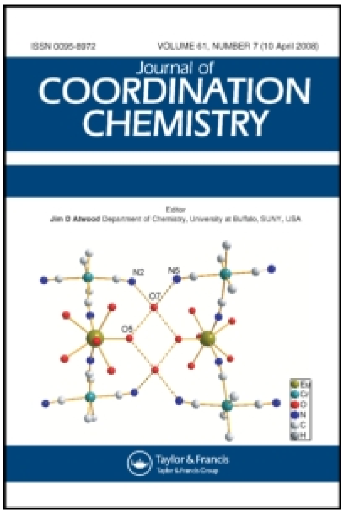

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, structures and magnetic properties of two copper(II) complexes with pyrazole and pivalate ligands

Jian-Hao Zhou[a]; Zheng Liu[a]; Yi-Zhi Li[a]; You Song[a]; Xue-Tai Chen[ab]; Xiao-Zeng You[a]
[a] Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P.R. China [b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou 350002, P.R. China

To cite this Article Zhou, Jian-Hao , Liu, Zheng , Li, Yi-Zhi , Song, You , Chen, Xue-Tai and You, Xiao-Zeng(2006) 'Synthesis, structures and magnetic properties of two copper(II) complexes with pyrazole and pivalate ligands', Journal of Coordination Chemistry, 59: 2, 147 — 156

To link to this Article: DOI: 10.1080/00958970500266206

URL: http://dx.doi.org/10.1080/00958970500266206

Journal of Coordination Chemistry
Vol. 59, No. 2, January 2006, 147–156

Synthesis, structures and magnetic properties of two copper(II) complexes with pyrazole and pivalate ligands

JIAN-HAO ZHOU†, ZHENG LIU†, YI-ZHI LI†, YOU SONG†,
XUE-TAI CHEN*†‡ and XIAO-ZENG YOU†

†Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing 210093, P.R. China
‡State Key Laboratory of Structural Chemistry, Fujian Institute of
Research on the Structure of Matter, Fuzhou 350002, P.R. China

(*Received 29 November 2004; revised 31 March 2005; in final form 18 July 2005*)

The copper(II) complexes, $[Cu^{II}_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(Hpz)(Me_3CCOO)_2]\cdot(Me_3CCOOH)_2$ (**1**) (Hpz = pyrazole) and $Cu^{II}(Hpz^*)_2(Me_3CCOO)_2$ (**2**) (Hpz* = 3,5-dimethylpyrazole), were obtained from the reactions of $Cu(NO_3)_2\cdot 3H_2O$ with Me_3CCOOK and Hpz/Hpz* in ethanol. The complex **1** is made up of a trinuclear core $[Cu_3(\mu_3\text{-}OH)]^{5+}$ with a nearly isosceles triangle, surrounded by three bidentate bridging pyrazolate ligands. Two adjacent molecules of **1** are connected by hydrogen bonds to form a dimer. The magnetic susceptibility of **1** was studied, showing antiferromagnetic behavior in the 1.8–300 K range. The complex **2** shows a *trans*-N_2O_2 square-planar geometry for the Cu(II) center. The crystal structure of **2** exhibits a one-dimensional chain arrangement mediated by intermolecular H-bonds.

Keywords: Copper(II) complex; Pyrazole; Pivalic acid; Crystal structure; Magnetism

1. Introduction

Metal complexes with pyrazole and its derivatives have attracted much research interest for their versatile coordination chemistry and interesting properties [1–3]. Pyrazole and its derivatives exhibit several coordination modes, particularly as the bridging unit to link metal ions to form polynuclear metal complexes [3]. Recently, polynuclear copper(II) complexes have received increasing attention for their interesting magnetic properties [4] and biological relevance [5]. Trinuclear copper(II) complexes have been of particular significance for their simulation of the bioactive sites of a number of multicopper blue oxidases [5]. Several copper(II)–pyralato complexes with different nuclearity including the $[Cu^{II}_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3]^{2+}$ (Hpz = pyrazole) core have been reported [6–17]. On the other hand, carboxylate ligand is particularly useful in the build-up of novel polynuclear metal complexes due to its bridging capability [18].

---

*Corresponding author. Email: xtchen@netra.nju.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500266206

We have been interested in the self-assembly of novel polynuclear metal complexes employing both pyrazole and carboxylate as bridging ligands [19]. As a part of our research on metal complexes with pyrazole and carboxylate ligands [19], we report here the synthesis and crystal structures of two copper(II) complexes, $[Cu^{II}_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(Hpz)(Me_3CCOO)_2]\cdot(Me_3CCOOH)_2$ (**1**) and $Cu^{II}(Hpz^*)_2(Me_3CCOO)_2$ (**2**) (Hpz* = 3,5-dimethylpyrazole). The magnetic properties of **1** are also reported.

