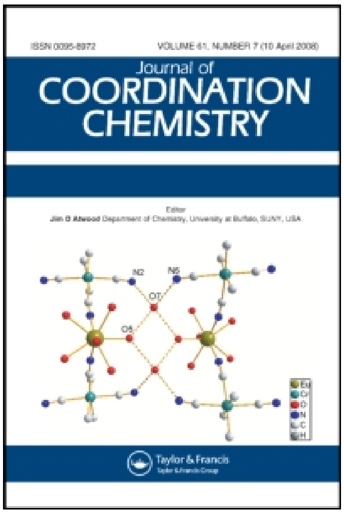

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure, and magnetism of a binuclear Cu(II) complex with a single end-to-end bridged azido ligand

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To cite this Article Li, Jin-Min and Jin, Xia(2009) 'Synthesis, crystal structure, and magnetism of a binuclear Cu(II) complex with a single end-to-end bridged azido ligand', Journal of Coordination Chemistry, 62: 16, 2610 — 2615, First published on: 24 May 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970902923305

URL: http://dx.doi.org/10.1080/00958970902923305

Journal of Coordination Chemistry
Vol. 62, No. 16, 20 August 2009, 2610–2615

Synthesis, crystal structure, and magnetism of a binuclear Cu(II) complex with a single end-to-end bridged azido ligand

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(*Received 24 November 2008; in final form 15 January 2009*)

A binuclear copper(II) complex, $[Cu_2(\mu_{1,3}\text{-}N_3)(N_3)(pmp)_2(ClO_4)]ClO_4$ (pmp = 2-((pyridin-2-yl) methoxy)-1,10-phenanthroline), was synthesized with a single azide as end-to-end bridge ligand, and pmp and perchlorate as ligands. In the crystal, Cu(II) is in a distorted square pyramidal geometry, and a single azide bridges equatorial-axial linking two Cu(II) ions with separation of 5.851 Å. There are $\pi-\pi$ stacking interactions involving 1,10-phenanthroline rings. The variable-temperature (2–300 K) magnetic susceptibilities were analyzed using a binuclear Cu(II) magnetic formula and it indicates that there is a very weak ferromagnetic coupling with $2J = 2.82\,\mathrm{cm}^{-1}$.

Keywords: Magnetism; Copper(II) complex; Crystal structure; Azide ligand

1. Introduction

Molecular magnetism has attracted considerable attention with major advances in theoretical description and application as new molecular-based materials [1–4], but the structure-magnetic relations are not yet understood. Therefore, it is necessary to synthesize a large number of complexes with different ligands and study their magnetic properties in order to obtain the delicate rules between structure and magnetism.

Azide is a versatile bridging ligand and a large number of complexes have been prepared and their magnetic coupling properties have been studied [5–8]; some key factors that tune the magnetic coupling sign have been obtained. For example, the end-on bridge coordination mode generally creates a ferromagnetic coupling while the end-to-end bridge coordination mode shows an anti-ferromagnetic interaction. Most reported complexes with azide as bridge deal with double azido-bridged coordination [9–11] and only limited complexes have single end-to-end azido-bridges [11–13]. Only five papers [14–18] report complexes with single end-to-end azido-bridges with copper(II) magnetic coupling, with some exhibiting weak ferromagnetic coupling [14–17] and one anti-ferromagnetic interaction [18]. Therefore, the factors that

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970902923305

govern magnetic coupling are not clear for this kind of complex. We selected 2-((pyridin-2-yl)methoxy)-1,10-phenanthroline as ligand and synthesized the title binuclear copper(II) complex as the first binuclear copper(II) complex with a single end-to-end azido-bridge. Herein we report its synthesis, crystal structure, and magnetic coupling mechanism.

2. Experimental

2.1. *General*

2-((Pyridin-2-yl)methoxy)-1,10-phenanthroline was prepared according to the literature method [19]; other chemicals are of analytical grade and used without purification. Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000–500 cm^{-1} region using KBr discs. C, H, and N elemental analyses were carried out on a Perkin–Elmer 240 instrument. Variable-temperature magnetic susceptibilities of microcrystalline powder samples were measured in a magnetic field of 1 kOe in the temperature range of 2–300 K on a MPMS-7SQUID magnetometer. The data were corrected for magnetization of the sample holder and for diamagnetic contributions estimated from Pascal's constants.

