Structure and magnetic properties of a *syn–anti* carboxylate bridged linear trinuclear copper(II) complex with ferromagnetic exchange interaction

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Abstract

The synthesis, crystal structure and magnetic properties are reported for the trinuclear compound $[Cu(H_2O)_4\{Cu(HL)(H_2O)(ClO_4)\}_2][ClO_4]_2\cdot 2H_2O$, where HL is the monodeprotonated form of 6-methylamino-1,3-dimethyl-5-[(2′-carboxyphenyl)azo]uracil. The compound crystallizes in the triclinic system, space group $P\bar{1}$, with cell constants $a=7.824(3)$, $b=12.278(3)$, $c=13.705(9)$ Å, $\alpha=104.34(3)$, $\beta=91.80(3)$, $\gamma=103.37(5)$° and $Z=1$. The structure was solved and refined to $R=0.071$ ($R_w=0.064$). The structure consists of trinuclear $[Cu(H_2O)_4\{Cu(HL)(H_2O)(ClO_4)\}_2]^{2+}$ cations, non-coordinated perchlorate anions and crystal water molecules, held together by a network of hydrogen bonds. The central copper is in an elongated octahedral CuO_6 chromophore and the terminal copper atoms in distorted square-pyramidal $CuNO_4$ chromophores. Adjacent copper atoms are linked by carboxylate groups in a *syn–anti* conformation. From the magnetic susceptibility measurements, the complex is found to exhibit weak ferromagnetic interaction between nearest-neighbour copper(II) ions. The magnitude and nature of the exchange coupling are discussed on the basis of the structural data.

Introduction

Studies on structural and magnetic properties of polynuclear transition metal complexes, aimed at understanding the structural and chemical factors governing electronic exchange coupling mediated by multiatom bridging ligands, are of continuing interest for bioinorganic chemists, investigating the structure and role of polymetallic active sites in biological processes, and inorganic chemists, seeking to design new molecular materials exhibiting unusual magnetic, optical and electrical properties, that are bound to their molecular nature [1–3].

Among multiatom bridging ligands, carboxylate has been extensively studied. It is well known that carboxylate group can exhibit different types of bridging conformation: monoatomic, triatomic *syn–syn*, *anti–anti* and *syn–anti* (Fig. 1). Numerous examples exist of well structurally characterized copper(II) complexes involving the last triatomic bridging mode, but only a few of them so far have been studied magnetically. These were characterized by feeble exchange interactions that can be either ferromagnetic [4–10] or antiferromagnetic [11–14]. Generally, the *syn–anti* configuration favours the formation of either chain or layer compounds. However, when the carboxylate group is incorporated into a polydentate ligand it is forced to adopt the *syn–anti* configuration and a variety of oligomeric copper(II) complexes can be obtained. Thus, we have succeeded in preparing di-, tetra- and hexanuclear copper(II) complexes from the ligands H_2L^1 and H_2L^2 (Fig. 2) [7, 15]. Within this framework, and following our current study on multiatombridged exchange-coupled systems, we report here the synthesis, X-ray and magnetic analyses of a novel trinuclear copper(II) sys-

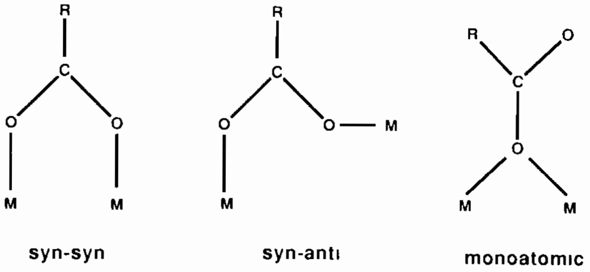

Fig. 1. Some important types of carboxylate bridging conformations.

