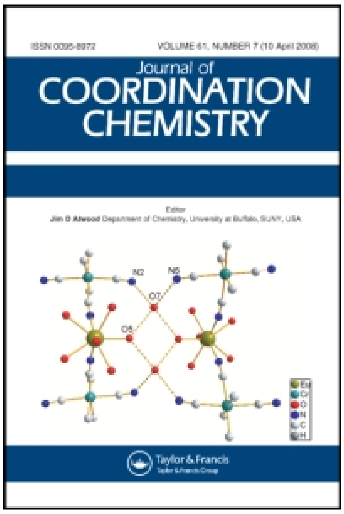

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Synthesis, crystal structure, and magnetism of a binuclear Cu(II) complex with double azido as asymmetric basal-apical end-on bridged ligand

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Synthesis, crystal structure, and magnetism of a binuclear Cu(II) complex with double azido as asymmetric basal–apical end-on bridged ligand

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A new binuclear copper(II) complex, $[Cu_2(\mu_{1,1}\text{-}N_3)_2(PP)_2)] \cdot 2ClO_4$ (PP = 2,6-dipyrazol-1-yl-pyridine), was synthesized with double azide as asymmetric end-on bridge ligand and 2,6-dipyrazol-1-yl-pyridine as the terminal ligand. The crystal structure was determined by X-ray crystallography. Cu(II) is located in a distorted square pyramidal geometry, and azide bridges the equatorial-axial linking two Cu(II) atoms with a separation of 3.3595(11) Å. The fitting for the data of the variable-temperature (2–300 K) magnetic susceptibilities by using the Curie–Weiss law gives the Weiss temperature $\theta = -7.830$ K, indicating a very weak anti-ferromagnetic interaction between the bridging Cu(II) complexes.

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

1. Introduction

Major advancements have been made in the theoretical description and application of molecular magnetism in new molecular-based materials [1, 2]. To understand the magnetic coupling mechanism, a large number of copper(II) complexes with different bridging ligands have been synthesized and their magnetic coupling properties were studied [3–11]. Copper(II) complexes [12, 13] with azide as a bridge play an important role in the correlation between structure and magnetic coupling, and the key factors that tune the sign of magnetic coupling have been obtained. For example, end-to-end bridging shows an anti-ferromagnetic interaction, while end-on bridging generally creates a ferromagnetic coupling for Cu–N–Cu angles lower than 108° and an anti-ferromagnetic coupling for Cu–N–Cu angles larger than 108° [14, 15]. Copper(II) complexes with the double end-on coordination only occur for basal–basal coordination [16–18] and not basal–apical coordination [19–31]; no correlation between magnetism and coordination has been obtained for the basal–apical coordination. Therefore, synthesizing these complexes and studying their magnetism can further

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enhance the understanding of the correlation between the coordination structure and magnetism. We have synthesized the title complex and herein we report its crystal structure and magnetism.

2. Experimental

2.1. *Materials*

2,6-Dipyrazol-1-yl-pyridine was synthesized by using pyrazole, and 2,6-dichloropyridine [32] and other chemicals are of analytical grade and used without purification.

2.2. *Synthesis of* $[Cu_2(\mu_{1,1}\text{-}N_3)_2(PP)_2)] \cdot 2ClO_4$

When $Cu(ClO_4) \cdot 6H_2O$ (0.0723 g, 0.195 mmol), NaN_3 (0.0130 g, 0.200 mmol) and 2,6-dipyrazol-1-yl-pyridine (0.0426 g, 0.202 mmol) were dissolved in 5 mL methanol, respectively, and mixed, a green precipitate was appeared immediately. The deposits were disappeared when 15 mL H_2O was added to the mixture and stirred for a few minutes. Green single crystals were obtained after the filtrate was allowed to stand at room temperature for 1 week. Anal. Calcd (%) for $C_{22}H_{18}Cl_2Cu_2N_{16}O_8$: C, 31.74; H, 2.18; N, 26.92. Found (%): C, 32.10; H, 2.49; N, 27.35.

2.3. *Physical measurements*

Infrared spectra were recorded on 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. Variable-temperature magnetic susceptibilities of microcrystalline powder samples were measured in a magnetic field of 1 kOe from 2 to 300 K on a MPMS-7SQUID magnetometer. The data were corrected for the magnetization of the sample holder and for diamagnetic contributions which were estimated from Pascal's constants.

2.4. *X-ray crystallography*

$C_{22}H_{18}Cl_2Cu_2N_{16}O_8$, Mr = 832.50, Monoclinic, space group $P2_1/n$, $a = 8.9326(19)$, $b = 14.696(3)$, $c = 11.857(3)$ Å, $\beta = 107.845(3)°$, $V = 1481.6(5)$ Å^3, $\mu = 1.695\ mm^{-1}$, $F(000) = 836$, Largest difference peak = 0.961 e Å^{-3}, Largest difference hole = −0.578 e Å^{-3}.

