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Poly[[tris(di-2-pyridylamine)tris(μ-5-sulfonato salicylato)tricopper(II)] trihydrate]

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Key indicators

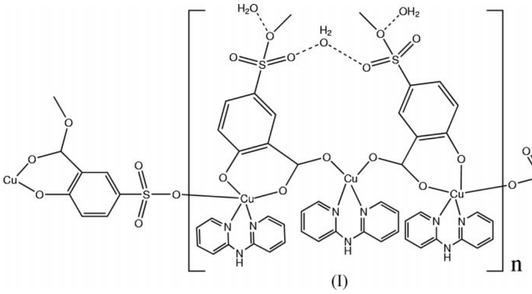
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
H-atom completeness 90%
R factor = 0.042
wR factor = 0.102
Data-to-parameter ratio = 14.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $[Cu_3(C_{10}H_9N_3)_3(C_7H_3O_6S)_2]\cdot 3H_2O$, $[Cu_3(ssal)_2(dpa)_3]$ units (dpa is 2,2′-dipyridylamine and ssal is 5-sulfonatosalicylate) are found, which consist of one crystallographically independent ssal anion, and two each of crystallographically independent dpa ligands and Cu atoms, the unit lying on a twofold rotation axis. One Cu atom is four-coordinated by one dpa ligand and one ssal anion within a square-planar geometry, whereas the second Cu atom is coordinated by one dpa ligand and two ssal anions which are related by symmetry. The first Cu atom has one longer contact to one O atom of a symmetry-related sulfonate group and is, therefore, five-coordinated within a distorted square-pyramidal coordination. The $[Cu_3(ssal)_2(dpa)_3]$ units are connected *via* the sulfonate groups into layers which are parallel to the *ab* plane. These layers are further connected by O—H$\cdots$O and N—H$\cdots$O hydrogen bonding *via* the water molecules.

Comment

Recently, the synthesis of complexes with sulfonates has attracted much attention, due to their versatile coordination behaviour compared with that of carboxylate groups (Haynes *et al.*, 2004; Koshima *et al.*, 2004). Complexes with 5-sulfosalicylic acid, a ligand with a combination of hydroxyl, carboxyl and sulfonate groups, show interesting coordination geometries (Toraishi *et al.*, 2004; Zheng *et al.*, 2003) and their coordination frameworks include discrete cation–anion complexes (Smith *et al.*, 2004; Ma *et al.*, 2003), dimers (Li *et al.*, 2004; Nothenberg *et al.*, 2000) or one-dimensional ladders (Chen *et al.*, 2003; Hecht, 2004; Wang *et al.*, 2004; Starynowicz, 2000). In our own work, we have prepared and structurally characterized the title compound, (I).



(I)

In the crystal structure of (I), trinuclear $[Cu_3(ssal)_2(dpa)_3]$ units are found, which consist of two crystallographically independent Cu atoms (Fig. 1). Atom Cu1, on a twofold rotation axis, is four-coordinated by two N atoms of one dpa

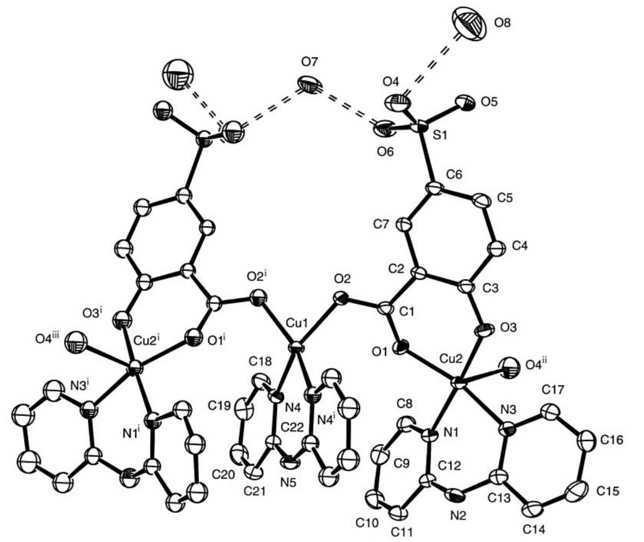


Figure 1

A view of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. Dashed lines indicate hydrogen bonding and H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (iii) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

ligand and two carboxylate O atoms of two symmetry-related ssal anions within a distorted tetrahedral geometry. Atom Cu1 exhibits two longer distances to two O atoms of 2.902 (2) Å, which are too long for a significant interaction.