2. Experimental

Pyrazole and pivalic acid were purchased from the Acros Chemical Co. and used without further purification. Me_3CCOOK was synthesized in water by treatment of Me_3CCOOH with KOH in 1 : 1 molar ratio. 3,5-dimethylpyrazole was prepared according to literature methods [20].

2.1. *Synthesis of 1 and 2*

To a 10 mL ethanol solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.136 g, 0.56 mmol) was added Me_3CCOOK (0.236 g, 1.68 mmol) and pyrazole (0.076 g, 1.12 mmol) while stirring. The resulting solution was stirred at room temperature for 5 h and then filtered. Blue crystals of **1** were obtained by slow evaporation of the resulting solution. Yield 75%. Anal. Calcd for $C_{32}H_{52}Cu_3N_8O_9$ (%): C, 43.51; H, 5.93; N, 12.68. Found: C, 43.73; H, 6.20; N, 12.51.

To a 10 mL ethanol solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.136 g, 0.56 mmol) was added Me_3CCOOK (0.158 g, 1.12 mmol) and 3,5-dimethylpyrazole (0.108 g, 1.12 mmol) while stirring. The resulting solution was stirred at room temperature for 5 h and then filtered. Some uncharacterized green material created by slow evaporation of the mother liquor was filtered off, before violet crystals of **2** were obtained. Yield 60%. Anal. Calcd for $C_{20}H_{34}CuN_4O_4$ (%): C, 52.44; H, 7.48; N, 12.23. Found: C, 52.65; H, 7.76; N, 12.41.

2.2. *Physical measurements*

Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. Magnetic susceptibilities on powder samples of **1** were carried out with a Quantum Design MPMS-XL SQUID magnetometer in the 1.8–300 K range. The applied magnetic field was 2 KG, and the data were corrected for diamagnetism using Pascal's constants and the temperature independent paramagnetism estimated at 60×10^{-6} emu mol^{-1} per Cu(II) ion.

2.3. *X-ray crystallography*

The data for **1** and **2** were collected on a Bruker SMART-CCD diffractometer with graphite monochromated Mo-Kα ($\lambda = 0.710732$ Å) and corrected for absorption using the SADABS program [21]. The two structures were solved by direct methods and refined on F^2 against all reflections by full-matrix least-squares methods

Table 1. Crystal data and structure refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_{32}H_{52}Cu_3N_8O_9$	$C_{20}H_{34}CuN_4O_4$
Formula mass	883.44	458.05
Crystal size (mm)	0.07 × 0.17 × 0.32	0.10 × 0.10 × 0.33
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.682(2)	5.9440(16)
b (Å)	12.976(3)	10.004(3)
c (Å)	16.989(3)	10.615(3)
α (°)	75.753(4)	96.572(5)
β (°)	88.698(4)	106.123(4)
γ (°)	66.465(3)	99.429(4)
V (Å^3)	2084.9(7)	589.6(3)
T (K)	293(2)	293(2)
Z	2	1
D_{Calcd} (g cm^{-3})	1.407	1.290
μ(Mo-Kα) (cm^{-1})	1.572	0.957
F(000)	918	243
θ range	2.09 to 25.25	2.09 to 25.09
Limiting indices	$-12 \le h \le 12$, $-15 \le k \le 15$, $-20 \le l \le 10$	$-7 \le h \le 7$, $-11 \le k \le 11$, $-12 \le l \le 8$
Total reflections	10659	2967
Independent reflections	7407	2078
Observations [$I > 2\sigma(I)$]	6193	1950
R_{int}	0.0213	0.066
Data/restraints/parameters	7407/0/574	2078/0/138
Goodness-of-fit on F^2	1.022	1.000
Final $R1/wR2$ indices [$I > 2\sigma(I)$]	0.0548/0.1435	0.0512/0.1347
$R1/wR2$ indices (all data)	0.0687/0.1498	0.0537/0.1370
Largest diff. peak/hole [e Å^{-3}]	0.56/−0.92	0.63/−0.54

with SHELXTL program [22]. The hydrogen atoms H9A, H7B and H3B in **1** were found in a difference Fourier map and not refined; the remaining hydrogens in both compounds were positioned geometrically and refined in the riding-model approximation. All non-hydrogen atoms were refined anisotropically. Some disorder was detected for the carbon atoms of the t-butyl groups in **1**, which were refined over two sites (see table 2 for positional data), yielding occupation factors of 0.582(15), 0.582(15), 0.554(12), 0.554(12), 0.554(12), 0.63(3), 0.63(3), 0.63(3) and 0.56(8) for C13, C14, C18, C19, C20, C23, C24, C25 and C29, respectively. Crystal data and structure refinement details of **1** and **2** are summarized in table 1. The selected bond lengths and angles of **1** and **2** are given in table 2.

