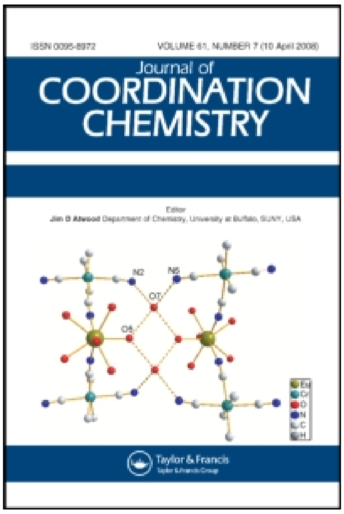

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Synthesis, crystal structure and magnetic properties of a trinuclear Cu(II)-pyrazolate complex containing μ_3-OH

Qi-Ji Zhou[a]; Yan-Zhao Liu[a]; Run-Ling Wang[a]; Jing-Wei Fu[a]; Jing-Yuan Xu[a]; Jian-Shi Lou[a]
[a] College of Pharmacy, Tianjin Medical University, Tianjin 300070, P.R. China

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Synthesis, crystal structure and magnetic properties of a trinuclear Cu(II)-pyrazolate complex containing μ_3-OH

QI-JI ZHOU, YAN-ZHAO LIU, RUN-LING WANG, JING-WEI FU,
JING-YUAN XU* and JIAN-SHI LOU*

College of Pharmacy, Tianjin Medical University, Tianjin 300070, P.R. China

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A new pyrazolate-bridged quasi-hexacopper(II) complex $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(pzH)_3(\mu_3\text{-}ClO_4)]_2(\mu\text{-}ClO_4)_2 \cdot (CH_3OH)_{0.33} \cdot (C_2H_5OH)_{0.66} \cdot H_2O$ (pz = pyrazolate), **1**, has been isolated and characterized by single crystal X-ray diffraction, elemental analysis, IR and UV–visible spectra and magnetic susceptibilities. The complex crystallizes in the orthorhombic system, space group Pbca (D_{2h}^{15}, No. 61), $a = 17.771(4)$ Å, $b = 16.143(4)$ Å, $c = 25.502(6)$ Å, $V = 7316(3)$ Å^3, $Z = 8$, $F(000) = 3521$, $D_c = 1.576\,\mathrm{g\,cm^{-3}}$. The structure of **1** consists of two $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(pzH)_3(\mu_3\text{-}ClO_4)]^{2+}$ trimers, which are weakly bridged by two perchlorate ions *via* centrosymmetric operation to form a trigonal prism with the six Cu atoms at six vertexes. Magnetic measurements were performed in the temperature range 2–300 K. The experimental data above 9 K could be satisfactorily reproduced by using an isotropic exchange model, $H = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_1\hat{S}_3)$ (**1**), with parameters of $J = -241.91\,\mathrm{cm^{-1}}$, $ZJ' = -23.04\,\mathrm{cm^{-1}}$ and $g = 2.07$, showing strong antiferromagnetic behaviors in Cu_3 unit and weak intertrimer magnetic interaction.

Keywords: Tricopper complex; Crystal structure; Antiferromagnetic behavior; Spin frustration

1. Introduction

Polynuclear copper complexes have attracted considerable attention because of their interesting magnetic properties and relevance to the active sites of a number of copper-containing metalloproteins such as ascorbate oxidase, laccase, ceruloplasmin and particulate methane monooxygenase (p-MMO) [1–3]. Cyclic-tricopper systems can be regarded as geometrically frustrated, offering the opportunity to elucidate magnetic exchange models [4–8]. In an equilateral triangular Cu_3 unit, magnetic coupling parameter J is equal for any two neighbor spins and if J is negative, which favors the spin antiparallel correlation, then only two of the three spin constraints can be satisfied simultaneously, so the system is geometrically frustrated. In order to further investigate magnetostructural correlations of the frustrated systems it is necessary to obtain more data of such examples. Additionally, triangular Cu(II) complexes play a fundamental

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*Corresponding authors. Email: jyxem@yahoo.com.cn; jianshilou@sina.com

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role in several catalytic biological processes, especially for the methane monooxygenases (MMOs), which catalyze the facile conversion of methane to methanol under ambient conditions [9]; extensive efforts at full characterization and its mechanism of action have not succeeded to date [10–12].