Atom Cu2 is coordinated by two N atoms of one dpa ligand, one phenolate and one carboxylate O atom of one ssal anion, and one O atom of a sulfonate group of a symmetry-related ssal anion, within a distorted square-pyramidal geometry. Atoms O1, O3, N1 and N3 occupy the basal plane, while the sulfonate O atom is located in the apical position of the pyramid. Atom Cu2 and the coordinated dpa ligand, as well as the ssal anion, are located in general positions.

Atom Cu1 bridges two neighbouring [Cu(ssal)(dpa)] units into trinuclear $[Cu_3(ssal)_2(dpa)_3]$ units, with a Cu1$\cdots$Cu2 distance of 4.6431 (5) Å. The dihedral angle between the two pyridyl rings of the dpa ligand bonded to Cu1 is 10.7 (1)°, while that between the two pyridyl rings of the dpa ligand bonded to Cu2 is 27.0 (1)°.

In the trinuclear unit, each ssal anion is fully deprotonated and acts as a bridging ligand *via* its sulfonate, phenolate and carboxylate O atoms. The phenolate and one carboxylate O atom, as well as atom Cu2, form a six-membered chelate ring, which deviates slightly from planarity. The Cu2—O3 distance to the phenolate O atom is slightly shorter than that to the carboxylate O atom (Table 1); this difference is also found in, for example, $Na[Cu(ssal)(H_2O)_3]\cdot 0.5H_2O$ (Marzotto *et al.*, 2001). The $[Cu_3(ssal)_2(dpa)_3]$ units are connected *via* the sulfonate groups into layers parallel to the *ab* plane (Fig. 2).

The structure also contains water molecules. Water atom O7 is located on a twofold axis, while water atom O8 is located in a general position. For atom O8, the H atoms could not be located in the difference map. The water molecules connect the $[Cu_3(ssal)_2(dpa)_3]$ units *via* O—H$\cdots$O and N—H$\cdots$O hydrogen bonding (Table 2).

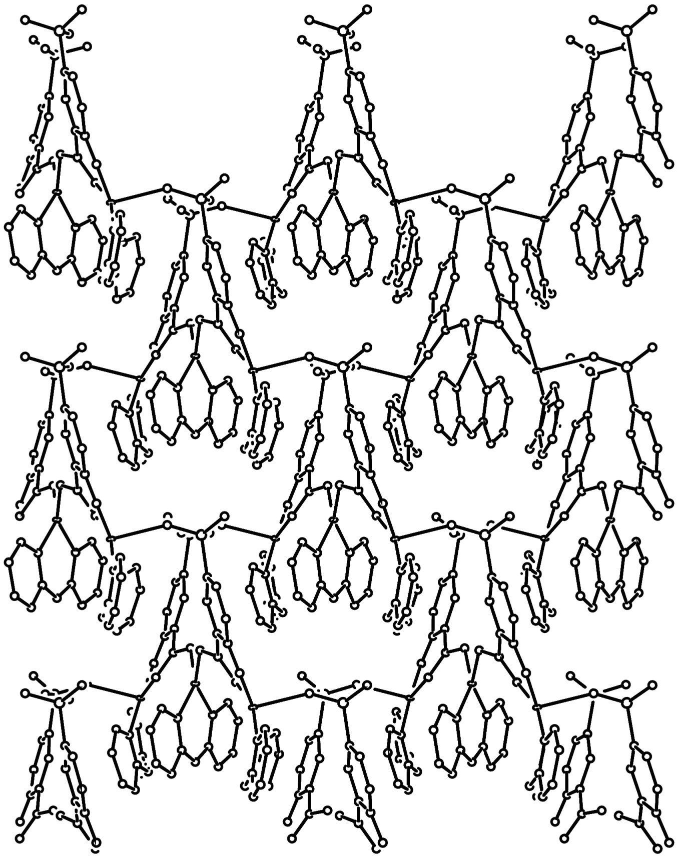


Figure 2

A view of the crystal structure of (I), along the *c* axis. The H atoms and water molecules have been omitted for clarity.

