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Key indicators

Single-crystal X-ray study
 T = 295 K
 Mean $\sigma(C-C)$ = 0.010 Å
 H-atom completeness 97%
 Disorder in solvent or counterion
 R factor = 0.070
 wR factor = 0.161
 Data-to-parameter ratio = 11.8

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

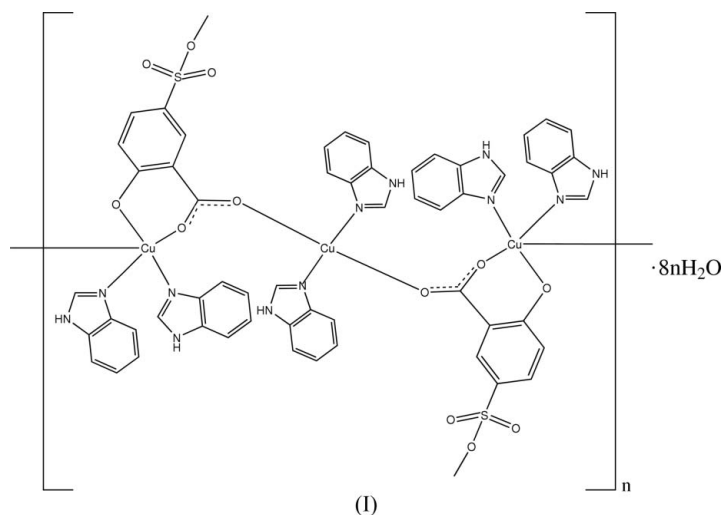
**catena-Poly[[hexakis(1*H*-benzimidazole)-
 bis(μ^2 -5-sulfonatosalicylato)tricopper(II)]
 octahydrate]**

The crystal structure of the title compound, $\{[Cu_3(C_7H_3O_6S)_2(C_7H_6N_2)_6] \cdot 8H_2O\}_n$, is built of trinuclear complexes $[Cu_3(bz)_6(ssal)_2]$ (bz = benzimidazole and ssal = 5-sulfonatosalicylate trianion) and uncoordinated water molecules. The molecule of the complex occupies a special position on a crystallographic inversion centre. The Cu atom located on the inversion centre has a square planar coordination made up of the two N atoms of monodentate benzimidazole ligands and the O atoms of two bridging salicylates. The other crystallographically independent Cu atom has a square pyramidal environment formed by the N atoms of two more monodentate benzimidazole ligands, two chelate O atoms of the bridging salicylate and the sulfonate O atom of the sulfonatosalicylate ligand belonging to the neighbouring trimetallic complex. The latter coordination links the molecules of the complex into infinite chains running along the *a* axis. These chains are further connected by O–H...O and N–H...O hydrogen bonding into a three-dimensional network.

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Comment

5-Sulfosalicylate complexes have lately been receiving considerable attention, and numerous complexes of this kind have been synthesized (Gao *et al.*, 2005; Smith *et al.*, 2005). Among these, two copper complexes with trinuclear units, $[Cu_3(2,2'-bipy)_2(ssal)_2(H_2O)_4] \cdot 4H_2O$, (II) (Wang *et al.*, 2004), and $[Cu_3(dpa)_3(ssal)_2] \cdot 3H_2O$, (III) (Fan & Zhu, 2005) (2,2'-bipy = 2,2'-bipyridine and dpa = 2,2'-dipyridylamine), were reported. We present here a third 5-sulfonatosalicylate copper complex with the trinuclear Cu_3 motif, (I).



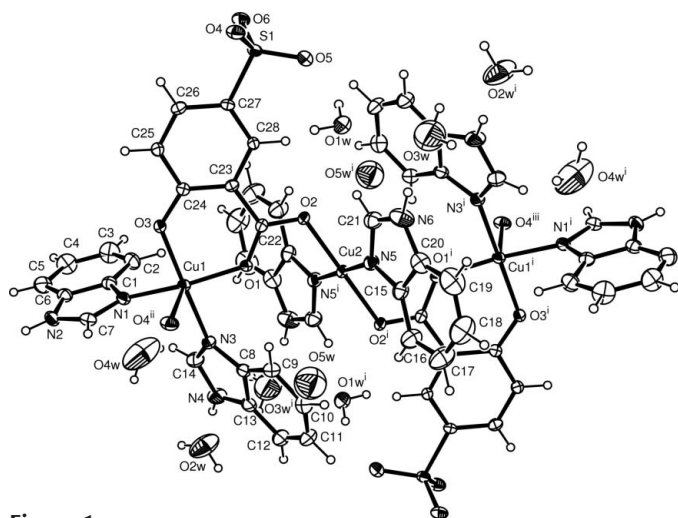


Figure 1
ORTEP-3 (Farrugia, 1997) view of the structure of (I). Displacement ellipsoids are drawn at the 30% probability level. The minor component of the disordered water molecule has been omitted for clarity. [Symmetry codes (i): $1 - x, 1 - y, 2 - z$; (ii): $-x, 1 - y, 2 - z$; (iii): $1 + x, y, z$.]

The crystal structure of the title compound is built of centrosymmetric trinuclear complexes, $[\text{Cu}_3(\text{bz})_6(\text{ssal})_2]$ (bz = benzimidazole and ssal = 5-sulfonatosalicylate trianion), and uncoordinated water molecules; a fragment of the structure of (I) with the trinuclear complex and water molecules is shown in Fig. 1.