In our recent efforts to obtain polynuclear complexes for single-molecule magnets (SMMs), we have used pyrazolate compounds. In the present work, a new spin-frustrated system, $[Cu_3(\mu_3\text{-OH})(\mu\text{-pz})_3(pzH)_3(\mu_3\text{-ClO}_4)]_2(\mu\text{-ClO}_4)_2\cdot(CH_3OH)_{0.33}\cdot(C_2H_5OH)_{0.66}\cdot H_2O$, **1**, has been isolated and characterized. Magnetic susceptibility measurements were carried out to further understand magnetic exchange-coupling and provide more magnetic data about spin-frustration of trinuclear Cu(II) complexes.

2. Experimental

2.1. *Materials and measurements*

Reagents were purchased commercially and used without purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer and the amount of Cu(II) measured on a Hitachi-180–80 atomic absorption spectrometry (AAS) analyzer. IR spectra were recorded on a Shimadzu IR-408 spectrometer as KBr pellets. Electronic spectra were recorded on a Perkin-Elmer Hitachi-240 spectrophotometer. Variable-temperature magnetic susceptibilities over 2–300 K were measured on an MPMS-7 SQUID magnetometer.

2.2. *Synthesis of 1*

$Cu(ClO_4)_2\cdot 6H_2O$ (0.8 mmol) and pyrazole (1.2 mmol) were dissolved in methanol (10 ml) under stirring to give a blue solution, and then 5 mL water solution of NaOH (0.2 mmol) was added. The resulting solution was stirred at ambient temperature for 2 h, followed by filtration to remove the insoluble materials. After evaporation in air, dark blue needlelike crystals formed, which were recrystallized in ethanol to get suitable crystals for X-ray analysis and air dried (Yield: 47%). Elemental analysis (%) calcd for **1**: C, 27.16; H, 3.06; N, 19.37. Found: C, 26.93; H, 3.21; N, 19.44. Atomic absorption spectrometry (AAS) analysis found Cu 21.96%. IR(cm^{-1}, KBr): 3370(s), 3250(s, br), 3135(m), 1623(w), 1526(w), 1472(m), 1406(m), 1382(m), 1356(m), 1278(m), 1125(vs), 1114(vs), 1063(vs), 939(m), 775(s), 697(w), 627(s), 476(w), 422(w).

2.3. *X-ray crystallography*

Diffraction data were collected on a Bruker SMART 1000 CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined with full-matrix least-squares using the SHELXS-97 and SHELXL-97 programs (G.M. Sheldrick, SHELXS-97/SHELXL-97, Program for the Solution of Crystal Structures, University of Gottingen, 1997). Details of crystal parameters, data collection and refinement for **1** are summarized in table 1. Selected bond lengths and angles are listed in table 2.

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

Empirical formula	$C_{19.63}H_{26.38}Cl_2Cu_3N_{12}O_{11}$
Formula weight	867.92
Crystal system	Orthorhombic
Space group	*Pbca* (D_{2h}^{15}, No. 61)
Unit cell dimensions (Å, °)	
a	17.771(4)
b	16.143(4)
c	25.502(6)
α	90.00
β	90.00
γ	90.00
V (Å^3), Z	7316(3), 8
D_{Calcd} (g cm^{-3})	1.576
μ (mm^{-1})	1.939
T (K)	294
$F(000)$	3497
Reflections collected	35928
Unique reflections	6397
R_{int}	0.0932
Goodness-of-fit on F^2	1.002
$R_1{}^{a}/wR_2{}^{b}$ [$I>2\sigma(I)$]	0.0576/0.1500
R_1/wR_2 [all data]	0.1203/0.1957
Largest peak and hole (e Å^{-3})	0.779/–0.562

[a] $R=\sum\|F_o|-|F_c\|/\sum|F_o|$. [b] $R_w=|\sum w(|F_o|^2-|F_c|^2)|/\sum|w(F_o)^2|^{1/2}$, where $w=1/[\sigma^2(F_o)^2+(aP)^2+bP]$. $P=(F_o^2+2F_c^2)/3$.