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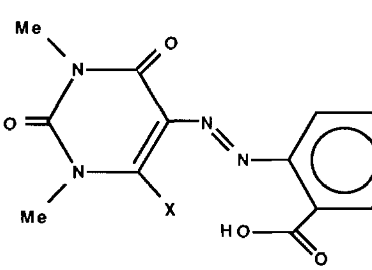

$X = NHMe, H_2L, X = NH_2, H_2L^1, X = OH, H_2L^2$

Fig. 2. Schematic representation of the ligands: H_2L = 6-methylamino-1,3-dimethyl-5-[(2′-carboxyphenyl)azo]uracil, H_2L^1 = 6-amino-1,3-dimethyl-5-[(2′carboxyphenyl)azo]uracil and H_2L^2 = 5-[(2′-carboxyphenyl)azo]-1,3-dimethylbarbituric acid.

tem, $[Cu(H_2O)_4\{Cu(HL)(H_2O)(ClO_4)\}_2][ClO_4]_2 \cdot 2H_2O$, where H_2L (Fig. 2) is a ligand closely related to the aforementioned H_2L^1 and H_2L^2. This compound represents the first example of a linear copper(II) trimer with *syn-anti* carboxylate bridges. Besides this, the compound is of interest since its magnetic behaviour clearly indicates that the copper ions are ferromagnetically coupled, which is rare among the trinuclear copper(II) complexes reported so far [4, 16, 17].

Experimental

Syntheses

The ligand H_2L was synthesized by coupling diazotized anthranilic acid with 6-methylamino-1,3-dimethyluracil. The compound was recrystallized from hot pyridine with a yield of 80%. *Anal.* Found: C, 52.7; H, 4.8; N, 22.1. Calc. for $C_{14}H_{15}N_5O_4$: C, 53.0; H, 4.7; N, 22.1%. IR (KBr, cm^{-1}): 3600–3200 br, ν(O–H) + ν(N–H); 1720, ν(C(2)=O); 1653, ν(C(4)=O); 1467, ν(N=N); 1351, ν(C–O) + δ(OH).

The complex was prepared by adding copper perchlorate hexahydrate (0.74 g, 2 mmol) to a stirred suspension of freshly prepared H_2L (0.32 g, 1 mmol) in 50 ml of a methanol–water mixture (4:1) at ambient temperature. Slow evaporation of the resulting black solution yielded well developed black crystals suitable for X-ray diffraction study. *Anal.* Found: C, 24.5; H, 3.5; N, 10.1; Cu, 13.8. Calc. for $C_{28}H_{44}N_{10}O_{32}Cl_4Cu_3$: C, 24.6; H, 3.3; N, 10.3; Cu, 14.0%. IR (KBr, cm^{-1}): 3600–3200 br, ν(O–H) + ν(N–H); 1720, ν(C(2)=O); 1600, ν(C(4)=O); 1580, ν_{as}(COO); 1380, ν(N=N); 1364, ν_s(COO); 1108, ν(Cl–O).

Physical measurements

Magnetic susceptibility data were collected on powder samples of the title compound with use of a SQUID-based sample magnetometer on a QUANTUM design model MPMS instrument. All data were corrected for the diamagnetism of the ligands (-492×10^{-6} cgsu) and TIP (taken as 60×10^{-6} cgsu/Cu atom). EPR spectra were recorded at X-band frequencies with a Bruker 200 TT spectrometer operating at 9.4–9.5 GHz. Copper was determined thermogravimetrically, as CuO, using a Mettler TG-50 thermobalance.

Crystal data

$C_{28}H_{44}N_{10}O_{32}Cl_4Cu_3$, triclinic, $a = 7.824(3)$, $b = 12.278(3)$, $c = 13.705(9)$ Å; $\alpha = 104.34(3)$, $\beta = 91.80(3)$, $\gamma = 103.37(5)°$; $V = 1235(1)$ Å^3, space group $P\bar{1}$, $Z = 1$, $D_c = 1.835$ g cm^{-3}, μ(Mo Kα) = 1.66 mm^{-1}, crystal dimensions: $0.40 \times 0.28 \times 0.20$ mm.

X-ray data collection and structure determination

Single crystal data collection was performed at ambient temperature (295 K) with a Nicolet P3F four-circle diffractometer using graphite monochromatized Mo Kα ($\lambda = 0.71069$) radiation. The lattice parameters were calculated by least-squares refinement of 25 well-centred reflections in the range $9 < \theta < 14°$. The data were collected by ω scan mode ($\theta_{max} = 27.5°$) with variable scan rate from 1.5 to 10.0° min^{-1}. Intensities of three standard reflections measured after 60 reflections showed variation less than 3%. A total of 3857 reflections was considered as observed with $|F| > 2\sigma(F_o)$. The data were corrected for Lorentz and polarization effects, as well as for absorption (empirical correction). Minimal and maximal transmission factors were 0.61 and 1.00, respectively.