A suitable single crystal with dimensions of $0.18 \times 0.16 \times 0.13\ mm^3$ 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 a graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) in the range of $4.56 < 2\theta < 54.00°$. A total of 8517 reflections were collected, of which 3202 were independent ($R_{int} = 0.045$) and 2388 observed reflections with $I > 2\sigma(I)$ were used in the structure analysis. Corrections for *Lp* factors were applied and all the non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens were placed in the calculated positions and refined as riding. The final refinements, including hydrogens, converged to $R = 0.0564$, $wR = 0.1479$, $w = 1/\sigma^2(F_o) + (0.0851P)^2 + 0.6530P$, where $P = (F_o^2 + 2F_c^2)/3$, the largest peak 0.961 e Å^{-3} and hole −0.578 e Å^{-3}; $(\Delta/\sigma) = 0.001$. The goodness-of-fit was on $F^2 = 1.034$. The program SHELXTL (Bruker, 2001) was used for structure solution and refinement.

3. Results and discussion

3.1. *IR spectrum*

The coordination mode of azide to a transition metal can be indicated by its infrared spectrum, and in general a strong sharp peak that appears above 2055 cm^{-1} means $\mu_{1,1}$ bridge, whereas a peak below 2055 cm^{-1} implies terminal coordination. The present complex shows a single sharp peak at 2043 cm^{-1}, the lower frequency attributed to the highly asymmetric nature of the azide bridge. The infrared peak of the present azide bridge ligand is very similar to that of the azide bridge complexes [21] with basal–apical coordination. Strong and broad peaks at 1119 and 1078 cm^{-1} arise from perchlorate, whereas vibrations of C=N and C=C for 2,6-dipyrazol-1yl-pyridine appear at 1622, 1484, and 1403 cm^{-1}.

3.2. *Crystal structure*

Figure 1 shows the coordination diagram, with Cu1 coordinated by N3, N4, N6, N8, and N3A, with N4, N6, and N8 from a 2,6-dipyrazol-1-yl-pyridine and N3 and N3A from two different azides. Data in table 1 show that Cu–N3A is obviously longer than the other four Cu1–N bonds; Cu1 assumes a distorted square-pyramidal geometry and N3A is located at the apex of the pyramid. N3, N4, N6, and N8 and Cu1 lie in a distorted square plane in which the five atoms deviate from the mean plane by −0.0522(15), 0.0650(18), −0.0794(22), 0.0675(19), −0.0010(16) Å, respectively.

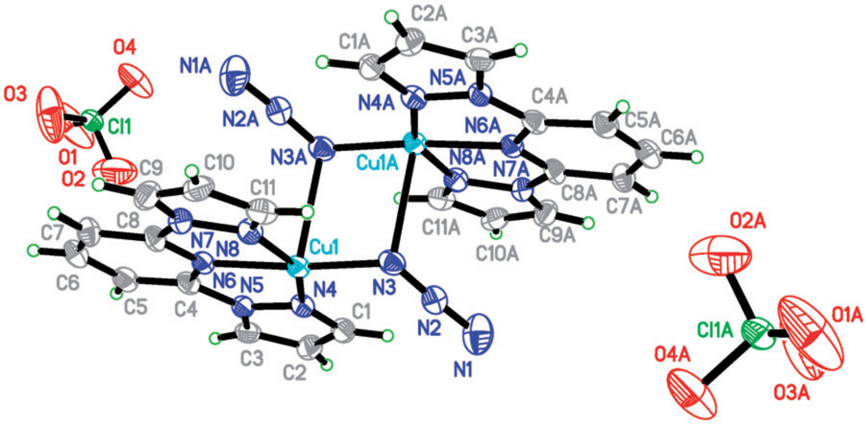

Figure 1. Coordination diagram of the binuclear complex with atom numbering scheme.

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

Cu1–N3	1.926(4)	Cu1–N6	1.960(3)	Cu1–N4	2.031(4)
Cu1–N8	2.061(4)	Cu1–N3A	2.491(4)	N1–N2	1.150(6)
N2–N3	1.178(5)				
N3–Cu1–N6	174.72(16)	N3–Cu1–N4	104.90(16)		
N6–Cu1–N4	78.88(15)	N3–Cu1–N8	98.59(16)		
N6–Cu1–N8	77.90(15)	N4–Cu1–N8	156.29(15)		
N3–Cu1–N3A	81.79(15)	N4–Cu1–N3A	96.99(14)		
N6–Cu1–N3A	94.17(13)	N8–Cu1–N3A	89.40(15)		
Cu1–N3–Cu1A	98.21(18)	N1–N2–N3	177.1(5)		

Symmetric code: N3A and Cu1A: $2-x$, $2-y$, $2-z$.