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

Cu(1)–N(12)	1.932(6)	Cu(1)–N(3)	1.940(6)
Cu(1)–O(1)	1.994(4)	Cu(1)–N(1)	2.012(6)
Cu(2)–N(11)	1.950(6)	Cu(2)–N(8)	1.958(6)
Cu(2)–O(1)	2.000(4)	Cu(2)–N(9)	2.013(6)
Cu(3)–N(7)	1.930(6)	Cu(3)–N(4)	1.943(6)
Cu(3)–O(1)	2.007(4)	Cu(3)–N(5)	2.011(6)
N(12)–Cu(1)–N(3)	173.9(3)	N(12)–Cu(1)–O(1)	88.3(2)
N(3)–Cu(1)–O(1)	87.7(2)	N(12)–Cu(1)–N(1)	93.3(2)
N(3)–Cu(1)–N(1)	91.3(2)	O(1)–Cu(1)–N(1)	172.4(2)
O(1)–Cu(3)–N(5)	177.8(3)	Cu(1)–O(1)–Cu(3)	115.6(2)

3. Results and discussion

3.1. *Crystal structure of 1*

Complex **1** crystallizes in the orthorhombic system with space group P_{bca} (D_{2h}^{15}, No. 61) and can be described as a discrete neutral centrosymmetric hexacopper structure (figure 1), in which two trinuclear $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3]^{2+}$ units are weakly bridged by two perchlorate ions with distances of Cu1–O5 2.664(9) Å and Cu2–O2 2.542(9) Å. The Cu_3 core structure fits well to the model structure of particulate methane monooxygenase (p-MMO), which was supported by the density functional theory (DFT) calculations of Chan [13]. Each tricopper unit has a μ_3-OH at its center, with Cu–O bond lengths of 1.994(4)–2.007(4) Å and Cu–O(H)–Cu angles of 114.3(2)°–115.6(2)° (figure 2). The μ_3-O(H) is displaced out of the Cu_3-plane by

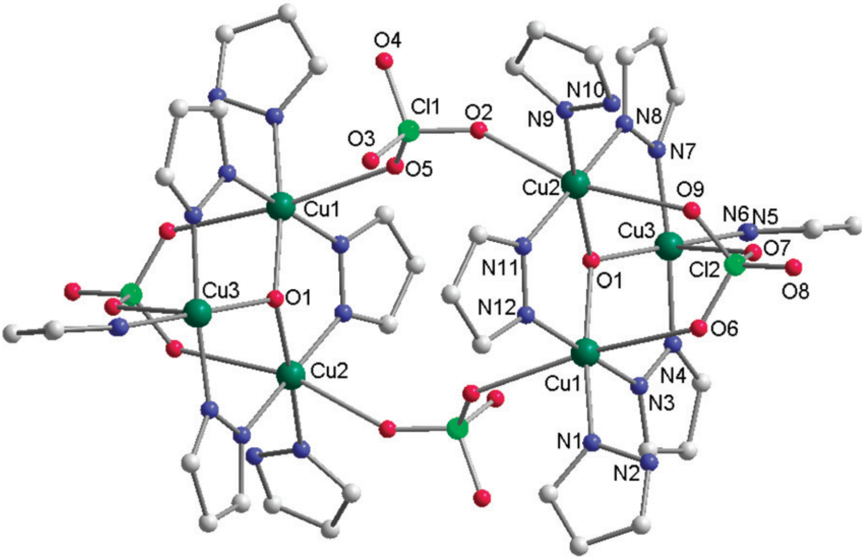

Figure 1. A perspective view of **1**. The non-coordinated solvent molecules and H atoms are omitted for clarity.

