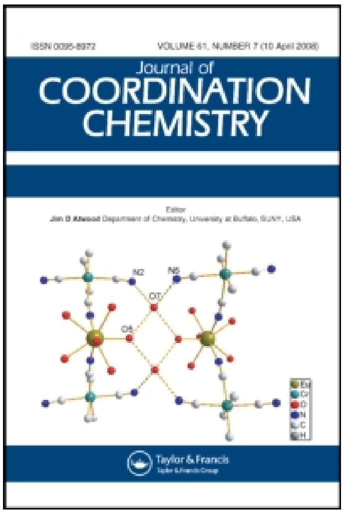

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A new double asymmetric $\mu_{1,1}$-azido bridged binuclear copper(II) complex: crystal structure and magnetic properties

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A new double asymmetric $\mu_{1,1}$-azido bridged binuclear copper(II) complex: crystal structure and magnetic properties

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A new double asymmetric $\mu_{1,1}$-azido bridged binuclear copper(II) complex, $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{Him2-py})_2(N_3)_2]$ (Him2-py = 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-hydroxy), has been synthesized and characterized structurally and magnetically. The crystal structure shows this complex is binuclear with copper(II) in a distorted square-pyramidal geometry, bridged by double asymmetric end-on azide ligands. The variable temperature magnetic susceptibility analyses reveal weak antiferromagnetic interaction mediated by the bridge.

Keywords: Asymmetric azide bridge; Copper(II) complex; Crystal structure; Magnetic properties

1. Introduction

The design and synthesis of polynuclear transition metal complexes attract attention for understanding structural and chemical factors that govern magnetic exchange coupling between paramagnetic centers and for developing new functional molecular-based materials [1]. In this context, azide as a versatile bridge and good mediator to transmit magnetic coupling, has evoked considerable interest [2]. The azide can bind metal ions in the modes of $\mu_{1,1}$(end-on, EO) [3], $\mu_{1,3}$(end-to-end, EE) [4], $\mu_{1,1,1}$ [5], $\mu_{1,1,3}$ [6] and others. Normally, the end-to-end mode gives antiferromagnetic coupling while the end-on transmits ferromagnetic coupling. For the copper-azide system, complexes with double symmetric end-to-end bridges are strongly antiferromagnetic. Those with double symmetric end-on bridges are usually strongly ferromagnetic; however, the ferromagnetic exchange coupling is expected to decrease with increasing Cu–N–Cu bridge angle, and the end-on azido bridge can transmit antiferromagnetic coupling when the bridge angles are around 108° [7–9]. More recent DFT calculations suggest a lower angle (~104°) [10]. For complexes with double asymmetric end-on bridges involving short and long Cu–N bonds, the situations are less clear since literature for this bridging mode is limited. New complexes with this kind of coordination are

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necessary to draw clearer magneto-structural conclusions. Hence we report herein the synthesis, structure and magnetic properties of a new binuclear complex with asymmetric double end-on azide bridges $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{Him2-py})_2(N_3)_2]$ (**1**), where Him2-py is 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-hydroxy.

2. Experimental

2.1. *General*

All reagents were purchased from commercial sources and used as received. 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1,3-dihydroxy (H_2im2-py) was prepared by the literature method [11]. Elemental analysis for carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer elemental analyzer model 240. The infrared spectra were recorded in KBr pellets in the range 4000–400 cm^{-1} on a Bruker Tensor 27 IR spectrometer. Variable-temperature magnetic susceptibilities were measured on a MPMS XL-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal′s constants for all constituent atoms.

