metal-organic papers

Poly[[diaquabis(1,10-phenanthroline)bis(μ_3-5-sulfonatosalicylato)tricopper(II)] tetrahydrate]

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The structure of the title compound, $\{[Cu_3(C_7H_3O_6S)_2$-$(C_{12}H_8N_2)_2(H_2O)_2]\cdot 4H_2O\}_n$, consists of centrosymmetric trinuclear $[Cu_3(ssal)_2(phen)_2(H_2O)_2]$ (phen is 1,10-phenanthroline and ssal is the 5-sulfonatosalicylate trianion) building units and non-coordinated water molecules. The central ($\bar{1}$ site symmetry) Cu atom is octahedrally coordinated and the other unique Cu atom adopts a square-pyramidal geometry. The μ_3-ssal ligands link trinuclear units into a chain running along the a axis via bridging sulfonate groups. The chains are connected by O—H$\cdots$O bonds into a three-dimensional network.

Comment

Metal complexes of the salicylate ion and its derivatives have been extensively studied from both structural and biological viewpoints (Zhu et $al.$, 2002, 2003; Zhu & Kitagawa, 2002). Our own recent work has focused on 5-sulfosalicylate metal complexes. Some of these, along with previously studied phases, contain the completely deprotonated 5-sulfonatosalicylate (ssal^{3-}) anion (Fan & Zhu, 2005a,b,c; Fan et $al.$, 2005; Marzotto et $al.$, 2001; Sun et $al.$, 1995; Wang, Zhang, Li et $al.$, 2004; Wang, Zhang, Song & Ju, 2004). However, there are only three complexes with trinuclear motifs, namely $[Cu_3(2,2'$-bipy)$_2$(ssal)$_2$(H$_2$O)$_4]\cdot 4H_2O$, (II) (Wang, Zhang, Li et $al.$, 2004), $[Cu_3(dpa)_3(ssal)_2]\cdot 3H_2O$, (III) (Fan & Zhu, 2005$a$), and $[Cu_3(bz)_6(ssal)_2]\cdot 8H_2O$, (IV) (Fan & Zhu, 2005$b$) (2,2'-bipy is 2,2'-bipyridine, dpa is 2,2'-dipyridylamine and bz is benzimidazole). We present here the structure of the title compound, (I), which is another example of a Cu^{2+}/ssal^{3-} complex with a trinuclear motif. The three previously reported copper complexes with trinuclear units are discussed in more detail by Fan & Zhu (2005b).
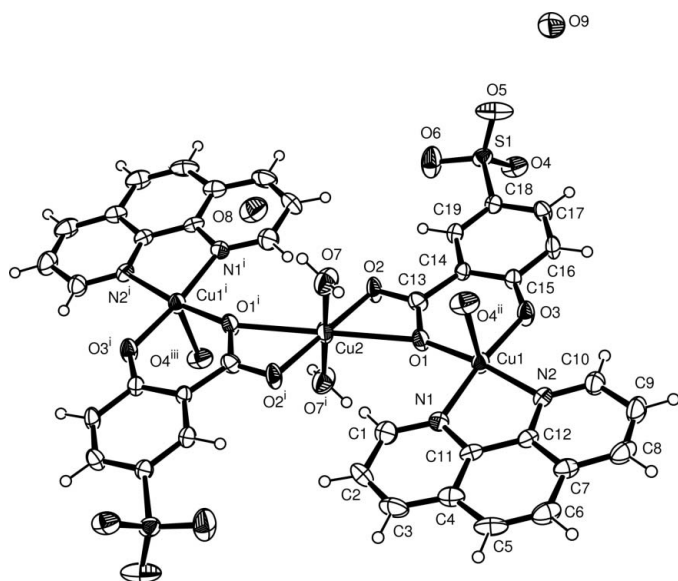

(I)
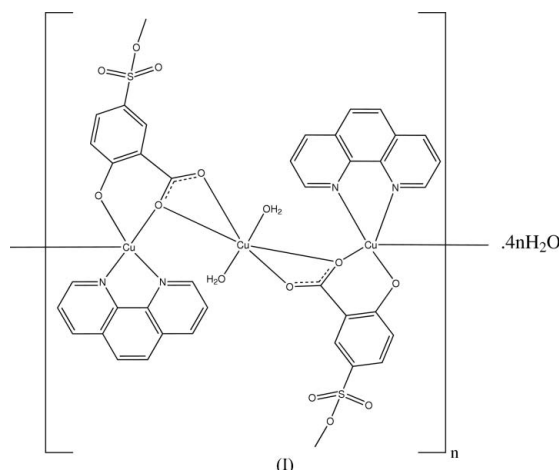
Figure 1
View of a segment of (I). Displacement ellipsoids are drawn at the 40% probability level. The minor disorder components are not shown. [Symmetry codes: (i) $-x$, $1 - y$, $1 - z$; (ii) $1 + x$, y, z; (iii) $-1 - x$, $1 - y$, $1 - z$.]

Figure 2
View of the one-dimensional chain in (I). H atoms and non-coordinated water molecules have been omitted for clarity.

(I) were obtained after the vessel had cooled to room temperature. Analysis calculated for $C_{38}H_{34}Cu_3N_4O_{18}S_2$: C 41.90, H 3.14, N 5.14%; found: C 41.48, H 2.95, N 4.66%.