The distortion degree of the coordination polyhedron from square pyramid to trigonal bipyramid can be assessed by the Addison parameter [33] ($\tau = (\beta - \alpha)/60 = 0.31$). Figure 1 reveals that this binuclear Cu(II) complex resulted from a pair of mononuclear units related by a crystallographic inversion center, which lies in the middle of Cu1 and Cu1A. In the binuclear Cu(II) complex, azide is an end-on bridging ligand linking Cu(II) with a separation of 3.3595(11) Å. The significant difference between the bond lengths of Cu1–N3 (1.926(4) Å) and Cu1–N3A (2.491(4) Å) further indicates the asymmetric basal–apical end-on coordination for azide. The Cu1–N3–Cu1A angle is 98.21(18)°, in the range of other basal–apical Cu(II) complexes. Table 2 details the Cu–N bond lengths (basal and apical) and the angles Cu–N–Cu of binuclear copper(II) complexes with double azides in asymmetric basal–apical end-on coordination.

3.3. *Magnetic property*

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 2.51 BM, which is slightly larger than that of uncoupled binuclear Cu(II) ion (2.45 BM for $g_{\text{av}} = 2$) at room temperature. The μ_{eff} values slowly decrease as temperature drops until 12.0 K with $\mu_{\text{eff}} = 2.18$ BM, and then the μ_{eff} values increase slightly as temperature decreases, reaching the maximum of 2.25 BM at 2.0 K. The behavior below 12 K may be attributed to the presence of a paramagnetic impurity [34] and the behavior above 12 K suggests that there is a weak anti-ferromagnetic interaction between the bridging binuclear Cu(II) ions. Fitting susceptibility data with the Curie–Weiss law gives the Weiss constant $\theta = -7.83$ K as shown in figure 3, indicating a very weak anti-ferromagnetic coupling between the bridging binuclear Cu(II) ions. For Cu(II) complexes with double azide basal–apical end-on bridging, no clear correlation between the structure and magnetism has been obtained to date, although the correlation of relevant magnetism with Cu–N bond lengths (basal and apical) and angles Cu–N–Cu are shown in table 2. The magnetic coupling of the present complex is similar to that of the related complexes; for this type of complex there is ferromagnetic and anti-ferromagnetic coupling, generally very weak with maximum J absolute values ($H = -JS_1S_2$) of only 35.0 cm^{-1}. From the reported magnetic data that deal with binuclear Cu(II) complexes

Table 2. Selected magneto-structural data for binuclear square-pyramidal complexes with azide as double basal–apical end-on bridges.

Complex	Cu–N (azido, basal, Å)	Cu–N (azido, apical, Å)	Cu–N–Cu (°)	J (cm^{-1})	References
1	1.975(4)	2.536(4)	96.7(2)	Weak	[19]
2	1.954(7)	2.269(6)	96.3(3)	$\theta = 0.5$ K	[20]
3	2.039(7)	2.440(7)	90.5(2)	−1.8	[21]
4	2.020(4)	2.546(5)	86.8(9)	−3.1	[21]
5	2.060(8)	2.475(9)	93.6(2)	+2.9	[21]
6	1.999	2.443(9)	88.3	−2.63	[22]
7	1.985	2.447(6)	93.0	−1.79	[22]
8	2.016	2.550(8)	90.8	−5.37	[22]
9	2.022(4)	2.398(4)	101.0(2)	Weak anti-ferromagnetic	[23]
10	1.998(3)	2.505(3)	89.1	−8.5(5)	[24]
11	2.010(3)	2.473(3)		−4.84	[25]
12	2.019(4)	2.551(4)	86.9(1)	24	[26]
13	1.990(9)	2.569(9)	90.4	−4.2	[27]
14	2.098(3)	2.513(4)	92.50(13)	−16.8	[28]
15	1.993(3)	2.500(3)	92.0(1)	35.0	[29]
16	2.016(4)	2.381(4)	98.84(15)	−3.06	[30]
17	1.926(4)	2.491(4)	98.21(18)	$\theta = -7.830$ K	This study

