$ *vs.* T and $1/\chi_m$ *vs.* T of **1** measured in an applied field of 1000 Oe. The solid lines represent the best fitting based on parameters discussed in the text.

linked through four EE azido bridges to four neighboring dimers, resulting in a neutral single EE and double EO alternating bridged layer-like 2-D structure. The EE azide takes an asymmetric bridging mode with two terminal nitrogen atoms locating at the apical and basal positions of the square pyramid surrounding two coppers, leading to two Cu–N bonds with different length.

In the Cu_2^{II} dimer, the Cu···Cu separation is 3.111(2) Å and the bridging angle Cu(1)–N(1)–Cu(1A) is 102.16(8)°. The Cu···Cu separation through EE azido bridge is 5.610(2) Å and the two corresponding angles are 121.59(16)° for N(5)–N(4)–Cu(1) and 126.51(16)° for N(5)–N(6)–Cu(1 C) [x, $-y+1/2$, $z+1/2$], respectively. The torsion angle by two Cu(II) ions and pseudo-linear EE azido bridge is 67.6°. The significant difference between **1** and $[Cu(L)(N_3)_2]_n$ [18e] is the Cu–N–N angle and Cu–N_3–Cu torsion. The Cu–N–N angles in $[Cu(L)(N_3)_2]_n$ [18e] are 121.5(3)° and 144.6(3)°, and the Cu–N_3–Cu torsion is 102.1°, respectively.

3.2. *Magnetic properties*

The $\chi_m T$ *versus* T and $1/\chi_m$ *versus* T curves for **1** are shown in figure 3, in which χ_m is the mole susceptibility of per Cu_2^{II} unit. At room temperature, the $\chi_m T$ value is 0.80 emu K mol^{-1}, near the expected value (0.75 emu K mol^{-1} and $g=2.0$) for two uncoupled Cu(II) ions. With decreasing temperature, the $\chi_m T$ value increases smoothly until 25 K. Then the $\chi_m T$ value increases quickly and reaches maximum 2.90 emu K mol^{-1} at 2.5 K, significantly higher than the expected value of 1.0 emu K mol^{-1} for two ferromagnetic coupled Cu(II) ions ($S_T=1$ and $g=2.0$), suggesting the occurrence of ferromagnetic ordering. Finally, $\chi_m T$ decreases to 2.04 emu K mol^{-1} at 2.0 K due to anisotropic zero-field splitting and/or interlayer antiferromagnetic interactions.

The field-cooled magnetic susceptibilities with applied fields of 50 and 1000 Oe show a maximum at *ca* 2.5 K (figure 4), which demonstrates that there exists a phase transition at *ca* 2.5 K. The absence of a peak for curves under 2500 Oe shows the metamagnetic behavior of the complex, and the critical field (H_c) to overcome the

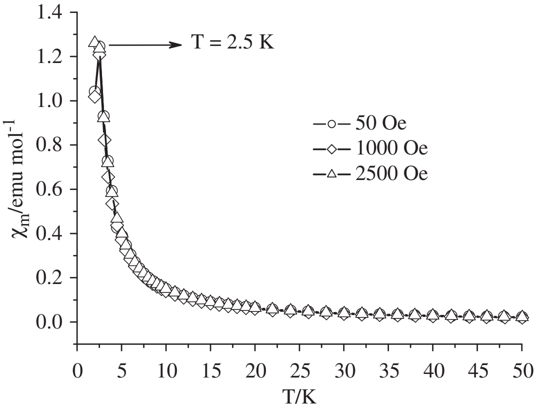


Figure 4. Field-cooled magnetic susceptibilities of **1**.

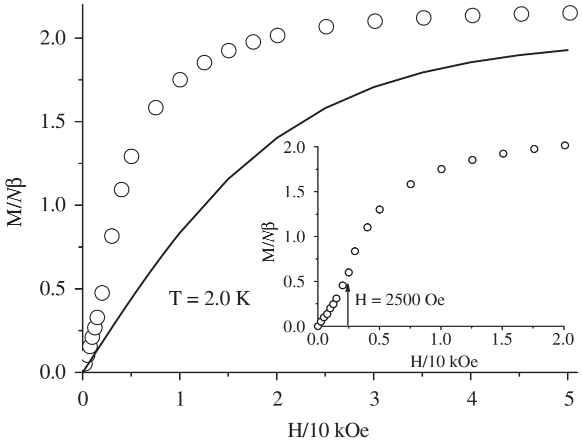
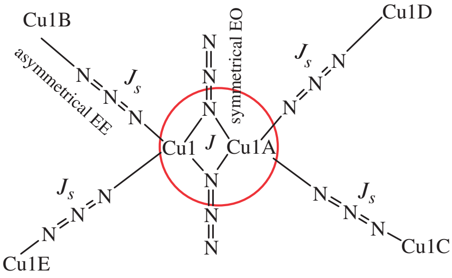


Figure 5. Field dependence of magnetization of **1** at 2.0 K. The solid line denotes the Brillouin function based on $g = 2.0$ and $S_T = 1$.