3. Results and discussion

3.1. *Crystal structures*

The crystal structure determination reveals that **1** consists of a nine-membered [Cu–N–N]$_3$ metallacycle with a μ_3-OH group (see figure 1 and table 2). The remaining coordination site in the square planar geometry on Cu1(Cu2) is occupied by an oxygen atom from one pivalate ligand, whereas that on Cu3 is occupied by a nitrogen atom from one pyrazole molecule. The μ_3-O atom is located 0.567 Å above the Cu$_3$ plane, which is close to that of [Cu$^{II}_3$(μ_3-OH)(μ-pz)$_3$(MeCOO)$_2$(Hpz)] (0.563 Å) [6].

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

Compound **1**			
Cu(1)–N(1)	1.928(4)	Cu(3)–N(6)	1.939(4)
Cu(1)–N(5)	1.938(4)	Cu(3)–N(4)	1.946(4)
Cu(1)–O(1)	1.968(3)	Cu(3)–N(7)	1.994(4)
Cu(1)–O(3)	1.975(3)	Cu(3)–O(3)	2.000(3)
Cu(2)–N(2)	1.934(4)	Cu1 ··· Cu3	3.2950(8)
Cu(2)–N(3)	1.947(4)	Cu1 ··· Cu2	3.3839(9)
Cu(2)–O(2)	1.996(3)	Cu2 ··· Cu3	3.2504(9)
Cu(2)–O(3)	2.008(3)		
N(1)–Cu(1)–N(5)	162.05(16)	O(2)–Cu(2)–O(3)	170.88(12)
N(1)–Cu(1)–O(1)	90.75(15)	N(6)–Cu(3)–N(4)	163.24(15)
N(5)–Cu(1)–O(1)	94.62(16)	N(6)–Cu(3)–N(7)	94.67(18)
N(1)–Cu(1)–O(3)	90.16(14)	N(4)–Cu(3)–N(7)	91.64(17)
N(5)–Cu(1)–O(3)	88.00(14)	N(6)–Cu(3)–O(3)	88.84(14)
O(1)–Cu(1)–O(3)	168.43(12)	N(4)–Cu(3)–O(3)	87.80(13)
N(2)–Cu(2)–N(3)	169.83(15)	N(7)–Cu(3)–O(3)	169.21(14)
N(2)–Cu(2)–O(2)	92.36(15)	Cu(1)–O(3)–Cu(3)	111.98(13)
N(3)–Cu(2)–O(2)	92.60(15)	Cu(1)–O(3)–Cu(2)	116.32(14)
N(2)–Cu(2)–O(3)	90.16(14)	Cu(3)–O(3)–Cu(2)	108.40(12)
N(3)–Cu(2)–O(3)	86.32(14)		
Compound **2**			
Cu(1)–O(1)#1	1.962(2)	Cu(1)–N(1)#1	1.985(3)
Cu(1)–O(1)	1.962(2)	Cu(1)–N(1)	1.985(3)
O(1)#1–Cu(1)–O(1)	180.00(8)	O(1)#1–Cu(1)–N(1)	90.39(10)
O(1)#1–Cu(1)–N(1)#1	89.61(10)	O(1)–Cu(1)–N(1)	89.61(10)
O(1)–Cu(1)–N(1)#1	90.39(10)	N(1)#1–Cu(1)–N(1)	180.000(1)

Symmetry code: #1: $-x+1, -y+1, -z+1$.