Experimental

A mixure of $Cu(CH_3COO)_2\cdot H_2O$ (0.041 g, 0.20 mmol), 5-sulfosalicylic acid dihydrate (0.050 g, 0.20 mmol), 2,2′-dipyridylamine (0.034 g, 0.20 mmol) and water (10 ml) was heated at 413 K for 72 h in a 20 ml Teflon-lined stainless steel autoclave. After cooling, green plate-shaped crystals of (I) had formed and these were filtered off.

Crystal data

$[Cu_3(C_{10}H_9N_3)_3(C_7H_3O_6S)_2]\cdot 3H_2O$
$M_r = 1188.58$
Monoclinic, $C2/c$
$a = 11.3447$ (10) Å
$b = 13.4618$ (11) Å
$c = 29.910$ (3) Å
$\beta = 98.650$ (2)°
$V = 4516.0$ (7) Å^3
$Z = 4$
$D_x = 1.748$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3596 reflections
$\theta = 4.8$–53.8°
$\mu = 1.58$ mm^{-1}
$T = 293$ (2) K
Plate, green
0.51 × 0.32 × 0.13 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.550$, $T_{max} = 0.816$
13 200 measured reflections
4979 independent reflections
3744 reflections with $I > 2\sigma I)$
$R_{int} = 0.087$
$\theta_{max} = 27.1$°
$h = -14 \rightarrow 13$
$k = -9 \rightarrow 17$
$l = -37 \rightarrow 38$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.102$
$S = 0.96$
4979 reflections
338 parameters
H-atoms treated by a mixture of independent and constrainted refinement
$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Extinction correction: none

Table 1
Selected geometric parameters (Å, °).

Cu1—O2	1.9447 (19)	Cu2—O1	1.942 (2)
Cu1—O2^{i}	1.9447 (19)	Cu2—N1	1.977 (2)
Cu1—N4	1.973 (2)	Cu2—N3	1.992 (2)
Cu1—N4^{i}	1.973 (2)	Cu2—O4^{ii}	2.318 (2)
Cu2—O3	1.900 (2)		
O2—Cu1—O2^{i}	86.67 (12)	O3—Cu2—N3	90.99 (10)
O2—Cu1—N4	152.71 (9)	O1—Cu2—N3	162.68 (10)
O2—Cu1—N4^{i}	96.15 (9)	N1—Cu2—N3	90.14 (10)
N4—Cu1—N4^{i}	93.59 (14)	O3—Cu2—O4^{ii}	93.59 (9)
O3—Cu2—O1	91.27 (8)	O1—Cu2—O4^{ii}	105.37 (9)
O3—Cu2—N1	176.10 (10)	N1—Cu2—O4^{ii}	90.10 (9)
O1—Cu2—N1	86.56 (9)	N3—Cu2—O4^{ii}	91.62 (10)

Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, y + \frac{1}{2}, z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O5^{iv}	0.81 (1)	2.06 (2)	2.833 (3)	159 (4)
N5—H5*A*···O7^{iv}	0.80 (1)	1.96 (1)	2.759 (5)	180
O7—H7*A*···O6^{i}	0.81 (3)	1.88 (3)	2.685 (3)	172 (5)
O8···O8^{v}			2.965 (8)	
O8···O4			2.908 (4)	

Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (iv) $x, y + 1, z$; (v) $-x - \frac{1}{2}, -y - \frac{1}{2}, -z$.

H atoms bonded to C atoms were positioned with idealized geometry, with C—H distances of 0.93 Å, and were refined using the riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms bound to water atom O7 and to the N atoms were located in a difference map and refined with restraints for the O—H and N—H distances of 0.82 (1) and 0.80 (1) Å, respectively, and with fixed isotropic displacement parameters of $U_{iso}(H) = 0.08$ and 0.05 Å^2, respectively. The H atoms of water atom O8 could not be located in the difference map and were not considered in the refinement, but they were included in the calculations of *F*(000), the molecular formula and derived results. However, the intermolecular O···O distances are in the normal range for O—H···O hydrogen bonding (Table 2).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT* and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WINGX* (Farrugia, 1999).

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