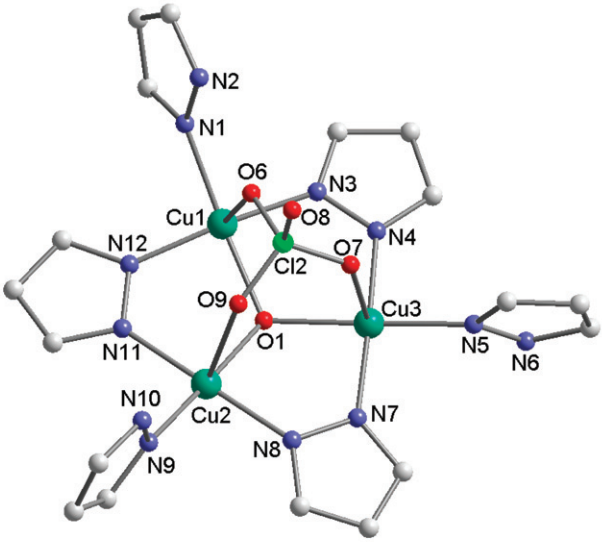

Figure 2. Close view of the trinuclear Cu(II) unit weak-coordinating with μ_3-ClO$_4$.

0.465 Å, which is shorter than the 0.605 Å in $[Cu_3(\mu_3\text{–}OH)(\mu\text{-pz})_3(\mu_4\text{-}NO_3)(pzH)_3]_2(\mu\text{-}NO_3)_2$, **2**, previously reported by Sakai *et al*. [14]. The Cu···Cu intratrimer distances are within the 3.355–3.386 Å range, which is ca 0.4 Å shorter than the Cu···Cu separations (3.66–3.90 Å) of the oxidized ascorbate oxidase with a triangular array of copper atoms [15, 16]. The bridged Cu–N bond lengths are within 1.929–1.958 Å (Cu1–N3 1.940(6) Å, Cu1–N12 1.932(6) Å, Cu2–N11 1.950(6) Å, Cu2–N8 1.958(6) Å,

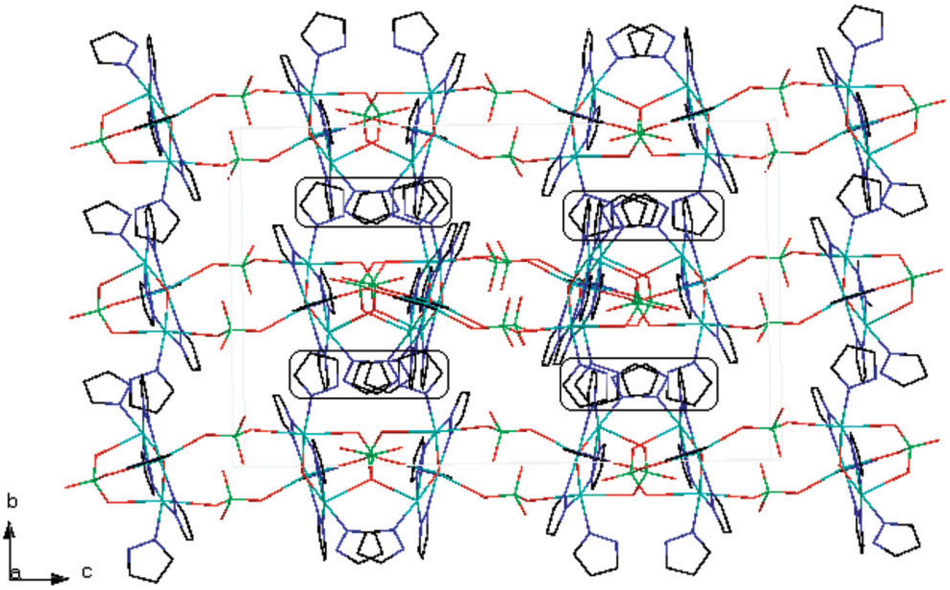

Figure 3. View showing the π–π interactions between pyrazole planes from the neighboring hexacopper(II) units for **1**.

Cu3–N7 1.930(6) Å and Cu3–N4 1.943(6) Å), which is very similar to **2** and the corresponding N–Cu–O(H) bridging angles range from 88.3° to 89.0°. One perchlorate is weakly bound to three Cu atoms of a trinuclear unit in a μ_3 mode with Cu1–O6 2.632(5) Å, Cu2–O9 2.646(5) Å and Cu3–O7 2.562(5) Å, which acts as an architectural truss to support the trimetric unit forming a stable frame (figure 2); the trinuclear unit is further coordinated by three terminal pyrazole ligands with similar bond lengths of Cu1–N1 2.012(6) Å, Cu2–N9 2.013(6) Å and Cu3–N5 2.011(6) Å. Also, the trinuclear unit is quite close to $[Cu_3(\mu_3\text{-}O)(pz)_3(Hpz)_3(\mu_1,\ \mu_2\text{-}ClO_4)](CH_3OH)$, **3**, reported by Shen *et al.* [17], which has a μ_3-O and different ClO_4^-coordination.