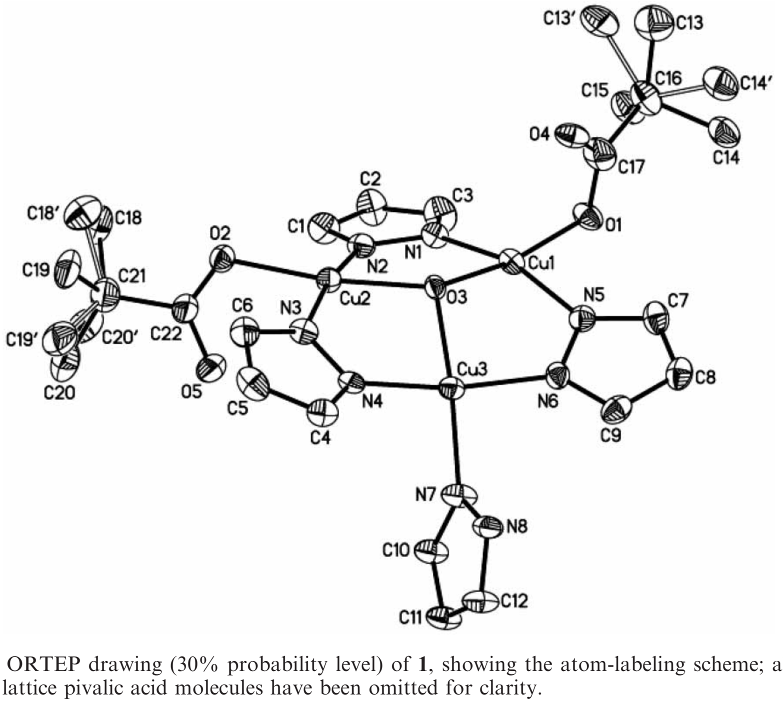

Figure 1. ORTEP drawing (30% probability level) of **1**, showing the atom-labeling scheme; all hydrogen atoms and lattice pivalic acid molecules have been omitted for clarity.

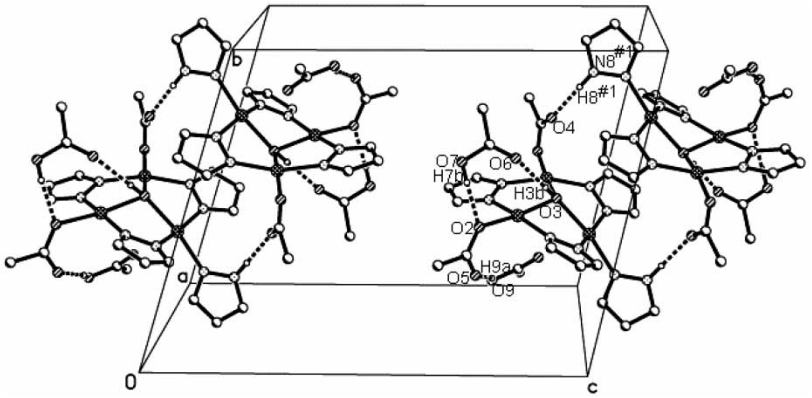

Figure 2. The dimer structure of **1** (symmetry code: #1 $1-x$, $1-y$, $2-z$). Dashed lines indicate hydrogen bonds. All methyl groups have been omitted for clarity.

Table 3. Hydrogen bond distances (Å) and hydrogen bond angles (°) for **1** and **2**.

D–H···A	D–H	H···A	D···A	D–H···A
Compound **1**				
N(8)–H(8)···O(4)#1	0.86	1.85	2.710(5)	175.3
O(3)–H(3B)···O(6)	0.85	2.21	3.062(5)	180.0
O(7)–H(7B)···O(2)	0.85	1.89	2.694(5)	157.9
O(9)–H(9A)···O(5)	0.85	1.84	2.650(5)	159.1
Compound **2**				
N(2)–H(2)···O(2)#2	0.86	1.96	2.746(4)	151.9

Symmetry codes: #1: $1-x$, $1-y$, $2-z$; #2: $-x+2$, $-y+1$, $-z+1$.

The deviations of Cu1 from the Cu1–N1–N5–O1–O3 plane (a), Cu2 from the Cu2–N2–N3–O2–O3 plane (b) and Cu3 from the Cu3–N4–N6–N7–O3 plane (c) are 0.0387(14), 0.0000(14) and −0.0345(15) Å, respectively. The dihedral angle of 6.05(17)° between (a) and (b) is smaller than those of 41.18(13)° between (a) and (c) and 47.22(11)° between (b) and (c). The Cu atoms define a nearly isosceles triangle with three Cu···Cu distances of 3.3839(9) Å (Cu1···Cu2), 3.2950(8) Å (Cu1···Cu3) and 3.2504(9) Å (Cu2···Cu3), respectively. The Cu–O3–Cu bond angles are similar [(Cu1–O3–Cu3) 111.98(13)°, (Cu2–O3–Cu3) 108.40(12)°, (Cu1–O3–Cu2) 116.32(14)°]. The average Cu–O3 bond distance 1.994(3) Å is longer than that reported for $[Cu^{II}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(MeCOO)_2(Hpz)]$ (1.967(5) Å) [6]. The average Cu···Cu distance of 3.3098 Å and Cu–O(H)–Cu bond angle in **1** are comparable with those found in complexes with a $[Cu^{II}_3(\mu_3\text{–OH})(\mu\text{-pz})_3]$ core (see table 4). In the crystal structure of **1**, there are hydrogen bonds between the trinuclear molecules and the two uncoordinated pivalic acids. Two trinuclear units are linked in dimers through intermolecular H-bonds (see figure 2 and table 3).