The structure was solved using the SHELXS system [18] and subsequent Fourier maps. Both perchlorate anions exhibit rotational disorder. In the weakly coordinated ClO_4^- ion all oxygen atoms occupy two positions having population parameters 0.53(1) and 0.47(1). The two forms of the non-coordinated ClO_4^- ion have the oxygen O(27) in common and they differ by rotation around the Cl(2)–O(27) bond. Each of the remaining three oxygen atoms occupies two positions with population parameters 0.78(2) and 0.22(2). All non-hydrogen atoms were refined anisotropically, with the exception of the oxygen atoms of the perchlorate anions which were refined isotropically. All hydrogen atoms except those belonging to the water molecules could be positioned. All hydrogen atoms were refined except those of O(31) which were included in calculations but not refined. All refinements were performed using the XTAL2.6 program system [19] on a Vax 8650 computer. The function minimized was $\Sigma\omega(\Delta F)^2$ ($\omega = 1/\sigma^2(F_o)$), resulting in a final $R = \Sigma|F_o - F_c|/\Sigma|F|$ value of 0.071 and $R_\omega = [(\Sigma\omega|F_o - F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$ value of 0.064, for 418 parameters. Atomic coordinates derived from the final cycle of refinement with their standard deviations are given in Table 1. See also ‘Supplementary material’.

TABLE 1. Atomic parameters and e.s.d.s. of the non-hydrogen atoms

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U^a (Å^2)
Cu(1)	0.0000	0 00000	0 00000	0.0459(4)
Cu(2)	0 1723(1)	0.41335(5)	0.13422(5)	0.0491(3)
N(1)	0 6535(6)	0.7947(4)	0.3324(4)	0.049(2)
C(1)	0.8054(9)	0.8820(5)	0 3961(5)	0.073(4)
C(2)	0.6310(8)	0.8045(5)	0.2356(4)	0.050(3)
O(2)	0.7277(6)	0 8800(3)	0 2061(3)	0.070(2)
N(3)	0.4914(6)	0.7256(4)	0.1740(3)	0.047(2)
C(3)	0.460(1)	0.7373(6)	0 0706(5)	0.074(4)
C(4)	0.3862(7)	0.6366(4)	0 2019(4)	0.043(2)
O(4)	0 2663(5)	0.5698(3)	0.1371(3)	0.054(2)
C(5)	0 4110(7)	0.6262(4)	0.3024(4)	0.039(2)
C(6)	0 5429(7)	0.7162(4)	0.3725(4)	0.042(2)
N(6)	0.5655(6)	0.7302(4)	0.4693(3)	0.048(2)
C(7)	0.4683(8)	0.6680(5)	0.5355(4)	0.052(3)
N(7)	0.3241(5)	0.5373(3)	0.3379(3)	0.037(2)
N(8)	0.2199(5)	0.4457(3)	0.2795(3)	0.037(2)
C(9)	0 1295(6)	0.3650(4)	0.3314(4)	0.034(2)
C(10)	0 0482(6)	0.2485(4)	0.2791(4)	0.034(2)
C(11)	−0.0525(7)	0.1777(4)	0.3309(4)	0.041(2)
C(12)	−0.0736(7)	0.2165(4)	0.4320(4)	0.044(3)
C(13)	0.0140(7)	0.3280(5)	0.4834(4)	0.044(2)
C(14)	0.1114(7)	0.4005(4)	0.4338(4)	0.039(2)
C(15)	0.0678(7)	0.1942(4)	0.1706(4)	0.036(2)
O(16)	0.1349(6)	0.2521(3)	0.1132(3)	0 057(2)
O(17)	0.0148(5)	0.0863(3)	0.1413(3)	0.050(2)
Cl(1)	−0.2707(2)	0.4494(1)	0.2052(1)	0.0580(7)
O(23)	−0.161(1)	0.3799(7)	0.1568(7)	0.075(3)
O(23)^b	−0.130(2)	0.450(1)	0.1410(9)	0.105(4)
O(24)	−0.305(1)	0.5269(9)	0.1528(8)	0.099(3)
O(24)^b	−0.422(1)	0.4610(8)	0.1523(7)	0.068(3)
O(25)	−0.248(1)	0.4842(9)	0.3102(8)	0.097(3)
O(25)^b	−0.301(2)	0.345(1)	0.227(1)	0.168(6)
O(26)	−0.441(2)	0 371(1)	0.199(1)	0.126(4)
O(26)^b	−0.182(2)	0.545(1)	0.271(1)	0.169(6)
Cl(2)	0 3431(2)	−0.0185(1)	0.3341(1)	0.0634(8)
O(27)	0.2317(7)	0.0548(5)	0.3653(4)	0.094(2)
O(28)	0.286(1)	−0.1222(7)	0.3614(6)	0.111(2)
O(28)^c	0.375(3)	−0.081(2)	0.411(2)	0 067(6)
O(29)	0.3384(9)	−0.0469(6)	0.2253(5)	0.100(2)
O(29)^c	0.287(3)	−0.102(2)	0.237(2)	0.088(7)
O(30)	0.516(1)	0.0347(7)	0.3713(6)	0.114(3)
O(30)^c	0.516(3)	0.064(2)	0.328(2)	0.067(6)
O(20)	0.2536(6)	0 0183(4)	0 0008(3)	0.067(2)
O(21)	0 0120(6)	−0.1578(4)	0.1029(3)	0.077(2)
O(22)	0.1152(8)	0.3842(4)	−0.0102(3)	0.089(3)
O(31)	0.5603(7)	0.1091(4)	0.1357(4)	0.086(3)