2.2. *Synthesis*

$[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{Him2-py})_2(N_3)_2]$ (**1**): An aqueous solution (10 mL) of NaN_3 (0.026 g, 0.4 mmol) was added to a methanol solution (20 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.0482 g, 0.2 mmol) and H_2im2-py (0.0476 g, 0.2 mmol). After the resulting solution was stirred for 2 h and filtered off, the filtrate was kept at room temperature for one week and deep green crystals were obtained. Yield 0.044 g (60%). Anal. Calcd for $C_{24}H_{34}Cu_2N_{18}O_2$(%): C, 39.29; H, 4.67; N, 34.34. Found C, 39.07; H, 4.33; N, 33.44. IR (KBr, cm^{-1}): $\nu = 3167$(s), 2066 (s), 1615(s), 1390 (s), 1320 (s).

2.3. *X-ray crystallographic study*

Single crystal X-ray diffraction data for **1** were collected on a Bruker SMART 1000 CCD diffractometer employing graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full matrix least-squares on F^2 using SHELXS 97 [12] and SHELXL 97 [13]. Non hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. The crystallographic data are listed in table 1, and selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of the crystal structure*

An ORTEP drawing of **1** is shown in figure 1. The crystal structure consists of binuclear units $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{Him2-py})_2(N_3)_2]$ in which the copper(II) ions are bridged by two

Table 1. Crystallographic data for **1**.

Empirical formula	$C_{12}H_{17}CuN_9O$
Formula weight	366.89
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions (Å, °)	
a	10.875(3)
b	7.266(2)
c	20.067(6)
β	93.521(4)
Volume (Å)	1582.6(8)
Z	4
Calculated density ($g\,cm^{-3}$)	1.540
Absorption coefficient (mm^{-1})	1.400
$F(000)$	756
Crystal size (mm^3)	0.28 × 0.20 × 0.16
Theta range for data collection (°)	2.68 – 26.48
Limiting indices	$-13 \le h \le 13$, $-6 \le k \le 9$, $-17 \le l \le 25$
Reflections collected/unique	8854/3251 [$R_{int} = 0.0256$]
Data/restraints/parameters	3251/1/216
Goodness-of-fit on F^2	1.022
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0315$, $wR_2 = 0.0724$
R indices (all data)	$R_1 = 0.0472$, $wR_2 = 0.0793$
Largest diff. peak and hole ($e\,Å^{-3}$)	0.299 and −0.265

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

Cu(1A)–N(4A)	1.961(2)	Cu(1A)–N(2A)	1.9999(18)
Cu(1A)–N(7A)	1.964(2)	Cu(1A)–N(1A)	2.049(2)
Cu(1A)–N(4B)	2.531	O(1A)–N(3A)	1.407(3)
O(1A)–H(1A)	0.839(10)		
N(4A)–Cu(1A)–N(7A)	94.71(10)	N(5A)–N(4A)–Cu(1A)	123.44(19)
N(4A)–Cu(1A)–N(2A)	169.32(9)	N(6A)–N(5A)–N(4A)	176.2(3)
N(7A)–Cu(1A)–N(2A)	95.57(9)	N(8A)–N(7A)–Cu(1A)	130.4(2)
N(4A)–Cu(1A)–N(1A)	90.07(9)	N(9A)–N(8A)–N(7A)	175.6(3)
N(7A)–Cu(1A)–N(1A)	173.90(9)	Cu(1A))–N(4A)–Cu(1B)	94.25(8)°

asymmetric azido ions in end-on fashion. The H_2im2-py changes to 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-hydroxy(Him-2-py) and coordinates to copper(II) by its two imino nitrogen atoms. The copper(II) ion has a 4 + 1 distorted square pyramidal environment with N(1A), N(2A), N(4A) and N(7A) in the basal plane where two nitrogen atoms (N(1A), N(2A)) are from Him2-py ligand and two nitrogen atoms are from two azido ligands; one (N(4A)) from the bridging azide, the other (N(7A)) from terminal azide. The Cu(1A)–N(1A), Cu(1A)–N(2A), Cu(1A)–N(7A) and Cu(1A)–N(4A) in-plane distances are 2.049(2), 1.9999(18), 1.964(2) and 1.961(2) Å, respectively. The axial position is occupied by one nitrogen atom (N(4B)) from the other azido bridge, the corresponding axial bond distance [2.531 Å for Cu(1A)–N(4B)] is longer than the equatorial bond distance. The copper atom is displaced toward the apical site by 0.0544 Å. The azido bridge is quasi-linear [176.2(3)° for N(4A)–N(5A)–N(6A)] and the bond angle Cu(1A)–N(4B)–Cu(1B) is 94.25(8)°. The copper—copper separation through double end-on azido bridges is 3.315 Å. Intermolecular hydrogen bonds are formed due to the short contacts (O(1A)–N′(9A): 2.798 Å) between the hydroxyl groups of Him2-py ligands and the azido groups of the neighboring dimers, which result in a two-dimensional network (figure 2).

