A mixed bridged trinuclear copper(II)–1,10-phenanthroline complex with a linear structure

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The title compound, diaqua-$1\kappa O,3\kappa O$-di-μ-hydroxido-1:$2\kappa^2$-$O:O$,2:$3\kappa^2 O:O$-di-μ-methacrylato-1:$2\kappa^2 O:O'$,2:$3\kappa^2 O:O'$-bis(1,10-phenanthroline)-$1\kappa^2 N,N'$;$3\kappa^2 N,N'$-tricopper(II) dinitrate dihydrate, $[Cu_3(C_4H_5O_2)_2(OH)_2(C_{12}H_8N_2)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$, has the central Cu atom on an inversion centre. The three Cu^{II} atoms are in a linear arrangement linked by methacrylate and hydroxide groups. The coordination environments of the Cu^{II} ions are five-coordinated distorted square-pyramidal for the outer Cu atoms and four-coordinated square-planar for the central Cu atom. All nitrate ions, hydroxide groups and water molecules are linked by hydrogen bonds, forming a linear structure. The complex exhibits ferromagnetic exchange coupling, which is helpful in elucidating magnetic interactions between copper ions and other metallic ions in heteronuclear complexes.

Comment

Molecular magnetic compounds have recently attracted attention and have been developed to a large extent (Miller & Drillon, 2001*a,b*, 2002; Bruda *et al.*, 2006; Narasimha *et al.*, 2006). In particular, ferromagnetic exchange coupling in the mixed bridged unit Cu^{II}–RO/RCO_2–Cu^{II} leads to a quartet ground state for the trinuclear system (Haase & Gehring, 1985). Because various ligands show different abilities for mediating electronic effects between copper ions, these coordination compounds display rich magnetic behaviour over various temperature ranges (Rao *et al.*, 2004; Setifi *et al.*, 2006; Chen *et al.*, 2006; Das *et al.*, 2006; Tao *et al.*, 2006). Efforts to obtain new compounds in which rare earth ions are coupled magnetically to transition metal ions and/or organic radicals are increasing rapidly (Mishra *et al.*, 2005; Mori *et al.*, 2005, 2006; Costes, Dahan & Wernsdorfer, 2006; Costes, Auchel *et al.*, 2006; Murugesu *et al.*, 2006; Yeung *et al.*, 2006). However, it is difficult to clarify what contributes most to the magnetic interaction between rare earth and transition metal ions,

because a change in magnetic properties depends on many factors.

(I)
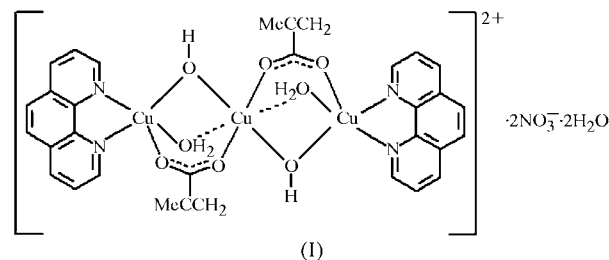
In recent years, we have pursued a research project investigating the structures and properties of heteronuclear complexes of rare earth and transition metals bridged by carboxyl groups (Wu *et al.*, 2002*a,b*, 2003, 2004; Zhu *et al.*, 2005). The title complex, (I), was obtained during the preparation of a dysprosium–copper–carboxyl compound. Its structure and magnetic properties are promising for the elucidation of the magnetic interaction between different 4*f* and 3*d* metallic ions in heteronuclear complexes.

The molecular structure and intramolecular arrangement of (I) are shown in Fig. 1. The symmetric centre of the molecule is situated at atom Cu1. The coordination environments of the Cu^{II} ions can be divided into two types. Outer atom Cu2 is in a CuN_2O_3 environment formed by two N atoms of a bidentate phenanthroline ligand and three O atoms from a water molecule, an α-methacrylate group and a hydroxide group, composing a distorted square-pyramidal geometry. Atoms O1, O2, N1 and N2 are in the equatorial plane and atom O5 occupies the vertex of the square pyramid. Atom Cu1 is coordinated by atoms O1, O1^{iii}, O3 and O3^{iii}, which constitute a square plane [symmetry code: (iii) $1 - x$, $-y$, $-z$]. It is noted that atoms O5 and O5^{iii} of the water molecules occupy the axial sites of an octahedral polyhedron if atom Cu1 is considered as six-coordinated (dashed lines in Fig. 1). The Cu1—O5 distance is 2.567 (2) Å. The three Cu^{II} ions in the molecule are in a linear arrangement linked by α-methacrylate and hydroxide groups to give two mixed bridged Cu2–OH/
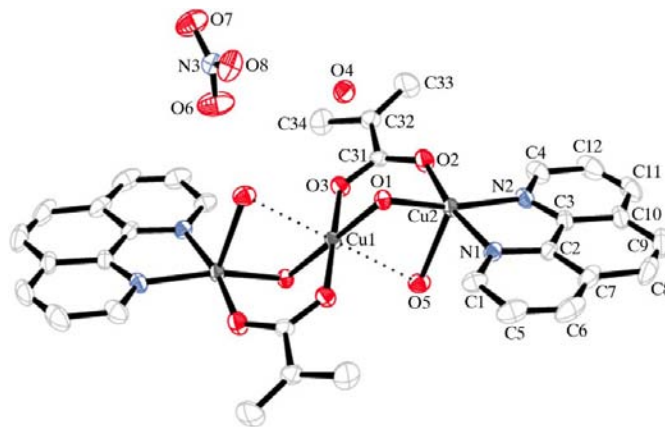

Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. Unlabelled atoms are related to labelled atoms by the symmetry code ($-x + 1$, $-y$, $-z$).

RCOO–Cu1 units with a Cu2$\cdots$Cu1 distance of 3.0275 Å. As Table 1 shows, the Cu—O bond lengths in the square planes are similar, with an average bond length of 1.9468 Å. The axial Cu—O distance is 2.287 (2) Å, which is obviously longer than those in the square planes. The two Cu—N distances are nearly the same, with an average value of 2.021 Å. All bond lengths are in agreement with those in other reports (Gehring *et al.*, 1993; Setifi *et al.*, 2006; Tao *et al.*, 2006). Electronic delocalization in the OCO fragment is complete, with two almost equivalent CO bond lengths [1.265 (4) Å for C31—O2 and 1.262 (3) Å for C31—O3]. The phenanthroline ligand adopts a bidentate coordination mode and possesses local C_{2v} symmetry.

A packing diagram for complex (I) is shown in Fig. 2. The copper complex cations are associated with their identical neighbours through stacking of the phenanthroline aromatic rings in an 'offset' manner. There is no evidence, however, of strong π–π stacking interactions. The aryl rings of neighbouring phenanthroline ligands are approximately parallel, with a dihedral angle of 0.82° and an approximate perpendicular distance of 3.687 Å.

Hydrogen bonds play an important role in the stability of the crystal structure of (I). As Fig. 3 shows, there are also many intermolecular hydrogen bonds between O atoms of the water molecules and O atoms of the nitrate ions or hydroxide groups. Atoms O1, O4, O5^{i}, O6^{ii}, N3^{ii} and O8^{ii} are interlinked by hydrogen bonds to form a six-ring cycle [symmetry codes: (i) $-1 + x, y, z$; (ii) $-x, -y, -z$]. Atoms O1^{ii}, O4^{ii}, O5^{iii}, O6, N3 and O8 are also joined together by hydrogen bonds to form another six-ring cycle. Meanwhile, there are two cycles linked by hydrogen bonds between atoms O4 and O8, and between O4^{ii} and O8^{ii}. These hydrogen bonds form a one-dimensional structure along the *a* axis, which is advantageous for decreasing the energy. The hydrogen-bond distances are in the range 2.731 (4)–2.970 (4) Å, with an average of 2.873 Å, which is in good agreement with typical values for O—H$\cdots$O interactions.
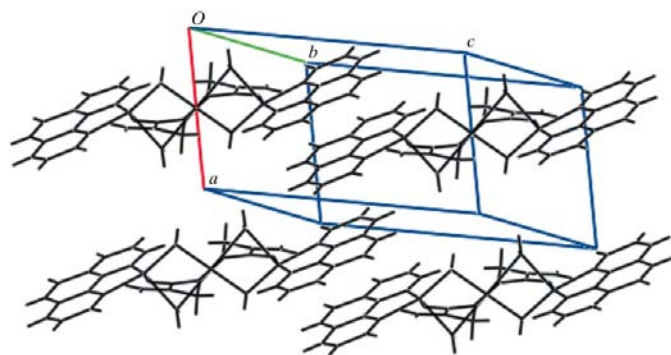

Figure 2
A packing diagram for complex (I), viewed along the *b* axis, showing the π–π interactions between the phenanthroline rings. Water molecules and nitrate ions have been omitted for clarity.
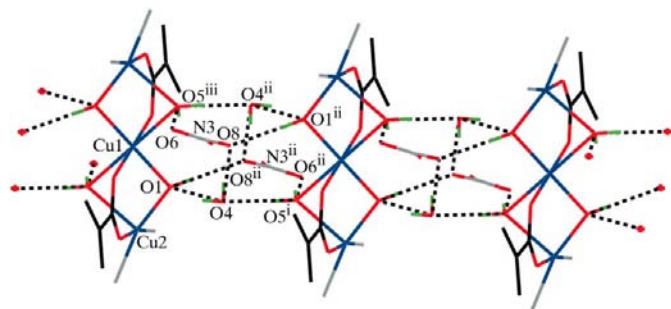

Figure 3
Intermolecular hydrogen bonds along the *a* axis. C atoms of the phenanthroline ligands have been omitted for clarity. [Symmetry codes: (i) $-1 + x, y, z$; (ii) $-x, -y, -z$; (iii) $1 - x, -y, -z$.]