Compound **2** is a four-coordinate mononuclear copper complex (see figure 3 and table 2). The copper in **2** is coordinated by two N atoms from two 3,5-dimethylpyrazole anions in a *trans*-configuration. The two remaining coordination sites in the square planar geometry are occupied by oxygen atoms from two pivalate ligands.

Table 4. The average Cu$\cdots$Cu distance (Å) and Cu–O(H)–Cu bond angle (°) of the compounds with a $[Cu^{II}_3(\mu_3\text{-}O(H))(\mu\text{-}pz)_3]$ core.

Compound	Av. Cu$\cdots$Cu	Av. Cu–O(H)–Cu	Reference
1	3.310	112.2	This work
$[Cu^{II}_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(Hpz)(MeCOOH)_2]$	3.256	112.1	[6]
$[PPN]\cdot[Cu^{II}_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3Cl_3]$	3.362	113.4	[7]
$[Bu_4N]\cdot[Cu^{II}_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3Cl_3]$	3.360	113.8	[7]
$[Et_3NH]\cdot[Cu^{II}_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3Cl_3(Hpz)]$	3.315	111.1	[7]
$[Cu^{II}_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(Hpz)(\mu_4\text{-}NO_3)]_2\cdot(\mu\text{-}NO_3)_2$	3.303	111.2	[8]
$[Cu^{II}_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$	3.351	114.5	[9]
$[Cu^{II}_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(py)_2Cl_2]\cdot py$, (py = pyridine)	3.251	109.6	[10]

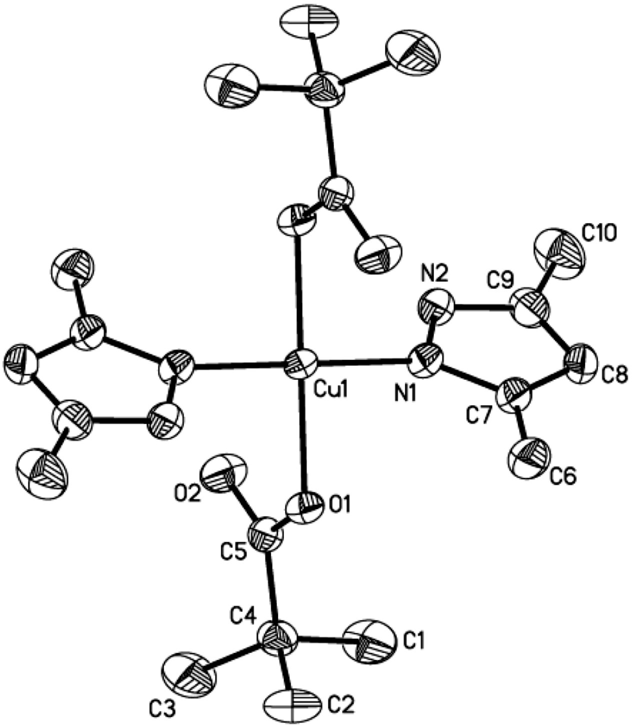

Figure 3. ORTEP drawing (30% probability level) of **2**, showing the atom-labeling scheme; all hydrogen atoms have been omitted for clarity.

The average Cu–N bond distance (1.985(3) Å) is shorter than that reported for $[Cu(Hpz^*)_4(H_2O)]\cdot(ClO_4)_2$ (2.023 Å) [23]. The N–H group of **2** forms an H-bond with the oxygen atom of the neighboring pivalate ligands as shown in figure 4 (see table 3 for geometric data), which leads to a one-dimensional chain structure for **2**.

