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Poly[[di-μ-aqua-tetraaquadi-μ-hydroxido-bis(μ_3-3-nitrophthalato)-tricopper(II)] dihydrate]

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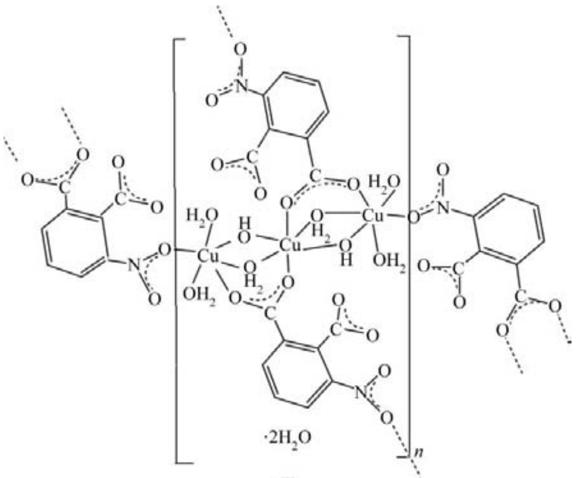
The novel title complex, $\{[Cu_3(C_8H_3NO_6)_2(OH)_2(H_2O)_6]\cdot 2H_2O\}_n$, has a one-dimensional polymeric double chain structure where the three Cu atoms are linked by μ_2-OH and μ_2-H_2O groups, and these trinuclear centres are bridged by two 3-nitrophthalate ligands. The asymmetric unit contains one and a half crystallographically independent Cu atoms (one lying on a centre of inversion), both coordinated by six O atoms and exhibiting distorted octahedral coordination geometries, but with different coordination environments. Each 3-nitrophthalate ligand connects to three Cu atoms through two O atoms of one carboxylate group and one O atom of the nitro group. The remaining carboxylate group is free and is involved in intrachain hydrogen bonds, reinforcing the chain linkage.

Comment

In constructing coordination polymers, aromatic dicarboxylic acids, such as *o*-phthalic, *m*-phthalic and *p*-phthalic acids, have been shown to produce a great variety of interesting structures (Zheng *et al.*, 2002; Wang *et al.*, 2001; Wan *et al.*, 2002, 2003; Hong & Do, 1997; Eddaoudi *et al.*, 2001). Among these isomeric forms of phthalate, the *o*-phthalate ligand, with two carboxylate groups in *ortho* positions, can bind metal ions in a diversity of bonding modes and thus lead to the formation of interesting network architectures (Baca *et al.*, 2004).

On the other hand, if an electron-withdrawing nitro group is also present in the ligand, it can not only coordinate metal ions in a variety of ways but also act as a hydrogen-bond acceptor, taking part in the formation of polymeric networks (Liu *et al.*, 2006). Recently, a series of lanthanide and transition metal complexes with 3-nitrophthalic acid were successfully obtained; however, in most of these complexes, the 3-nitrophthalate ligands are coordinated to the metal ions *via* the two carboxylate groups (Deng, Liu *et al.*, 2007; Deng, Wang *et al.*, 2007; Huang *et al.*, 2007; Song *et al.*, 2007). In this paper, we used 3-nitrophthalic acid as a rigid ligand and synthesized the one-dimensional coordination polymer poly[[di-μ-aqua-tetraaquadi-μ-hydroxido-bis(μ_3-3-nitrophthalato)tricopper(II)] dihydrate], (I), in which the nitro group of the 3-nitrophthalate anion is also coordinated to the metal ion.



(I)

The title complex exhibits a double chain structure. There are one and a half crystallographically independent Cu atoms in the asymmetric unit (one lying on an inversion centre), one complete 3-nitrophthalate anion, one hydroxy group and three coordinated water molecules, together with a free water molecule. Fig. 1 shows the full coordination environments of the Cu atoms in a symmetry-expanded view.

In the complex, the unique Cu atoms are both six-coordinated, but they have two different coordination environments. Atom Cu1 lies on the inversion centre and is coordinated to an O_6 donor set. Four equatorial sites are occupied by four O atoms from two monodentate carboxylate groups of two symmetry-related 3-nitrophthalate anions [O1 and O1^{i}; symmetry code: (i) $-x + 1, -y + 1, -z + 1$] and two coordinated water molecules (O7 and O7^{i}). The axial sites are occupied by two O atoms from two hydroxy groups. The equatorial Cu1—O distances are very similar and about 0.46 Å shorter than the axial distances (Table 1). For atom Cu2, the six O atoms belong to three water molecules, one carboxylate group of one 3-nitrophthalate anion, one nitro group of another 3-nitrophthalate anion and one hydroxy group. The Cu2—O_{water} and Cu2—$O_{carboxylate}$ distances are similar, but much shorter than the *trans*-positioned and unequal Cu2—$O_{hydroxyl}$ and Cu2—O_{nitro} distances (Table 1), with the latter being significantly longer than normal Cu—O bond lengths. For both unique Cu atoms, the coordination environment is a significantly distorted octahedron.