1: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L1)_2] \cdot 2[ClO_4]$ (L1 = 1-(imidazol-4-yl)-2-[(2-pyridylmethylene)amino]ethane).
2: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L2)_2] \cdot [PF_6]$ (L2 = 2,2′ : 6′2″-terpyridine).
3: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L3)_2]$ (HL3 = N-(3-aminopropyl)salicylaldimine).
4: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L4)_2]$ (HL4 = 7-amino-4-methyl-5-azahept-3-en-one).
5: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L5)_2]$ (HL5 = 8-amino-4-methyl-5-azaoct-3-en-one).
6: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L6)_2]$ (HL6 = N-[2-(ethylamino)ethyl]salicylaldimine).
7: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L7)_2]$ (HL7 = 7-(ethylamino)-4-methyl-5-azahept-3-en-2-one).
8: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L8)_2]$ (HL8 = 7-amino-4-methyl-5-azaoct-3-en-2-one).
9: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L9)_2] \cdot (ClO_4)_2$ (L9 = dipropylenetriamine).
10: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L10)_2]$ (L10 = 1-(N-salicylideneamino)-2-aminoethane).
11: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L11)_2(N_3)_2]$ (L11 = 1,3-diaminopropane).
12: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L12)_2]$ (L12 = 7-amino-4-methyl-5-aza-3-hepten-2-onato(1-)).
13: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L13)_2]$ (L13 = 1-(orth-hydroxyacetophenimine)-2-aminoethane).
14: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L14)_2]$ (L14 = methyldiethylenetriamine).
15: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L15)_2(N_3)_2]$ (L15 = 1-phenyl-2-(2-pyridyl)-1-azapropylene).
16: $[Cu_2(\mu_{1,1}\text{-}N_3)_2(L16)_2]$ (L16 = 1-(2-aminoethyl)piperidine).

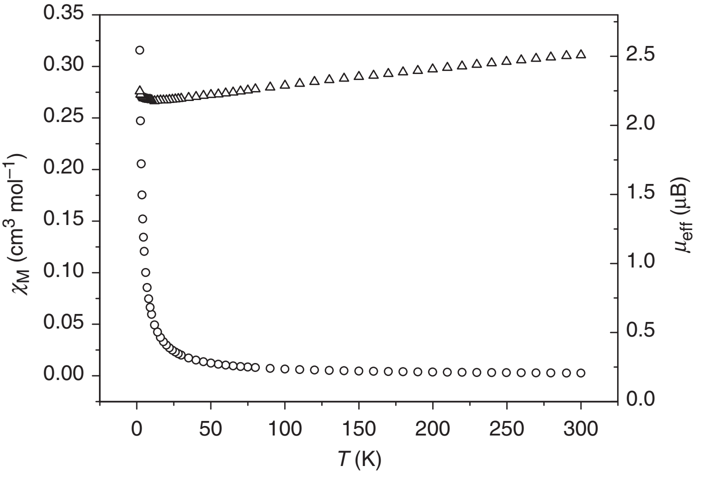

Figure 2. Plots of χ_M (open circle for experimental data) and μ_{eff} (triangle for experimental data) *vs.* T for the complex.

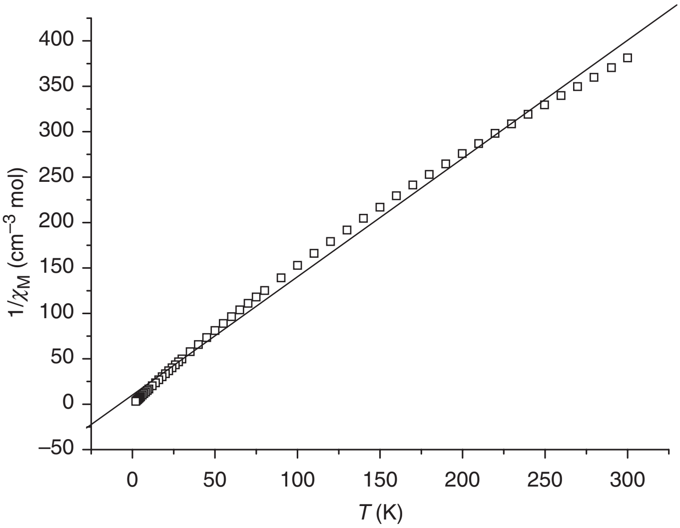

Figure 3. Thermal variation of the reciprocal susceptibility (open square for experimental data).

with double azides as basal–apical end-on bridges, it is hard to correlate the magnetism with the relevant bond parameters.

4. Conclusion

In this work, a new binuclear copper(II) complex was synthesized with asymmetric end-on bridge double azide and its crystal structure was determined. The magnetic study indicates that there is a very weak anti-ferromagnetic interaction between the bridged binuclear copper(II) complexes, similar to the relevant complexes with asymmetric end-on bridging double azide.

Supplementary material

CCDC 751330 contains detailed information of the crystallographic data for this article, and these data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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