interlayer antiferromagnetic interaction is less than 2500 Oe. The field-dependent magnetization was measured up to 50 kOe at 2.0 K (figure 5). The experimental curve is significantly higher than that of the Brillouin function based on $g = 2.0$ and $S_T = 1$, which confirms the overall ferromagnetic interactions and suggests the existence of magnetic ordering in **1**. The sigmoid shape of the magnetization curve under low field (figure 5, inset) is typical behavior of a metamagnet. The critical field is about 2500 Oe, in agreement with that obtained from field-cooled magnetic susceptibility measurements. Since the phase transition temperature is very low for **1**, further magnetic measurements have not been carried out. The magnetic behavior of **1** is similar to that of 2-D Ni(II) complex $[Ni(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3)(L)]_n$ (L = *N*,*N*-diethyl-*N*′-methylethylenediamine) [12].

From the molecular structure of **1**, the magnetic structure can be considered as uniform 2-D layers formed by binuclear copper(II) units and the dominating magnetic



Scheme 1. The magnetic coupling model for **1**.

coupling (J) occurring within the binuclear bridged by symmetrical basal-to-basal EO azide linkages (scheme 1). The magnetic exchange (J_s) between Cu_2^{II} units through a single EE linkage is weaker than that of the Cu_2^{II} unit ($J \gg J_s$) because of the longer Cu–Cu distance. Based on this analysis and assumption, the 2-D sheet-like **1** can be simplified as a simple binuclear Cu^{II}–Cu^{II} magnetic model with magnetic susceptibilities of **1** fitted by the following expression derived from the isotropic exchange spin Hamiltonian $\hat{H} = -2J\hat{S}_{Cu1}\hat{S}_{Cu1A}$. Magnetic coupling through single EE linkage (J_s) as a weak interaction together with interlayer magnetic coupling can beclassified to intermolecular magnetic interactions (zJ'). Moreover, it is easy to understand that J_s is dominating in zJ'.

$$\chi_d = \frac{2Ng^2\beta^2}{kT(3 + \exp(-2J/kT)} \tag{1}$$

$$\chi_m = \frac{\chi_d}{1 - \chi_d(2zJ'/Ng^2\beta^2)} \tag{2}$$

The best-fit parameters in the whole temperature range 2–300 K are $J = 20.81(2)\ \mathrm{cm}^{-1}$, $g = 2.05(1)$, $zJ' = 1.20(2)\ \mathrm{cm}^{-1}$ and $R = \sum[(\chi_m T)_{obsd.} - (\chi_m T)_{Calcd}]^2 / \sum[(\chi_m T)^2_{obsd.}] = 8.64 \times 10^{-5}$. The value of J, significantly larger than that of zJ', suggests that the above assumption of magnetic model for this compound is reasonable, and the transmitting magnetic interaction through the asymmetric EE azide bridge is weak.

The magneto-structural correlation for **1** can be explained based on previously reported results. Cu(II)–azide complexes with double symmetric EO bridges are ferromagnetic for bridging angle Cu–N_{azide}–Cu smaller than 108°, but can change to antiferromagnetic when the Cu–N_{azide}–Cu angle is larger than 108° [9a]. This empirical conclusion was confirmed by a density functional study, in which the critical Cu–N–Cu angle was found to be 104° [9b]. For **1**, the double symmetric EO bridging angle Cu–N_{azide}–Cu is 102.14(8)°, within the range of ferromagnetic interactions, and similar to that of a 1-D copper(II) complex $[Cu_3(\mu_{1,1}\text{-}N_3)_6(dmp)_2]_n$ reported recently by our group [17d].

For complexes with single asymmetric EO and EE bridges involving short and long Cu–N bonds, the magnetic coupling is less clear since these systems are rarely reported. Careful examination of the few examples reported to date reveals that magnetic exchange is either weak ferromagnetic or antiferromagnetic [21, 22]. According to the theoretical analysis proposed by Chaudhuri *et al.* [23], there exist ferro- and antiferromagnetic coupling channels for Cu–azide system with asymmetric EE azide bridges at the same time, and the nature of magnetic coupling is related to Cu–N–N bond angle and Cu–N_3–Cu torsion angle. The antiferromagnetic component of the superexchange may be drastically reduced for large Cu–N–N bond angles or large Cu–N_3–Cu torsion angle. The magnetic interactions in **1** are comparable to those of complexes $[Cu(L)(N_3)_2]_n$ [18e] and $[Cu(L)(\mu_{1,3}\text{-}N_3)(ClO_4)]_n$ [23].

4. Conclusion

Employing monodentate dmp as ancillary ligand and N_3^- as bridging group, a new 2-D copper complex with single asymmetrical EE and double symmetrical EO bridges has been obtained. Magnetic investigation indicates overall ferromagnetic interactions in the complex with both kinds of azide bridges (EE and EO) transmitting ferromagnetic coupling interactions. When the temperature is below 2.5 K, the complex demonstrates some metamagnetic behavior.

Supplementary material

Crystallographic data for the structure of **1** has been deposited at the Cambridge Crystallographic Data Center (CCDC 864802). This information can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, United Kingdom; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk

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