3.2. *Magnetic properties of 1*

The temperature dependence of the magnetic susceptibility of **1**, in the form of $\chi_m T$, is shown in figure 5. The room-temperature $\chi_m T$ product ($0.645\,cm^3\,K\,mol^{-1}$)

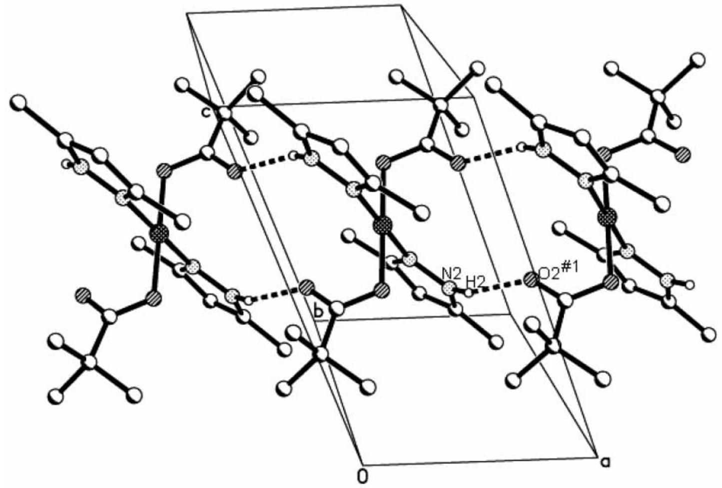

Figure 4. The one-dimensional chain structure of **2** (symmetry code: #1 $-x+2$, $-y+1$, $-z+1$). Dashed lines indicate hydrogen bonds.

is lower than expected for three uncoupled copper(II) ions. Upon cooling the product $\chi_{\mathrm{m}}T$ decreases steadily and then reaches 0.375 $\mathrm{cm^3\,K\,mol^{-1}}$ at 50 K, which is close to the spin-only value of 0.376 $\mathrm{cm^3\,K\,mol^{-1}}$ ($g = 2.0023$) for one unpaired electron. Below 50 K, the product $\chi_{\mathrm{m}}T$ further decreases to 0.344 $\mathrm{cm^3\,K\,mol^{-1}}$ (1.8 K). Apparently, the magnetic behavior reveals the antiferromagnetic behavior of **1** and the ground state is 1/2.

The HDVV model (equation 1) is used to analyze the magnetic susceptibility data of **1** (the Hamiltonian being $\hat{H} = -2J(\hat{S}1\hat{S}2) - 2J'(\hat{S}1\hat{S}3 + \hat{S}2\hat{S}3)$ for an isosceles triangle trinuclear copper(II)), where N, β, g and k have their usual meanings, and $\mathrm{TIP} = 180 \times 10^{-6}$ (fixed). The intermolecular interactions are taken into account for the experimental variation of $\chi_{\mathrm{m}}T$ at low temperature (equation 2),

$$\chi_{\mathrm{m}} = \left(\frac{N\beta^2 g^2}{4kT}\right)\frac{[(10\exp((2J+J')/kT) + \exp((2J-J')/kT) + 1)]}{(2\exp((2J+J')/kT) + \exp((2J-J')/kT) + 1)} + \mathrm{TIP} \tag{1}$$

$$\chi'_{\mathrm{m}} = \frac{\chi_{\mathrm{m}}}{[1 - (2zJ/N\beta^2 g^2 \chi_{\mathrm{m}})]} \tag{2}$$

The best set of parameters obtained (full line in figure 5a) gives $g = 1.988$, $J = -99.9\,\mathrm{cm^{-1}}$, $J' = -100.6\,\mathrm{cm^{-1}}$ and $zJ = -0.28\,\mathrm{cm^{-1}}$ with the agreement factor $R = 1.7 \times 10^{-4}$ ($R = \Sigma|(\chi_{\mathrm{m}}T)_{\mathrm{exp}} - (\chi_{\mathrm{m}}T)_{\mathrm{Calcd}}|^2/\Sigma(\chi_{\mathrm{m}}T)^2_{\mathrm{exp}}$). Apparently, the fitting is not satisfactory and the g value is too low. The product $\chi_{\mathrm{m}}T$ below 50 K is lower than the expected one unpaired electron, which suggests that other kinds of antiferromagnetic interactions are operative. A similar magnetic phenomenon has been reported [9, 10]. Antiferromagnetic interactions corresponding to intermolecular hydrogen bonding pathways might be a reason for this magnetic behavior of **1** at low temperature, considering that two adjacent molecules are connected by hydrogen bonds as shown in figure 2. Moreover, an antisymmetric interaction might exist in trinuclear copper(II) compounds, resulting in a smaller $\chi_{\mathrm{m}}T$ value than expected