In the present structure, there is only one type of 3-nitrophthalate anion, which adopts 1,3-bridging and monodentate modes to coordinate with the Cu atoms (see scheme). Atom O5 of the nitro group adopts a monodentate mode to connect with one Cu atom, and atoms O1 and O2 of one carboxylate

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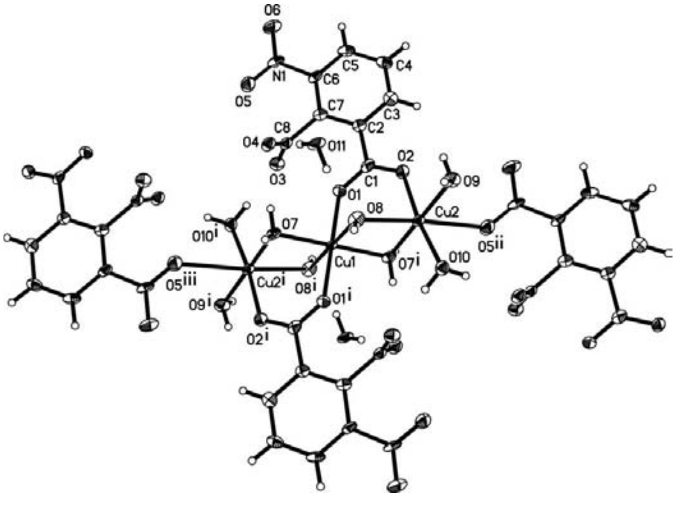

Figure 1
A view of the structure of (I), showing the atom-numbering scheme and the coordination environments of the Cu atoms. Displacement ellipsoids are drawn at the 70% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y-1, z$; (iii) $-x, 2-y, 1-z$.]

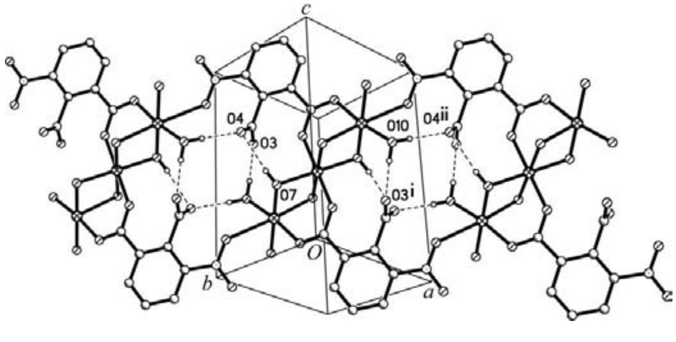

Figure 2
The one-dimensional double chain structure of complex (I), showing the intrachain hydrogen bonds (dashed lines), viewed approximately along the [111] direction. [Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y-1, z$.]

group adopt a 1,3-bridging mode to link two Cu atoms; the other carboxylate group of the 3-nitrophthalate anion is free. To the best of our knowledge, this type of coordination mode for the 3-nitrophthalate ligand has not been reported in the literature. There is a previously reported structure with a binding nitro group {$[K_2Cu(NPA)_2(H_2O)_4]_n$; H_2NPA is 3-nitrophthalic acid; Shen *et al.*, 2006}, but in the latter, the 3-nitrophthalate ligand coordinates to K and Cu ions with the nitro and both carboxylate groups.

In (I), a one-dimensional polymeric double chain structure with a trinuclear centre builds up, where the Cu atoms are linked by μ_2-OH and μ_2-H_2O groups and these trinuclear centres are further bridged by two 3-nitrophthalate ligands (Fig. 2). The Cu1$\cdots$Cu2 separation in the trinuclear unit is 3.041 (1) Å, which could be considered a weak interaction since it is in the range of the sum of the van der Waals radii of two Cu ions.