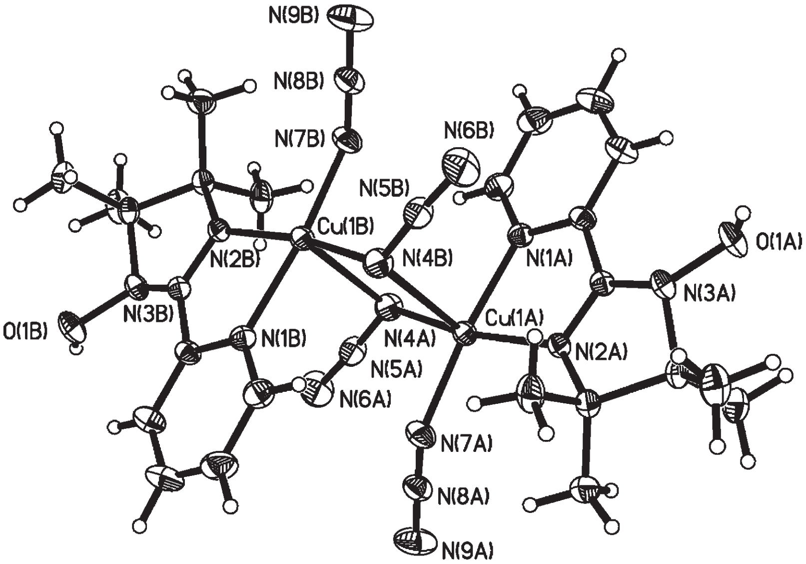

Figure 1. ORTEP drawing with 30% termal ellipsoid probability showing atom labeling of **1**.

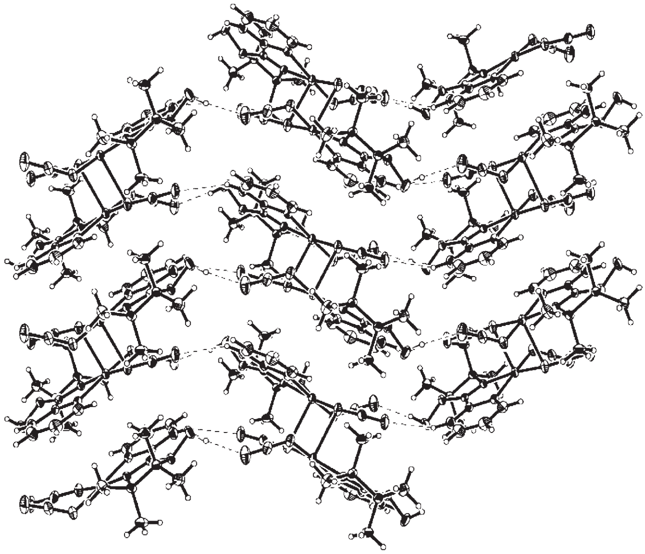

Figure 2. View showing two-dimensional network formed by hydrogen bonds in **1**.