The preference of all pyrazole groups to lie as far apart as possible supports a very open structure along the *ab* two-dimensional direction, exhibiting weak π–π stacking with the distance of 4.695 Å between the mono-coordinated pyrazole planes from the neighboring hexacopper(II) units to generate multi-dimensional arrays, as shown in figure 3.

3.2. *IR and electronic spectra*

IR spectra of **1** show absorptions in the range 1600–600 cm^{-1}, consistent with pz. A broad band in the 3400–3200 cm^{-1} region and a band at 1623 cm^{-1} are due to stretching and bending vibrations of O–H bonds, indicative of the presence of lattice water and methanol/ethanol solvent molecules in this complex. The sharp band at 3135 cm^{-1} shows N–H coming from the monodentate coordination of Hpz [18]. Bands in the 1530–1280 cm^{-1} area corresponding to pyrazole stretching vibrations generally showed a slight blue shift upon coordination to Cu^{2+}. In addition, considerable changes in absorption intensity of bending vibrations of C–H bonds were observed in the "fingerprint" area. Some bands observed between 476 and 422 cm^{-1} are likely due to Cu–O vibrations [19]. The typical absorptions of coordinated perchlorates were observed at 1063, 1114 and 1125 cm^{-1}. Electronic spectra in concentrated methanol show a weak broad absorption centered at ~656 nm ($\varepsilon = 183\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) in the visible region, which is attributable to the symmetry forbidden d–d transition of the Cu(II).

3.3. *Magnetic property*

Magnetic susceptibility measurements were performed on a polycrystalline sample of **1** from 2–300 K at 0.5 T field. Plots of χ_M and $\chi_M T$ *versus* T are shown in figure 4. The 300 K $\chi_M T$ value of 0.45 cm^3 K mol^{-1} is much lower than expected for three magnetically uncoupled copper(II) ions (ca 1.13 cm^3 K mol^{-1} assuming $g = 2.0$). Upon cooling, the $\chi_M T$ product steadily decreases to ca 0.37 cm^3 K mol^{-1} around 140–60 K, in good agreement with the spin-only value of 0.376 cm^3 K mol^{-1} for one unpaired electron. This behavior indicates a quite strong antiferromagnetic interaction between the Cu(II) ions, with the ground state of $S = 1/2$ per Cu_3 unit. $\chi_M T$ keeps decreasing monotonously below the former indicated temperatures, reaching a value of 0.21 cm^3 K mol^{-1} at 2.0 K; this has been observed in similar compounds [20, 21] and discussed earlier [22], probably due to weak antiferromagnetic interactions between Cu_3 trimers ($S = 1/2$). Since the three copper atoms of the [Cu_3O] unit define a *quasi* equilateral triangle, the three Cu(II) ions can be considered equivalent. The appropriate spin Hamiltonian with an isotropic exchange interaction is given as

$$H = -2J\left(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_1\hat{S}_3\right) \tag{1}$$