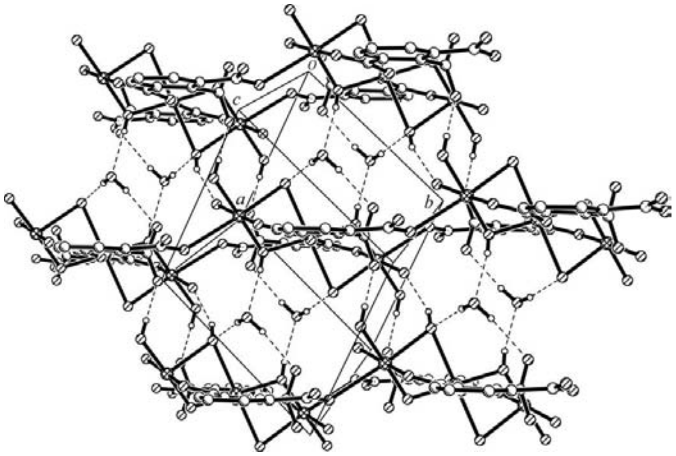

Figure 3
A packing diagram for (I), showing the hydrogen-bond interactions (dashed lines) linking the chains.

In the double chain, 3-nitrophthalate anions interconnect with Cu atoms, forming two different types of ring, *viz.* a six-membered one containing two Cu atoms and a 20-membered ring containing four Cu atoms, which alternate along the infinite one-dimensional array. The chains are further stabilized by intrachain hydrogen bonds involving the free carboxylate groups as acceptors and coordinated water molecules or hydroxy groups as donors (Table 2).

Fig. 3 shows a view of the packing of the title compound. There are a number of distinct hydrogen-bond interactions involving the ligands, both intrachain (reinforcing the chain linkage) and interchain (assembling these one-dimensional chains into a three-dimensional network structure). Free water molecules (O11) reside between layers and also enter into hydrogen bonding with the free carboxylate group (O3), coordinated water molecules (O7) and the hydroxy group (O8), further stabilizing the three-dimensional supramolecular network.

Experimental

The addition of anhydrous sodium carbonate (0.53 g, 5 mmol) to a stirred solution of copper nitrate hexahydrate (1.20 g, 4 mol) in water (20 ml) produced a blue precipitate, which was filtered off and washed with distilled water. The precipitate was subsequently added to a stirred solution of 3-nitrophthalic acid (0.53 g, 2.5 mol) in boiling water (15 ml) over a period of 20 min. After filtration, slow evaporation over a period of two weeks at room temperature yielded blue block-shaped crystals of (I).

Crystal data

$[Cu_3(C_8H_3NO_6)_2(OH)_2(H_2O)_6]\cdot 2H_2O$
$M_r = 786.99$
Triclinic, $P\overline{1}$
$a = 7.2192$ (14) Å
$b = 8.3899$ (17) Å
$c = 11.191$ (2) Å
$\alpha = 74.81$ (3)°
$\beta = 84.38$ (3)°
$\gamma = 74.77$ (3)°
$V = 630.9$ (2) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 2.61$ mm^{-1}
$T = 133$ (2) K
0.16 × 0.12 × 0.08 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
$T_{\min} = 0.702$, $T_{\max} = 0.815$
3616 measured reflections
2192 independent reflections
1757 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.108$
$S = 1.03$
2192 reflections
196 parameters
6 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.83$ e Å^{-3}
$\Delta\rho_{\min} = -0.69$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—O7	1.944 (2)	Cu2—O10	1.984 (3)
Cu1—O1	1.948 (3)	Cu2—O9	1.996 (3)
Cu1—O8	2.408 (3)	Cu2—O8	2.336 (3)
Cu2—O7$^{\rm i}$	1.916 (2)	Cu2—O5$^{\rm ii}$	2.603 (3)
Cu2—O2	1.958 (3)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H11*B*···O4	0.85	2.08	2.918 (4)	172
O11—H11*A*···O8	0.85	1.83	2.665 (4)	166
O10—H10*B*···O4$^{\rm ii}$	0.85	1.80	2.631 (3)	163
O10—H10*A*···O3$^{\rm i}$	0.85	1.78	2.632 (3)	177
O9—H9*A*···O3$^{\rm iv}$	0.84	1.79	2.634 (4)	178
O9—H9*B*···O2	0.84	2.21	2.652 (3)	113
O8—H8*A*···O10$^{\rm v}$	0.84	2.15	2.951 (4)	160
O7—H7*B*···O11$^{\rm vi}$	0.85	1.97	2.739 (4)	150
O7—H7*A*···O4	0.84	2.14	2.969 (4)	170

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

All water H atoms were found in difference Fourier maps and were kept fixed during refinement, with O—H distances in the range 0.84–0.85 Å and $U_{\rm iso}$(H) values equal to $1.2U_{\rm eq}$(O). H atoms of CH groups were idealized and treated as riding, with C—H distances of 0.93 Å and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C). Pseudo-isotropic displacement-parameter restraints, with a standard uncertainty of 0.001 Å^2, were applied to atom C8.

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3085). Services for accessing these data are described at the back of the journal.

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