$^aU = 1/3\Sigma_i\Sigma_j U_{ij}(a_i^* a_j^*)(\mathbf{a}_i \cdot \mathbf{a}_j)$. ^{b}Atoms with occupation factor of 0.47. ^{c}Atoms with occupation factor of 0.22

Results and discussion

Description of the structure

The crystal structure of the compound consists of linear trinuclear $[Cu(H_2O)_4\{Cu(HL)(H_2O)(ClO_4)\}_2]^{2+}$ cations, non-coordinated perchlorate anions and crystal water molecules, held together by a network of hydrogen bonds. A view of the asymmetric unit is shown in Fig. 3 together with the numbering system, while a perspective view of the trinuclear unit is given in Fig. 4. Selected bond lengths and angles are listed in Table 2.

The complex has a C_i symmetry, with the Cu(1) atom located on the centre of symmetry. This central copper atom is joined to the other two by two bridging carboxylate groups in a *syn–anti* conformation, resulting in a Cu · · · Cu separation between nearest neighbours of 4.797(1) Å.

The sites of the central and terminal copper ions are non-equivalent. The coordination polyhedron of the central copper atom, CuO_6, has a symmetry close to D_{4h}, with four strong bonds in an exact plane at *c.* 1.95 Å, which are formed with O(17) and O(17)^I ($I = -x, -y, -z$) atoms belonging to the bridging carboxylate groups and O(20) and O(20)^I atoms from two water molecules, and two weak axial bonds to O(21) and O(21)^I from another water molecule at 2.680(5) Å. The O(21)–Cu–O(21)^I axis is tilted 13.6° from the normal to the equatorial plane. The two outer copper atoms are (4+1) five-coordinated and have identical environments, $CuNO_4$, because of the crystallographic inversion symmetry. Four short bonds, ranging from 1.88 to 1.94 Å, are formed with O(4), N(8) and O(16) atoms from the monodeprotonated HL ligand and the O(22) atom from a water molecule, while a disordered perchlorate anion is coordinated through the O(23) atom at a longer distance of *c.* 2.6 Å. All the Cu–O and Cu–N metal–ligand distances are similar to those found in related complexes [7, 8]. The (4+1) coordination of Cu(2) is compatible with two idealized geometries: square-pyramidal and trigonal-bipyramidal. According to the procedure proposed by Muetterties and Guggenberg [20], the shape of the polyhedron can be considered as square-pyramidal, since the coordination polyhedron is located at *c.* 21% of the $C_{4v} \leftrightarrow D_{3h}$ deformation pathway. In a square-pyramidal description, the axial position is occupied by O(23) whereas N(8), O(4), O(16) and O(22) define the basal plane; the maximum deviation from planarity of the latter atoms being *c.* 0.15 Å. As usual, the copper ion is lifted by 0.102(1) Å from the mean basal plane toward the axial donor. The dihedral angle of the mean equatorial planes around Cu(1) and Cu(2) is 94.9(3)°.