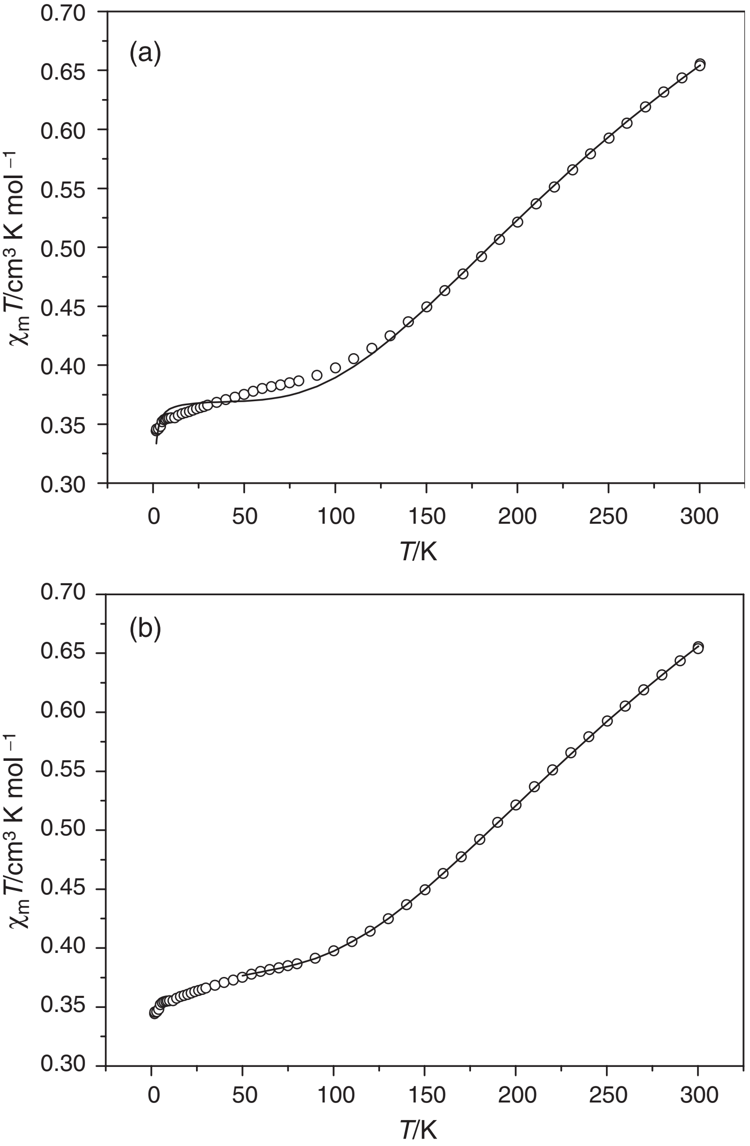

Figure 5. Plots of $\chi_m T$ *vs.* T for **1** with (a) simulation curve of the data in the range 1.8–300 K and (b) simulation curve of the data in the range 50–300 K. The solid lines represent the simulation curve and the points of the experimental data.

for one unpaired electron [24–26]. Therefore, the reason for the magnetic behavior at low temperatures is complex in this case.

A satisfactory fit is accomplished on the experimental data in the range 50–300 K (full line in figure 5b), leading to acceptable parameters: $g = 2.047$, $J = -117.7\,\text{cm}^{-1}$, $J' = -90.3\,\text{cm}^{-1}$ and $zJ = -3.0\,\text{cm}^{-1}$ with $R = 1.5 \times 10^{-6}$. In the Cu_3OH complexes, the $Cu_3(\mu_3\text{-}OH)$ core determines the magnetic properties [6, 12] and the Cu–O(H)–Cu angle is an important structure parameter to imply the value of the exchange parameter J_{Cu-Cu} [7, 27]: larger Cu–O(H)–Cu angles suggest more negative J values. The J value ($-117.7\,cm^{-1}$) is more negative than the J' value ($-90.3\,cm^{-1}$), consistent with the fact that the angle Cu1–O3–Cu2 (116.32(14)°) is larger than the other two (Cu1–O3–Cu3 111.98(13)°, Cu3–O3–Cu2 108.40(12)°).

Supplementary material

Crystallographic data of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Deposition codes: 256202 for **1** and 256201 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223-336-033: E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

The authors thank the reviewers for very helpful comments. This work was supported by Natural Science Grant of Jiangsu Province (BK 2004087) and Grant of Instruments of Nanjing University.