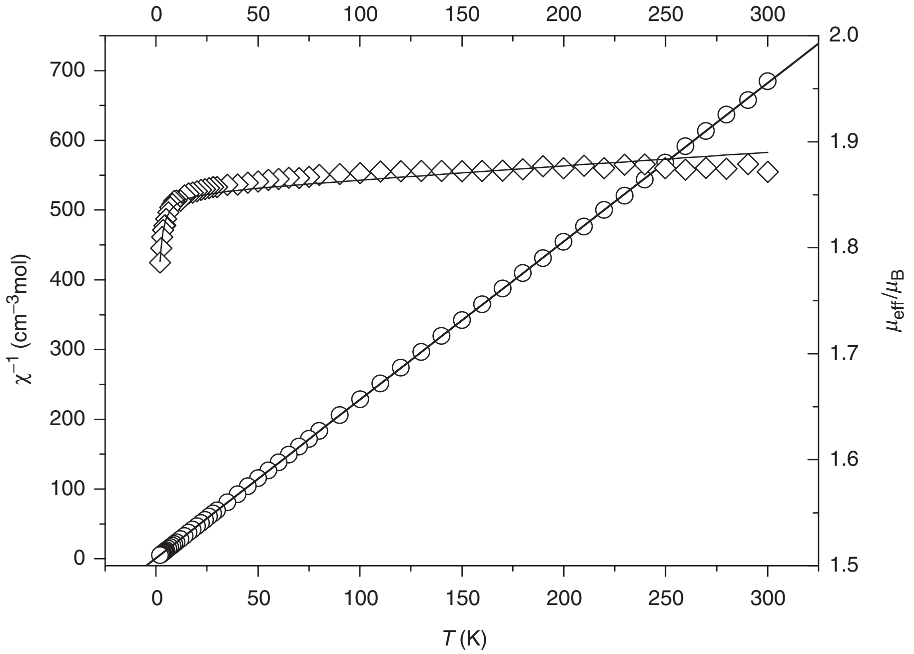

Figure 3. Plots of $\chi^{-1}{}_M$ (o) and μ_{eff} (◇) *vs.* T of **1**. The solid line corresponds to the best fit.

3.2. *Magnetic properties*

The temperature dependence of the magnetic susceptibility for the complex was measured in the temperature range 2.0–300 K in the applied field of 2000 G. The magnetic susceptibility data in the form of $1/\chi_M$ and μ_{eff} *versus* T plots are given in figure 3. At room temperature, the μ_{eff} value is 2.65 μ_B, which is slightly higher than expected (2.45 μ_B) for two isolated $S = 1/2$ spins assuming $g = 2.00$. This value smoothly decreases upon cooling and reaches 2.52 μ_B at 2.0 K. The magnetic susceptibility data follows the Curie–Weiss law with $C = 0.88\,\text{cm}^3\,\text{K}\,\text{mol}^{-1}$ and $\Theta = -0.50$ K. The C value corresponds to the value expected for copper(II) ion with $g = 2.16$. The results suggest antiferromagnetic interaction between copper(II) ions. To estimate the magnitude of the antiferromagnetic coupling, the magnetic susceptibility data were fit to the Bleaney–Bowers equation [14] for two interacting copper(II) ions with the Hamiltonian in the form $\hat{H} = -J\hat{S}_1\hat{S}_2$. The magnetic susceptibility equation for such a dimeric system can be expressed as

$$x_{\text{bi}} = \frac{2\text{N}g^2\beta^2}{kT[3 + \exp(-J/\text{kT})]}$$

Considering intermolecular magnetic interaction, the mean field approximation, zJ', was introduced. The magnetic susceptibility of the complex is

$$\chi_M = \frac{\chi_{\text{bi}}}{[1 - zJ'x_{\text{bi}}/\text{N}g^2\beta^2)]}$$

The best fit of the experimental data leads to $g = 2.15$, $J = -0.30\,\text{cm}^{-1}$, $zJ' = -0.06\,\text{cm}^{-1}$, and $R = 2.96 \times 10^{-6}$ (R value is defined as $[(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calc}}]^2/\Sigma[(\chi_M)_{\text{obs}}]^2$). The results

Table 3. Structural and magnetic parameters for Cu(II)-$\mu_{1,1}$-N_3 complexes involving only asymmetric azido bridges ($\hat{H} = -J\hat{S}_1\hat{S}_2$).