As previously noted, each pair of adjacent copper ions within the trimer is bridged by a carboxylate group in the *syn–anti* conformation. The copper atoms are displaced from the carboxylate plane by 0.257(2) and 0.398(1) Å for Cu(1) and Cu(2), respectively. Moreover, this plane forms dihedral angles of 109.8(3) and 25.6(2)° with the equatorial planes around Cu(1) and Cu(2), respectively.

As for the coordination mode of the ligand, it is noteworthy that, unlike the closely related ligand

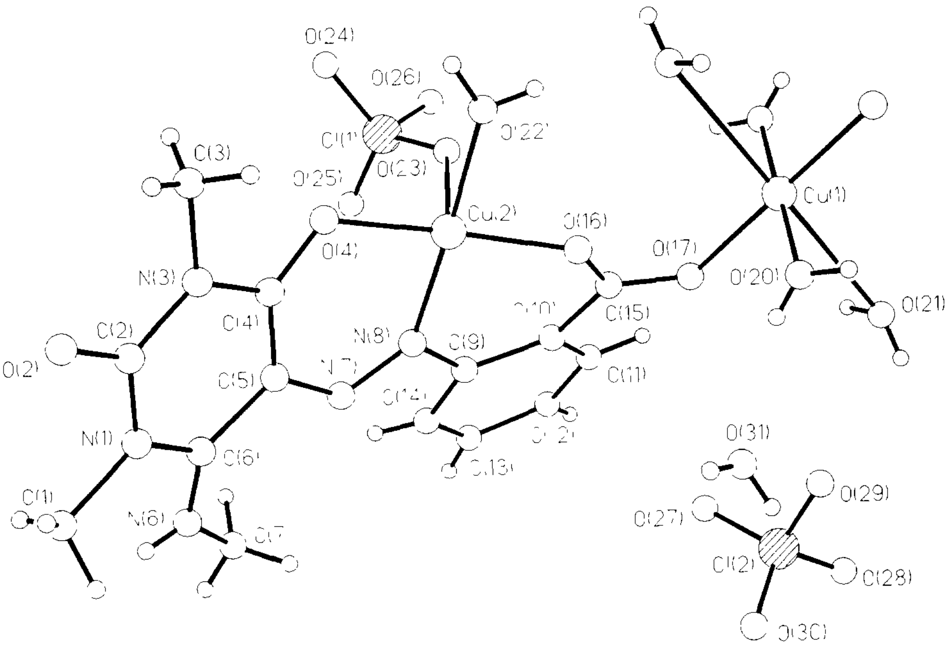

Fig. 3. A perspective view of the asymmetric unit For the disordered perchlorate anions only one set of oxygen atoms are drawn.

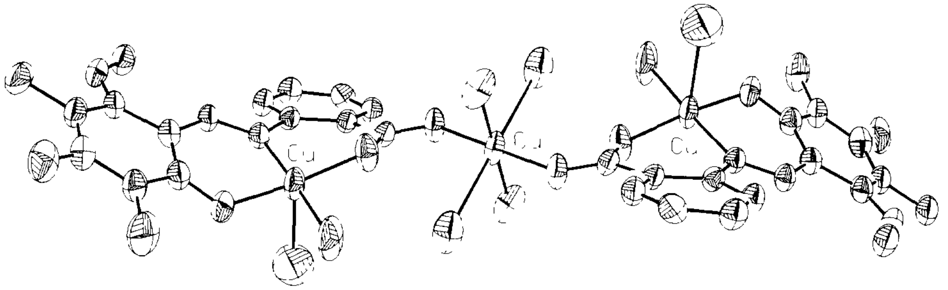

Fig. 4. A perspective view of the trinuclear unit. Perchlorate anions (except the oxygen O(23)), non-coordinated water molecules and hydrogen atoms have been omitted for clarity.