Experimental

An aqueous solution (1 ml) of Cu(NO$_3$)$_2$ (188 mg, 1 mmol) was added to a solution of Dy(C$_4$H$_5$O$_2$)$_3$(H$_2$O)$_6$ (81.7 mg, 0.16 mmol) in water (3 ml) with stirring. An ethanol solution (1 ml) of phenanthroline (15.1 mg, 0.076 mmol) was added to the mixture. The resulting solution was filtered and the filtrate was allowed to stand at room temperature. After two weeks, blue needle-shaped crystals of (I) suitable for X-ray crystallographic study were obtained. Temperature-dependent magnetic susceptibilities were collected from the pure crystal sample in the 5–300 K range using a Quantum Design PPMS-9 magnetometer in an applied field of 20 kOe (1 Oe = 79.58 A m^{-1}). An effective magnetic moment of 3.589 μ_B was observed at 300 K. With decreasing temperature, the $\mu_{eff}(T)$ functions increase and reach 3.859 μ_B at 18 K, and then decrease rapidly to 3.54 μ_B at 5 K. Such behaviour is characteristic of predominantly ferromagnetic exchange coupling in Cu$_3^{II}$ systems (Haase & Gehring, 1985). The observed susceptibility data are well fitted to the Curie–Weiss law [$\chi_m = C/(T - \theta)$], with Weiss constant $\theta = 3.52$ K. IR: ν(OH) 3650–2900, ν(C=C) 1645, ν(COO)$_{as}$ 1541, ν(COO)$_s$ 1426, ν(NO$_3$) 1384 cm^{-1}.

Crystal data

[Cu$_3$(C$_4$H$_5$O$_2$)$_2$(OH)$_2$(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)$_2$](NO$_3$)$_2$·2H$_2$O	$\beta = 81.596$ (2)°
$M_r = 951.29$	$\gamma = 70.529$ (2)°
Triclinic, $P\bar{1}$	$V = 922.94$ (12) Å^3
$a = 7.3779$ (5) Å	$Z = 1$
$b = 11.1570$ (9) Å	Mo $K\alpha$ radiation
$c = 12.5830$ (9) Å	$\mu = 1.79$ mm^{-1}
$\alpha = 71.081$ (2)°	$T = 293$ (2) K
	$0.35 \times 0.08 \times 0.02$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	8975 measured reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	4172 independent reflections
$T_{min} = 0.572$, $T_{max} = 0.965$	3356 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.120$	
$S = 1.13$	$\Delta\rho_{max} = 0.53$ e Å^{-3}
4172 reflections	$\Delta\rho_{min} = -0.54$ e Å^{-3}
271 parameters	

The H atoms of the hydrocarbon groups were placed in calculated positions, with C—H = 0.96 Å for the methyl group or 0.93 Å for the

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9367 (19)	Cu2—N1	2.013 (2)
Cu1—O3	1.9725 (19)	Cu2—N2	2.028 (2)
Cu1—Cu2	3.0275 (4)	Cu2—O5	2.287 (2)
Cu2—O1	1.9304 (19)	O2—C31	1.265 (4)
Cu2—O2	1.932 (2)	O3—C31	1.262 (3)
O1—Cu1—O3	90.83 (8)	N1—Cu2—N2	81.39 (11)
O1—Cu2—O2	90.91 (9)	O1—Cu2—O5	90.65 (8)
O1—Cu2—N1	97.49 (9)	O2—Cu2—O5	94.87 (10)
O2—Cu2—N1	169.20 (10)	N1—Cu2—O5	91.82 (9)
O1—Cu2—N2	164.93 (9)	N2—Cu2—O5	104.39 (9)
O2—Cu2—N2	88.74 (10)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H101$\cdots$O8[ii]	0.94	2.03	2.970 (4)	177
O4—H401$\cdots$O8	0.93	1.99	2.910 (3)	171
O4—H402$\cdots$O1	0.87	2.00	2.819 (4)	157
O5—H501$\cdots$O4[iii]	0.92	1.84	2.731 (4)	166
O5—H502$\cdots$O6[i]	0.96	1.99	2.936 (4)	168

Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x, -y, -z$; (iii) $x + 1, y, z$.

terminal CH_2 group, and they were included in the final cycles of refinement in a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). The H atoms of the water molecules were located in a difference Fourier map, and their coordinates and displacement parameters were fixed during structure refinement using a riding model, with $U_{iso}(H) = 1.2U_{eq}(O)$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *CrystalStructure* (Rigaku/MSC & Rigaku, 2002); data reduction: *CrystalStructure*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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