2.2. *Preparation of $[Cu_2(\mu_{1,3}\text{-}N_3)(N_3)(pmp)_2(ClO_4)]ClO_4$*

Total of 8 mL H_2O solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.1267 g, 0.342 mmol) was added to 10 mL methanol solution containing 2-((pyridin-2-yl)methoxy)-1,10-phenanthroline (0.0973 g, 0.339 mmol) and the mixed solution was stirred for a few minutes. Allowing the filtrate to stand at room temperature for 2 weeks, green single crystals were obtained. Anal. Calcd (%), $C_{36}H_{26}Cl_2Cu_2N_{12}O_{10}$: C, 43.91; H, 2.66; N, 17.07; Cu, 12.91. Found (%): C, 44.21; H, 2.81; N, 17.43; Cu, 13.48. IR (cm^{-1}): 2039 s, 1577 w, 1400 s, and 1079 s.

2.3. *Crystal structure determination*

A suitable single crystal with dimensions $0.31 \times 0.21 \times 0.16\ mm^3$ was selected and glued on the tip of a glass fiber. The crystal structure determination was carried out at 25°C on an X-ray diffractometer, Model Bruker Smart-1000 CCD, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) in the range of $3.10 < 2\theta < 52.00°$. A total of 10,663 reflections were collected, of which 7457 were independent ($R_{int} = 0.026$) and 5115 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 hydrogen atoms were placed in calculated positions and refined as riding. The programs for structure solution and refinement were SHELXTL (Bruker, 2001) [20]. A summary of the crystallographic data is given in table 1.

Table 1. Crystallographic data.

Formula	$C_{36}H_{26}Cl_2Cu_2N_{12}O_{10}$
Formula weight	984.67
Temperature (K)	298(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	11.9790(19)
b	12.3147(19)
c	14.558(2)
α	80.124(2)
β	66.901(2)
γ	89.916(2)
Volume (Å^3)	1940.9(5),
Z	2
Calcd density (mg m^{-3})	1.685
Absorption coefficient (mm^{-1})	1.309
F(000)	996
Crystal size (mm^3)	$0.31 \times 0.21 \times 0.16$
θ range for data collection (°)	1.55–26.00
Limiting indices	$-14 \leq h \leq 13$, $-11 \leq l \leq 15$, $-17 \leq k \leq 17$
Reflections collected	10,663
Independent reflection	7457
Data/restraints/parameters	7457/0/559
Goodness-of-fit on F^2	1.064
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0675$, $wR_2 = 0.1787$
R indices (all data)	$R_1 = 0.0980$, $wR_2 = 0.1964$
Largest difference peak and hole (e Å^{-3})	0.817 and -0.833

3. Results and discussion

3.1. *Crystal structure*

Figure 1 shows the coordination diagram, with Cu1 coordinated by N1, N7, N8, N9, and N12, in which atoms N7, N8, and N12 are from a pmp and N9 comes from an azide; N1 is the $\mu_{1,3}$-azido; Cu2 is coordinated by N3, N4, N5, N6, and O5, in which N4, N5, and N6 come from another pmp, N3 from the $\mu_{1,3}$-azido bridge ligand, and O5 from a perchlorate. The data in table 2 display that the bond lengths of Cu1–N1 and Cu2–O5 are longer than the other bonds. Cu1 and Cu2 assume a distorted square pyramidal geometry with N1 and O5 located on the apexes, respectively. Azide bridges Cu1 and Cu2 with separation of 5.851 Å. One end of the bridged azide coordinates the distorted square base and the other end on the apex of the other square pyramid; azide assumes an equatorial-axial bridge coordination, identical with reported copper(II) complexes [14–18, 21]. The angles between Cu(II) and bridging azide are 132.1(4)° and 123.5(4)° for Cu1–N1–N2 and Cu2–N3–N2, respectively, and the torsion angle Cu1–N1–N2–N3–Cu2 is 69.75(35)°. In the crystal there are π–π stacking interactions between adjacent complexes involving 1,10-phenanthroline rings; the relevant distances are $\mathrm{Cg1}\cdots\mathrm{Cg2}^{\mathrm{i}} = 3.545(3)$ Å and $\mathrm{Cg1}\cdots\mathrm{Cg2}^{\mathrm{i}}_{\mathrm{perp}} = 3.519$ Å [symmetry codes: (i) $1-x, 2-y, -z$; Cg1 and Cg2 are the centroids of the N8/C26–C30 and N7/C19–C23 rings, respectively; $\mathrm{Cg1}\cdots\mathrm{Cg2}^{\mathrm{i}}_{\mathrm{perp}}$ is the perpendicular distance from Cg1 ring to $\mathrm{Cg2}^{\mathrm{i}}$ ring plane].