References

[1] S. Trofimenko. *Chem. Rev.*, **93**, 943 (1993).
[2] R. Mukheerjee. *Coord. Chem. Rev.*, **203**, 151 (2000).
[3] G. La Monica, G.A. Ardizzoia. *Prog. Inorg. Chem.*, **46**, 151 (1997).
[4] L.K. Thompson. *Coord. Chem. Rev.*, **193**, 233 (2002).
[5] W. Kaim, J. Rall. *Angew. Chem. Int. Ed. Engl.*, **35**, 43 (1996).
[6] M. Casarin, C. Corvaja, C. di Nicola, D. Falcomer, L. Franco, M. Monari, L. Pandolfo, C. Pettinari, F. Piccinelli, P. Tagliatesta. *Inorg. Chem.*, **43**, 5865 (2004).
[7] P.A. Angaridis, P. Baran, R. Boča, F. Cervantes-Lee, W. Haase, G. Mezei, R.G. Raptis, R. Werner. *Inorg. Chem.*, **41**, 2219 (2002).
[8] K. Sakai, Y. Yamada, T. Tsubomura, M. Yabuki, M. Yamaguchi. *Inorg. Chem.*, **35**, 542 (1996).
[9] F.B. Hulsbergen, R.W.T. Ten Hoedt, G.C. Verschoor, J. Reedijk, A.L. Spek. *J. Chem. Soc., Dalton Trans.*, 539 (1983).
[10] M. Angaroni, G.A. Ardizzoia, T. Beringhelli, G. La Monica, D. Gatteschi, N. Masciocchi, M.J. Moret. *J. Chem. Soc., Dalton Trans.*, 3305 (1990).
[11] W.Z. Shen, L. Yi, P. Cheng, S.P. Yan, D.Z. Liao, Z.H. Jiang. *Inorg. Chem. Commun.*, **7**, 819 (2004).
[12] R. Boča, L. Dlháň, G. Mezei, T. Ortiz-Pérez, R.G. Raptis, J. Telser. *Inorg. Chem.*, **42**, 5801 (2003).
[13] G.A. Ardizzoia, M.A. Angaroni, G. La Monica, F. Cariati, S. Cenini, M. Moret, N. Masciocchi. *Inorg. Chem.*, **30**, 4347 (1991).
[14] X.M. Liu, J.A. McAllister, M.P. de Miranda, B.J. Whitaker, C.A. Kilner, M. Thornton-Pett, M.A. Halcrow. *Angew. Chem. Int. Ed. Engl.*, **41**, 756 (2002).
[15] X.M. Liu, J.A. McAllister, M.P. de Miranda, E.J.L. McInnes, C.A. Kilner, M.A. Halcrow. *Chem. Eur. J.*, **10**, 1827 (2004).
[16] V. Chandrasekhar, S. Kingsley. *Angew. Chem. Int. Ed. Engl.*, **39**, 2320 (2000).
[17] G. Mezei, P. Baran, R.G. Raptis. *Angew. Chem. Int. Ed. Engl.*, **43**, 574 (2004).
[18] R.E.P. Winpenny. *Adv. Inorg. Chem.*, **52**, 1 (2001).
[19] J. Li, J.H. Zhou, Y.Z. Li, L.H. Weng, X.T. Chen, Z. Yu, Z.L. Xue. *Inorg. Chem. Commun.*, **7**, 538 (2004).
[20] R.H. Wiley, P.E. Hexner. *Org. Synth. Col.*, **4**, 351 (1962).
[21] G.M. Sheldrick. *Program for Empirical Absorption Correction*, University of Göttingen, Germany (2000).
[22] G.M. Sheldrick. *Program for Crystal Structure Solution and Refinement*, University of Göttingen, Germany (2000).
[23] X.Y. Chen, W.Z. Shen, P. Cheng, S.P. Yan, D.Z. Liao, Z.H. Jiang. *Z. Anorg. Allg. Chem.*, **629**, 697 (2003).

[24] X.M. Liu, M.P. de Miranda, E.J.L. Mclnnes, C.A. Kilner, M.A. Halcrow. *J. Chem. Soc., Dalton Trans.*, 59 (2004).
[25] S. Ferrer, J.G. Haasnoot, J. Reedijk, E. Müller, M.B. Cingi, M. Lanfranchi, A.M.M. Lanfredi. *J. Ribas, Inorg. Chem.*, **39**, 1859 (2000).
[26] S. Ferrer, F. Lloret, I. Bertomeu, G. Alzuet, J. Borrás, S. García-Granda, M. Liu-González, J.G. Haasnoot. *Inorg. Chem.*, **41**, 5821 (2002).
[27] R.J. Butcher, C.J. O'Connor, E. Sinn. *Inorg. Chem.*, **20**, 537 (1981).