TABLE 2. Selected bonds (Å) and angles (°) with e.s d.s. in parentheses

Cu(1)–O(17)	1.949(3)	Cu(2)–O(22)	1.940(4)
Cu(1)–O(20)	1 944(4)	Cu(2)–O(23)	2.585(9)
Cu(1)–O(21)	2.680(5)	Cu(2)–O(23)[a]	2.51(1)
Cu(2)–O(4)	1.882(4)	C(15)–O(16)	1.237(7)
Cu(2)–N(8)	1.938(4)	C(15)–O(17)	1.249(6)
Cu(2)–O(16)	1.880(4)		
O(17)–Cu(1)–O(20)	93.6(2)	N(8)–Cu(2)–O(23)	89.0(2)
O(17)–Cu(1)–O(21)	76.0(2)	O(16)–Cu(2)–O(23)	85.7(3)
O(20)–Cu(1)–O(21)	84.6(2)	O(22)–Cu(2)–O(23)	88.8(3)
O(4)–Cu(2)–N(8)	91.2(2)	O(4)–Cu(2)–O(23)[a]	89.4(3)
O(4)–Cu(2)–O(22)	87.6(2)	N(8)–Cu(2)–O(23)[a]	95.0(3)
O(4)–Cu(2)–O(16)	164.0(2)	O(16)–Cu(2)–O(23)[a]	104.9(4)
N(8)–Cu(2)–O(16)	93.8(2)	O(22)–Cu(2)–O(23)[a]	82.4(3)
N(8)–Cu(2)–O(22)	177.3(2)	Cu(1)–O(17)–C(15)	123.0(4)
O(16)–Cu(2)–O(22)	87 4(2)	O(17)–C(15)–O(16)	121.4(4)
O(4)–Cu(2)–O(23)	109.4(3)	C(15)–O(16)–Cu(2)	126.5(3)

[a]Atom with occupation factor of 0.47.

6-amino-1,3-dimethyl-5-[2′-carboxyphenyl)azo]uracil, which usually coordinates to copper(II) ion in a double deprotonated tridentate fashion through the N(6) atom of the deprotonated amino group, N(8) and O(16) [7, 21], the H_2L ligand does it in a monodeprotonated fashion through O(4), N(8) and O(16), the methylamino group remaining undeprotonated. This behaviour seems to be due to the presence of a methyl group as substituent on the N(6) atom, since N(6) coordination to a copper ion would lead to a large steric interaction between N(1)–CH_3 and N(6)–CH_3 groups.

Bond distances and angles of the ligand do not noticeably differ from those reported by us for the complex $[Cu(Cl)(HL)(H_2O)]_2 \cdot 6H_2O$ [22], in which the ligand, within the mononuclear unit, is coordinated in the same fashion as in the complex discussed here. The pyrimidine and phenyl rings are nearly planar with maximum deviation from planarity less than 0.070(7)

Å. These planes are twisted by an angle of 31.6(2)° to each other.

Furthermore, the carboxylate group forms an angle of 12.4(1)° with respect to the phenyl ring.

Finally, a network of hydrogen bonds connects the trinuclear units, perchlorate anions and water molecules, packing the trimers along the *a* axis, the shortest intertrimer Cu · · · Cu distance being that of Cu(1) · · · Cu(1)^{II} (II $=x+1, y, z$) with a value of 7.824(3) Å. Hydrogen bonding distances are listed in Table 3.

Magnetic properties

The results of susceptibility measurements for $[Cu(H_2O)_4\{Cu(HL)(H_2O)(ClO_4)\}][ClO_4]_2 \cdot 2H_2O$ (Fig. 5) indicate ferromagnetic coupling at low temperatures given that $\chi_M T$ increases as T decreases. From 250 to *c.* 30 K, $\chi_M T$ remains practically constant and equal to 1.30 cm^3 mol^{-1} K, which is the value expected for three virtually independent copper(II) ions. Below 30 K, $\chi_M T$ increases, yielding an extrapolated value of *c.* 2.0 cm^3 mol^{-1} K at 0 K. This value would correspond to a state characterized by a spin of 3/2 with a *g* value of 2.07.

TABLE 3. Selected intra- and inter-molecular hydrogen bonds lengths (Å)

O(20) · · · O(31)	2.808
O(21) · · O(29)	2.860
O(29) · · · O(31)	2.819
O(31) · · O(30)^a	2.833
O(20) · · · O(31)^{III}	2 801
O(21) · · · O(22)^{IV}	2.688
O(21) · · O(2)^V	2.740
O(22) · · O(24)^{VI}	2.775
O(31) · · · O(25)^{bVII}	2.791

^{a}Atom with occupation factor of 0.22. ^{b}Atom with occupation factor of 0.47. III $=1-x, -y, -z$; IV $= -x, -y, -z$, V $=x-1, y-1, z$; VI $=x, y-1, z$; VII $=x+1, y, z$.