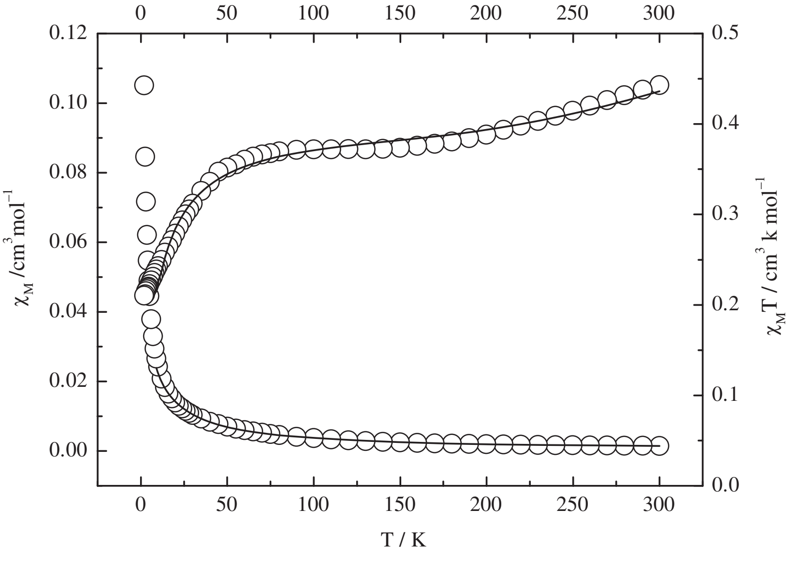

Figure 4. Plots of χ_M and $\chi_M T$ *vs.* T in the range 2–300 K at 5000 Oe for **1**.

The susceptibility as a function of temperature derived from this Hamiltonian can be expressed as equation (2)

$$\chi_{\mathrm{tri}} = \frac{N\beta^2 g^2}{4kT}\left[\frac{\mathbf{5} + \exp(-\mathbf{3J/kT})}{\mathbf{1} + \exp(-\mathbf{3J/kT})}\right]$$

$$\chi_{MF} = \frac{\chi_{\mathrm{tri}}}{1 - \dfrac{ZJ'\chi_{\mathrm{tri}}}{N\beta^2 g^2}} \tag{2}$$

where J is the exchange integral between copper(II) ions in the Cu_3 unit, ZJ' would account for intertrimer magnetic interaction resulting from weakly-coordinated bridging perchlorate, and the other symbols have their usual meanings. According to this assumption, the experimental data could be fitted satisfactorily in the temperature range 9–300 K. The best-fit parameters are $J = -241.91\,\mathrm{cm^{-1}}$, $ZJ' = -23.04\,\mathrm{cm^{-1}}$ and $g = 2.07$ with $R = \sum(\chi_{\mathrm{obsd}} - \chi_{\mathrm{cacld}})^2 / \sum \chi^2_{\mathrm{obsd}} = 5.76 \times 10^{-4}$. The coupling parameters thus obtained have been compared with those reported for analogous compounds as a function of certain structural features [21–24]. Magnetostructural correlations for trimers with the $Cu_3O(H)$ moiety have already been described in relation to the two potential bridges: the tridentate central oxygen and the bidentate N,N peripheral ligand. More flattened $Cu_3O(H)$ bridge and higher coplanarity of the coordination planes around each copper result in stronger magnetic interaction. So, for the central bridge of **1**, comparing with the literature, larger Cu–O(H)–Cu′ angles (av. 114.8°)/shorter O(H)···Cu3 plane distances (0.465 Å) give higher J values (ca–241.91 $\mathrm{cm^{-1}}$), quite consistent with the previous conclusion [20–22]. With respect to the coplanarity of the pheripheral ligands, again, it is difficult to derive conclusions due to the scarcity of data; in general terms, the J values of **1** with dihedral angles (av. 27.4°) between the least-squares planes defined by CuL_4 square-planar coordination are also in the expected range [22]. For the quasi-planar doubly triazole- or pyrazole-bridged systems, general agreement exists that the dominant pathway for antiferromagnetic exchange is provided by σ bonding between the copper $d_{x^2-y^2}$ and bridging ligand orbitals [25]. Similar N–Cu–O(H) bridging angles ranging from 88.3° to 89.0° lead to similar J values. As for the magnetic behavior below 60 K, the experimental observation that the magnetic moment drops below the value expected for one unpaired electron was tentatively assigned to antiferromagnetic interactions between spins of adjacent trinuclear entities, resulting from the bridging exchange of weakly-coordinated perchlorate at bond lengths of Cu1–O5 2.664(9) Å and Cu2–O2 2.542(9) Å, which is much stronger than that ($ZJ' = -0.28\,\mathrm{cm^{-1}}$) in the isosceles triangle $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(Hpz)(Me_3CCOO)_2]\cdot(Me_3CCOO)_2$ complex [23] corresponding to intermolecular hydrogen bonding pathways; a detailed study on this hypothesis is in progress.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-659582. 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].