The structure of (I) consists of centrosymmetric $[Cu_3(phen)_2(ssal)_2(H_2O)_2]$ (phen is 1,10-phenanthroline) trinuclear components and uncoordinated water molecules. A segment of the structure of (I) is shown in Fig. 1. There are two crystallographically independent Cu atoms in the asymmetric unit. Atom Cu2 occupies a special position (site symmetry $\bar{1}$), and has distorted octahedral coordination geometry defined by the four O atoms of two carboxylate groups and two O atoms of two water molecules. The other metal atom, Cu1, has a square-pyramidal geometry defined by the two N atoms of one phen ligand, and three O atoms from the carboxylate, phenolate and sulfonate groups of two $ssal^{3-}$ ligands. The O atom of the sulfonate group from the neighbouring trinuclear unit occupies the apical position.

In the trinuclear unit of (I), the Cu1···Cu2 separation is 4.2493 (7) Å, which is similar to the equivalent value of 4.2677 (6) Å in (II) but significantly smaller than the values of 4.6431 (5) and 4.6621 (6) Å for (III) and (IV), respectively. The μ_3 $ssal^{3-}$ ligands link the trinuclear units into a one-dimensional chain through sulfonate groups running along the a axis. In the chain, the phen and $ssal^{3-}$ ligands from a neighbouring trinuclear unit are nearly parallel, with a dihedral angle of 2.4 (2)°, and interact by way of π–π stacking with a centroid–centroid distance of about 3.50 Å. The structure is further consolidated into a three-dimensional framework by extensive O—H···O hydrogen bonding (Table 2).

Experimental

A mixture of $Cu(CH_3COO)_2 \cdot H_2O$ (0.041 g, 0.2 mmol), 5-sulfo-salicylic acid dihydrate (0.050 g, 0.2 mmol) and 1,10-phenanthroline (0.021 g, 0.11 mmol) in an aqueous solution (20 ml) was sealed in a 30 ml stainless steel reactor with a Teflon liner, then heated to 413 K and kept at this temperature for 24 h. Green block-shaped crystals of
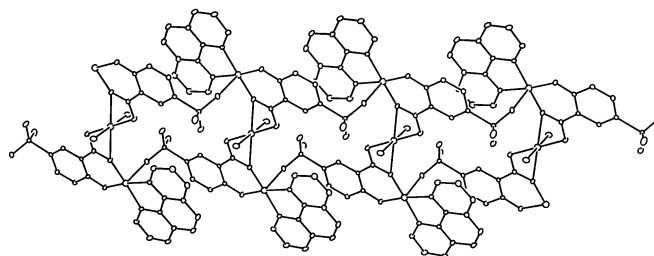
Crystal data

$[Cu_3(C_7H_3O_6S)_2(C_{12}H_8N_2)_2$- $(H_2O)_2]\cdot4H_2O$	$D_x = 1.771$ Mg m^{-3}
$M_r = 1089.43$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1522 reflections
$a = 8.7183$ (9) Å	$\theta = 2.4$–21.6°
$b = 14.0994$ (16) Å	$\mu = 1.74$ mm^{-1}
$c = 16.9212$ (18) Å	$T = 295$ (2) K
$\beta = 100.900$ (2)°	Block, green
$V = 2042.5$ (4) Å^3	$0.40 \times 0.34 \times 0.16$ mm
$Z = 2$	

Data collection

Bruker SMART APEX CCD diffractometer	3813 independent reflections
φ and ω scans	2341 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$R_{int} = 0.079$
	$\theta_{max} = 25.5°$
$T_{min} = 0.514$, $T_{max} = 0.759$	$h = -9 \rightarrow 10$
10606 measured reflections	$k = -17 \rightarrow 12$
	$l = -20 \rightarrow 19$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.051$	
$wR(F^2) = 0.116$	
$S = 0.94$	$w = 1/[\sigma^2(F_o^2) + (0.038P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3813 reflections	
321 parameters	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.70$ e Å^{-3}
	$\Delta\rho_{min} = -0.73$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—O3	1.887 (3)	Cu1—O4^{ii}	2.396 (4)
Cu1—O1	1.926 (3)	Cu2—O2	1.945 (3)
Cu1—N2	2.001 (4)	Cu2—O7	1.957 (4)
Cu1—N1	2.013 (4)	Cu2—O1	2.486 (3)

Symmetry code: (ii) $x + 1, y, z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7B···O6^{ii}	0.84 (4)	1.86 (5)	2.694 (5)	167 (5)
O7—H7A···O8	0.84 (1)	1.85 (2)	2.666 (13)	163 (3)
O7—H7A···O8$'$	0.84 (1)	1.89 (2)	2.729 (15)	172 (4)

Symmetry code: (ii) $x + 1, y, z$.

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All aromatic H atoms were positioned geometrically and refined as riding, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Some of the water H atoms were located in difference Fourier maps and were refined with distance restraints of O—H = 0.85 (1) Å and fixed isotropic displacement parameters of $U_{iso}(H) = 0.08$ Å^2. Water molecules O8 and O9 are disordered over two positions and their occupancies (sum constrained to unity) were refined to 0.61 (6):0.39 (6) and 0.66 (6):0.34 (6), respectively. The H atoms associated with these species were not located in the present study.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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