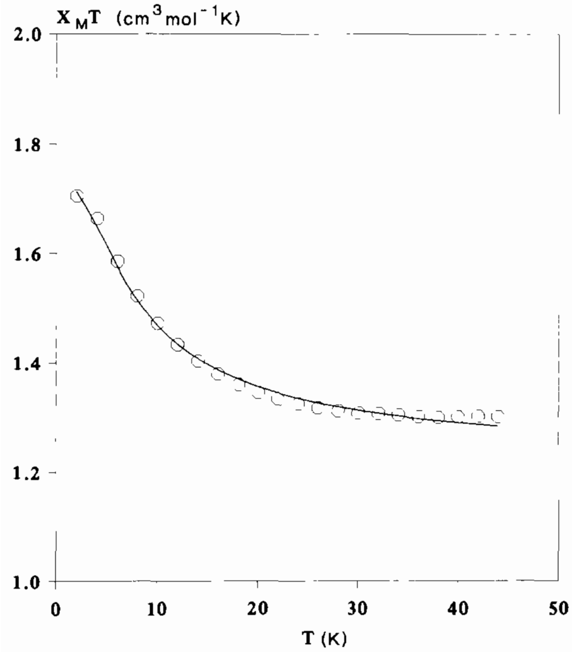

Fig. 5. Plot of the $\chi_M T$ product vs. temperature. The solid line was generated from the best-fit magnetic parameters.

The spin Hamiltonian appropriate to describe the exchange interaction in a linear symmetric copper(II) trimer like $[Cu(H_2O)_4\{Cu(HL)(H_2O)(ClO_4)\}_2][ClO_4]_2 \cdot 2H_2O$ is [23]:

$$\hat{\mathscr{H}} = -2J(\hat{S}_1\hat{S}_{2'}) + \hat{S}_1\hat{S}_{2'} - 2j(\hat{S}_2\hat{S}_{2'}) + \sum_{i=1}^{3}\beta g_i\hat{S}_i\vec{H}$$

where J and j describe the exchange interactions between adjacent and terminal copper ions, respectively, and g_i denotes the local g factors. Defining the spin operators

$\hat{S} = \hat{S}_1 + \hat{S}_2 + \hat{S}_{2'}$ and $\hat{S}^* = \hat{S}_2 + \hat{S}^*_{2'}$

for three interacting $s = 1/2$ centres, a quartet state $S = 3/2$ at $-J - 1/2j$ and two doublet states $S = 1/2$ ($S^* = 0$) and $S = 1/2$ ($S^* = 1$) at $3/2j$ and $2J - 1/2j$, respectively, are obtained. By use of the van Vleck equation one can easily obtain the following expression for the temperature dependence of the magnetic susceptibility, assuming that the g values for all three copper atoms are equal:

$$\chi_M = \left(\frac{N\beta^2 g^2}{4kT}\right) \frac{10 + \exp\left(\frac{-3J}{kT}\right) + \exp\left(\frac{-J-2j}{kT}\right)}{2 + \exp\left(\frac{-3J}{kT}\right) + \exp\left(\frac{-J-2j}{kT}\right)} \quad (1)$$

To take into account the intercluster exchange interactions a molecular field correction term is added to eqn. (1). The equation for the susceptibility then has the form:

$$\chi_M = \frac{\chi_c}{1 - (2zJ'/Ng^2\beta^2)\chi_c} \quad (2)$$

where χ_c is the susceptibility calculated from eqn. (1), J' is the intercluster-exchange constant and z is the number of interacting nearest neighbours.

The only effect of the j coupling is that of varying the energy of the excited doublet, then, its influence on the magnetic properties is negligible. In fact, J can be obtained with a reasonable accuracy but j is much less well determined [24]. In view of this, the magnetic data were fit to the theoretical expression by holding $j = 0$ and allowing g, J and J' to vary. The best fit to eqn. (2) to the data in the temperature range 2–50 K was found with $J = 2.7$ cm^{-1}, $J' = -0.1$ cm^{-1}, $g = 2.08$ and R, defined as $\Sigma(\chi_M T^{calc} - \chi_M T^{obs})^2/\Sigma(\chi_M T^{obs})$, equal to 4×10^{-5}.