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References

[1] D. Gatteschi, O. Kahn, J.S. Miller, F. Palacio. *Magnetic Molecular Materials*, Kluwer Academic, Dordrecht, The Netherlands (1991).

[2] K.D. Karlin, Z. Tyeklar (Eds.). *Bioinorganic Chemistry of Copper*, Chapman & Hall, New York (1993).

[3] E.I. Solomon, U.M. Sundaram, T.E. Machonkin. *Chem. Rev.*, **96**, 2563 (1996).

[4] A.P. Cole, D.E. Root, P. Mukherjee, E.I. Solomon, T.D.P. Stack. *Science.*, **273**, 1848 (1996).

[5] S. Ferrer, F. Lloret, I. Bertomeu, G. Alzuet, J. Borrás, S. García-Granda, M. Liu-González, J.G. Haasnoot. *Inorg. Chem.*, **41**, 5821 (2002).

[6] M.I. Belinsky. *Inorg. Chem.*, **43**, 739 (2004).

[7] J.E. Greedan. *J. Mater. Chem.*, **11**, 37 (2001).

[8] X. Liu, M.P. De Miranda, E.J.L. McInnes, C.A. Kilner, M.A. Halcrow. *Dalton Trans.*, 59 (2004).

[9] R.S. Hanson, T.E. Hanson. *Microbiol. Rev.*, **60**, 439 (1996).

[10] C.D. Nicola, Y.Y. Karabach, A.M. Kirillov, M. Monari, L. Pandolfo, C. Pettinari, A.J.L. Pombeiro. *Inorg. Chem.*, **46**, 221 (2007).

[11] G. Mezei, M. Rivera-Carrillo, R.G. Raptis. *Dalton Trans.*, 37 (2007).

[12] S. Gupta, A. Mukherjee, M. Nethaji, A.R. Chakravarty. *Polyhedron.*, **23**, 643 (2004).

[13] H.H.T. Nguyen, S.J. Elliott, J.H.K. Yip, S.I. Chan. *J. Biol. Chem.*, **273**, 7957 (1998).

[14] K. Sakai, Y. Yamada, T. Tsubomura, M. Yabuki, M. Yamaguchi. *Inorg. Chem.*, **35**, 542 (1996).

[15] A. Messerschmidt, H. Luecke, R. Huber. *J. Mol. Biol.*, **230**, 997 (1993).

[16] A. Messerschmidt, R. Ladenstein, R. Huber, M. Bolognesi, L. Avigliano, R. Petruzzelli, A. Rossi, A. Finazzi- Agró. *J. Mol. Biol.*, **224**, 179 (1992).

[17] W.Z. Shen, L. Yi, P. Cheng, S.P. Yan, D.Z. Liao, Z.H. Jiang. *Inorg. Chem. Commun.*, **7**, 819 (2004).

[18] R.A. Periana. *J. Mol. Catal.*, **220**, 7 (2004).

[19] K. Nakamoto. Application in Organometallic Chemistry. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edn, p. 271, Wiley-Interscience, New York (1997).

[20] F.B. Hulsbergen, R.W.M. ten Hoedt, J. Verschoor, J. Reedijk, A.L.J. Spek. *J. Chem. Soc., Dalton Trans.*, 539 (1983).

[21] M. Angaroni, G.A. Ardizzoia, T. Beringhelli, G. La Monica, D. Gatteschi, N. Masciocchi, M. Moret. *J. Chem. Soc., Dalton Trans.*, 3305 (1990).

[22] S. Ferrer, J.G. Haasnoot, J. Reedijk, E. Müller, M. Biagini Cingi, M. Lanfranchi, A.M.M. Lanfredi, J. Ribas. *Inorg. Chem.*, **39**, 1859 (2000).

[23] J.-H. Zhou, Z. Liu, Y.-Z. Li, Y. Song, X.-T. Chen, X.-Z. You. *J. Coord. Chem.*, **59**, 147 (2006).

[24] R.J. Butcher, C.J. O'Connor, E. Sinn. *Inorg. Chem.*, **20**, 537 (1981).

[25] Z. Xu, L.K. Thompson, D.O. Miller. *Inorg. Chem.*, **36**, 3985 (1997).