Complex	Short Cu–N(Å)	Long Cu–N(Å)	Cu–N–Cu angle (°)	J(cm^{-1})	Ref.
$[Cu_2(L1)_2(N_3)_2]$	1.998(3)	2.505(3)	89.1	−8.5	[16]
$[Cu_2(L2)_2(N_3)_2]$	1.990(9)	2.569(9)	90.4	−4.2	[17]
$[Cu_2(L3)_2(N_3)_2]$	1.988(4)	2.409(5)	96.2(2)	−12.18	[18]
$[Cu_2(L4)_2(N_3)_2]$	1.986(5)	2.318(5)	97.5(2)	−4.43	[18]
$[Cu_2(L5)_2(N_3)_2]$	2.039(7)	2.440(7)	90.5	−1.84	[19]
$[Cu_2(L6)_2(N_3)_2]$	1.988(10)	2.443(9)	88.3	−2.63	[20]
$[Cu_2(L7)_2(N_3)_2]$	1.985(6)	2.447(6)	93.0	−1.79	[20]
$[Cu_2(L8)_2(N_3)_2]$	2.016(4)	2.381(4)	98.8	−3.06	[21]
$[Cu_2(L9)_2(N_3)_2](ClO_4)_2$	1.972(7)	2.563(8)	98.31(8)	−3.20	[22]
$[Cu_2(L10)_2(N_3)_2(H_2O)_2](PF_6)_2$	1.927(6)	2.851(5)	95.0(7)	−5.80	[7]
$[Cu_2(L11)_2(N_3)_2](ClO_4)_2$	2.098(3)	2.513(4)	92.5	−16.8	[23]
$[Cu_2(L12)_2(N_3)_2]$	2.019(4)	2.551(4)	86.9(1)	+24.0	[24]
1	1.961(2)	2.531	94.25(8)	−0.30	This work

L1 = 1-(*N*-salicylideneamino)-2-aminoethane; L2 = 1-*N*-*ortho*-hydroxyacetophenimine)-2-aminoethane; L3 = *N*-pyridin-2-yl-methylene-propane-1,3-diamine; L4 = *N*-(1-pyridin-2-yl-ethylidene)propane-1,3-diamine; L5 = *N*-(3-aminopropyl) salicylaldimine; L6 = *N*-[2-(ethylamino)ethyl]salicylaldimine; L7 = 7-(ethylamino)-4-methyl-5-azaphept-3-en-2-one; L8 = 1-(2-aminoethyl)piperidine; L9 = *N*,*N*-*bis*(2-methylpyridyl)(3,5-dimethyl-2-hydroxybenzyl)amine; L10 = 2,2′: 6′,2″-terpyridine; L11 = methyldiethylenetriamine; L12 = 7-amino-4-methyl-5-aza-3-hepten-2-onato.

clearly indicate the magnetic interaction between copper(II) ions is weak antiferromagnetic, in agreement with recent DFT calculations which show that double asymmetric end-on bridges produce antiferromagnetic coupling for copper(II) complexes [15]. Table 3 summarizes the structural and magnetic data for double asymmetric end-on bridges in the literature for magnetostructural correlations. The dependence of the magnetic coupling upon Cu–N–Cu bridging angle established for the symmetric end-on azido bridge is invalid for the asymmetric one. The data are so scattered that it is impossible to establish any general magnetostructural correlation with these limited experimental data. However the magnitude of magnetic coupling between copper(II) ions bridged by asymmetric double azides not only depends on the Cu–N–Cu bridging angle, but also depends on the Cu–N bond lengths. The weak antiferromagnetic interaction in complex **1** can be attributed to the long Cu–N bond length (2.531 Å). It is necessary to prepare new similar complexes to further explore the structural correlations of this magnetic system.

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