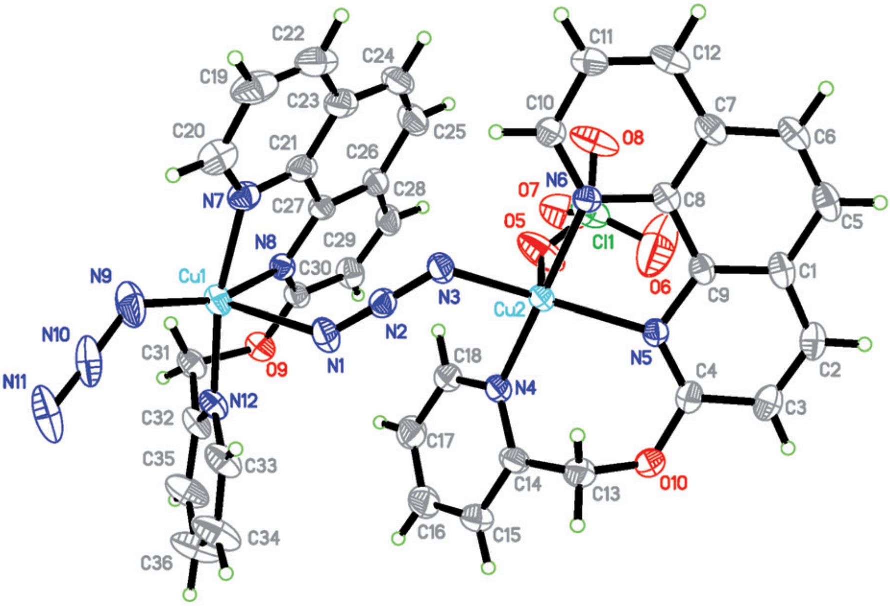

Figure 1. Coordination diagram of the binuclear complex with atom numbering scheme.

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

Cu1–N9	1.919(5)	Cu1–N12	1.971(4)	Cu1–N7	2.003(5)
Cu1–N8	2.093(4)	Cu1–N1	2.472(5)	Cu2–N6	1.975(4)
Cu2–N3	1.980(4)	Cu2–N4	2.009(4)	Cu2–N5	2.080(4)
Cu2–O5	2.323(5)				
N9–Cu1–N12	95.4(2)	N9–Cu1–N7	90.8(2)		
N12–Cu1–N7	168.54(18)	N9–Cu1–N8	159.0(2)		
N12–Cu1–N8	96.63(17)	N7–Cu1–N8	80.48(18)		
N9–Cu1–N1	101.3(2)	N12–Cu1–N1	87.61(17)		
N7–Cu1–N1	81.73(17)	N8–Cu1–N1	96.33(15)		
N6–Cu2–N3	89.47(17)	N6–Cu2–N4	171.97(18)		
N3–Cu2–N4	93.34(17)	N6–Cu2–N5	81.69(16)		
N3–Cu2–N5	153.2(2)	N4–Cu2–N5	98.89(17)		
N6–Cu2–O5	88.45(17)	N3–Cu2–O5	106.8(2)		
N4–Cu2–O5	83.54(18)	N5–Cu2–O5	98.17(19)		
Cu1–N1–N2	132.1(4)	Cu2–N3–N2	123.5(4)		
N1–N2–N3	177.8(6)				

3.2. *Magnetic property*

The variable-temperature (2−300 K) magnetic susceptibilities are shown in figure 2, where χ_M is the molar magnetic susceptibility per binuclear Cu(II) unit and μ_{eff} is the magnetic moment per binuclear Cu(II). The μ_{eff} value at 300 K is 2.72 B.M., slightly larger than that of uncoupled binuclear Cu(II) (2.45 B.M. for $g_{av} = 2$) at room temperature. The μ_{eff} values are almost unchanged with temperature to 10 K, and then the μ_{eff} values increase with decreasing temperature reaching the maximum of 2.79 B.M. at 4.5 K. Then the values decrease again with temperature decrease, implying