Owing to the low J value, the excited doublet states with $S^* = 0$ and $S^* = 1$ are very close in energy to the ground quartet state, with separations of 2.7 and 8.1

cm^{-1}, respectively. Therefore, all three multiplets are expected to contribute to the EPR spectra even at very low temperatures. The room temperature X-band EPR spectrum of a powdered sample of the compound exhibits an intense and quasi-isotropic signal centred at $g = 2.10$. Decreasing the temperature to 90 K does not alter the overall appearance of the spectrum but slightly increases its intensity and, at high gain, the half-field signal can be detected at $g = 4.12$. This signal would be attributable to $\Delta M_s = \pm 2$ transitions within the $S = 3/2$ ground state.

The presence of weak ferromagnetic coupling between adjacent copper ions in the compound is consistent with the nature of the magnetic orbitals (built up from d orbitals of the metals and the symmetry adapted linear contribution of the orbitals of the ligands) on Cu(1) and Cu(2), and the geometrical features of the Cu–O–C–O–Cu bridges.

Cu(1) has an elongated tetragonal geometry close to D_{4h}, in which the unpaired electron is adequately described by a $d_{x^2-y^2}$ type pointing along the Cu–O directions in the equatorial plane $\{CuO(17)O(20)O(17)^{I}O(20)^{I}\}$. On the other hand, the geometry of Cu(2) is not far removed from square-pyramidal. In this case, the unpaired electron lies primarily in a $d_{x^2-y^2}$ type orbital, pointing toward the nitrogen and oxygen atoms of the basal plane $\{CuN(8)O(4)O(16)O(22)\}$, with some admixture of dz^2 character. Thus, both magnetic orbitals on Cu(1) and Cu(2) are delocalized toward the 2p oxygen orbitals of the COO bridges (Fig. 6) and, then, the exchange coupling through the carboxylate groups might be operative. Moreover, the nature of the bridging group is also determinant for the intensity of the exchange interaction. According to Khan's model, the exchange coupling constant J, can be expressed as a sum of both ferromagnetic (J_F) and antiferromagnetic (J_{AF}) contributions $J = J_F + J_{AF}$ [25]. The ferromagnetic contribution is weak when the metal ions are bridged by polyatomic extended ligands [26] whereas the magnitude of the antiferromagnetic one is proportional to the square of the overlap integral between magnetic orbitals centred on nearest-neighbour metal ions. So, the sign and magnitude of J are governed, primarily, by that overlap. For a *syn–anti* conformation of the Cu–O–C–O′–Cu′ bridging network, as it occurs in our complex, the contribution of the 2p orbitals of O and O′ belonging to the magnetic orbitals centred on Cu and Cu′, respectively, are unfavourably oriented to give a strong overlap (Fig. 6) [27]. This would cause a reduction of the antiferromagnetic contribution and, consequently, one may expect weak interactions. In good accord with this, for the few well characterized copper(II) complexes with bridging *syn–anti* COO groups, the magnitudes of the exchange-coupling constants are small (from -8.5 to 6.5 cm^{-1}) [4–14]. It must be pointed out that, in the present complex, the non-planarity of Cu–O–C–O–Cu bridging network is also expected to decrease the overlap of the magnetic orbitals in the bridging region [8]. Therefore, both *syn–anti* conformation and non-planarity of the bridging network would reduce the antiferromagnetic contribution to such an extent that the ferromagnetic one would become predominant. Thus, the weak ferromagnetic coupling observed for the trimer complex can be explained from the structural features of the bridges between the copper atoms.

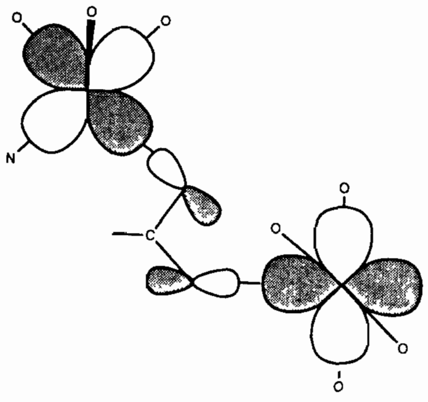

Fig. 6. Relative orientation of the copper(II) magnetic orbitals and their interaction through the carboxylate bridges with *syn–anti* conformation in $[Cu(H_2O)_4\{Cu(HL)(H_2O)(ClO_4)\}_2][ClO_4]_2 \cdot 2H_2O$

Supplementary material

Tables of hydrogen atom coordinates, atomic anisotropic thermal parameters, least-square plane equations, and observed and calculated structure factors are available from the authors on request.

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