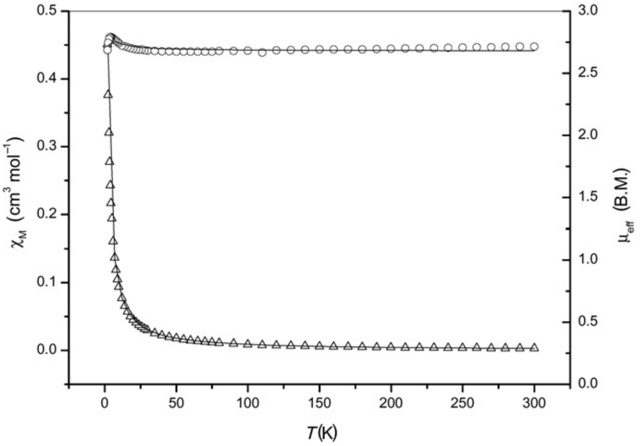

Figure 2. Plots of χ_M (triangle for experimental data, line for theoretical value) and μ_{eff} (open circle for experimental data, line for theoretical value) *vs.* T for the complex.

a very weak ferromagnetic exchange between bridged Cu(II) ions. The binuclear Cu(II) equation (3) was used to fit the experimental susceptibility data, which was obtained based on an isotropic Hamiltonian operator as presented in equation (1).

$$\widehat{H} = -2J\widehat{S}_{\mathrm{Cu1}}\widehat{S}_{\mathrm{Cu2}} \tag{1}$$

$$\chi'_{\mathrm{M}} = \frac{2Ng^2\beta^2}{\kappa T}\left[3 + \exp\left(\frac{-2J}{\kappa T}\right)\right]^{-1} \tag{2}$$

$$\chi_{\mathrm{M}} = \frac{\chi'_{\mathrm{M}}}{1 - \frac{\mathrm{z}J'\chi'_{\mathrm{M}}}{\mathrm{N}\mathrm{g}^2\beta^2}} \tag{3}$$

The symbols above have general meanings and the theoretical model gave a good fit for the experimental data with agreement factor $R = \sum(\chi_{\mathrm{Obs}} - \chi_{\mathrm{Calcd}})^2/(\chi_{\mathrm{Obs}})^2 = 3.4 \times 10^{-4}$, $g = 2.19$, $2J = 2.82\,\mathrm{cm}^{-1}$ and $zJ' = -0.52\,\mathrm{cm}^{-1}$. The value of $2J = 2.82\,\mathrm{cm}^{-1}$ implies that there is a very weak ferromagnetic coupling between the bridged Cu(II) ions. Relevant papers [15, 21] report that the magnetic coupling sign for single end-to-end azido-bridged coordination complexes mainly is dependent on the Cu–N–N angle and the Cu–N–N–N–Cu torsion angle, and especially Cu–N–N–N–Cu torsion angle plays a key role. Large Cu–N–N angle and large Cu–N–N–N–Cu torsion angle reduces anti-ferromagnetic interaction. When Cu–N–N–N–Cu torsion angle is 0° or 180° anti-ferromagnetic interaction reaches maximum, and when Cu–N–N–N–Cu torsion angle is 90° anti-ferromagnetic interaction becomes zero. Therefore, the ferromagnetic coupling of the present complex may be attributed to the larger Cu–N–N–N–Cu torsion angle [69.75(35)°]; when the Cu–N–N–N–Cu torsion angles are 50.0(4)° and 40.4(8)° the relevant complexes also show ferromagnetic interaction [15]. The very weak ferromagnetic coupling of the present complex may be due to the equatorial-axial azido-bridge mode [14–17]. In square pyramidal coordination geometry unpaired electron of Cu(II) is mainly located on $\mathrm{d}_{x^2-y^2}$ orbital and unpaired electron spin density of the d_{z^2} orbital is very low. Also, the axial bond length is relatively large. All the factors result in poor electron delocalization between the azido-bridged Cu(II) ions giving the very weak magnetic interaction of the present complex.

4. Conclusion

In this work, a new binuclear Cu(II) complex has been synthesized with azide as bridge and its crystal structure determined. The fitting of the variable-temperature (2–300 K) magnetic susceptibility data reveals a very weak ferromagnetic coupling between bridging Cu(II) ions. The weak ferromagnetic interaction is explained on the basis of its axial-equatorial bridge mode. This is the first binuclear copper(II) complex with a single end-to-end azido-bridged axial-equatorial coordination mode.

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