There are two crystallographically independent Cu atoms in each complex. One of them, Cu2, occupies a special position on a crystallographic inversion centre and has a square planar coordination, formed by the N atoms of two monodentate benzimidazole ligands [$\text{Cu2}-\text{N5} = 2.000$ (5) Å] and the O atoms of two bridging sulfonatosalicylates [$\text{Cu2}-\text{O2} = 1.965$ (3) Å]. The other crystallographically independent metal atom, Cu1, has a square pyramidal geometry formed by the N atoms of two more benzimidazole ligands [$\text{Cu1}-\text{N1} = 1.990$ (4) Å and $\text{Cu1}-\text{N3} = 2.004$ (4) Å], two O atoms of the chelate salicylate fragment [$\text{Cu1}-\text{O1} = 1.935$ (4) Å and $\text{Cu1}-\text{O3} = 1.920$ (3) Å] and the O atom of the sulfonate group of the neighbouring trinuclear complex in the apical position of the pyramid [$\text{Cu1}-\text{O4}^{\text{ii}} = 2.330$ (4) Å; symmetry code: (ii) $-x, 1 - y, 2 - z$]. The latter contact gives rise to infinite chains running along the *a* axis of the crystal structure. The structure is further consolidated into a three-dimensional framework by extensive $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding (Table 2).

Comparison of the two previously reported copper complexes with trinuclear units with (I) shows that the ssal ligands in these three complexes have different coordination modes. In (III), ssal is a μ_5 ligand, while in (I) and (II), the ssal anions are μ_3 ligands; therefore, the structures of (I) and (II) feature one-dimensional chains, whereas the structure of (III) is built of two-dimensional layers. In the trinuclear units the Cu atoms in special positions have four-, six- and four-coordinated environments with square planar, octahedral and distorted tetrahedral geometry for (I), (II) and (III), respectively. The Cu atoms in general positions have either square

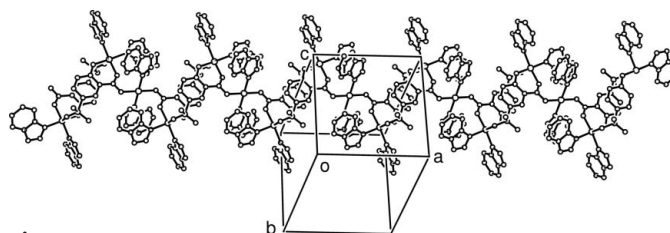


Figure 2
A view of the one-dimensional network in (I). H atoms and uncoordinated water molecules have been omitted for clarity.

pyramidal environments, as in (I) and (II), or octahedron geometry, as in (III). The comparison of bond lengths in these three complexes is given in Table 3.

Experimental

A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.170 g, 1 mmol), 5-sulfosalicylic acid dihydrate (0.126 g, 0.5 mmol), Na_2CO_3 (0.106 g, 1 mmol) and benzimidazole (0.236 g, 2 mmol) in water/methanol (*v/v* 2:1) solution (30 ml) was refluxed for 2 h and filtered. After the mixture had been left to stand for 1 d, green block-shaped crystals of (I) precipitated; these were used for the X-ray diffraction experiment.

Crystal data

$[\text{Cu}_3(\text{C}_7\text{H}_3\text{O}_6\text{S})_2(\text{C}_7\text{H}_6\text{N}_2)_6] \cdot 8\text{H}_2\text{O}$
 $M_r = 1473.88$
 Triclinic, $P\bar{1}$
 $a = 11.1489$ (6) Å
 $b = 11.9699$ (6) Å
 $c = 12.5693$ (6) Å
 $\alpha = 99.302$ (1)°
 $\beta = 93.690$ (1)°
 $\gamma = 107.155$ (1)°
 $V = 1570.48$ (14) Å³

$Z = 1$
 $D_x = 1.558$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5186 reflections
 $\theta = 2.2$ – 27.7°
 $\mu = 1.16$ mm⁻¹
 $T = 295$ (2) K
 Block, green
 $0.33 \times 0.21 \times 0.10$ mm

Data collection

Bruker APEX area-detector diffractometer
 φ and ω scan
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\text{min}} = 0.701$, $T_{\text{max}} = 0.893$
 11391 measured reflections

5475 independent reflections
 5149 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -13 \rightarrow 13$
 $k = -14 \rightarrow 14$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.070$
 $wR(F^2) = 0.161$
 $S = 1.22$
 5475 reflections
 464 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 6.6709P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.69$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.66$ e Å⁻³

Table 1

Selected bond angles (°).

O3—Cu1—O1	91.45 (15)	N3—Cu1—O4 ⁱⁱ	90.56 (17)
O3—Cu1—N1	87.16 (16)	O2—Cu2—O2 ⁱ	180 (1)
O1—Cu1—N1	166.81 (18)	O2—Cu2—N5	87.02 (17)
O3—Cu1—N3	172.30 (18)	O2 ⁱ —Cu2—N5	92.98 (17)
O1—Cu1—N3	88.85 (17)	N5—Cu2—N5 ⁱ	180 (1)
N1—Cu1—N3	90.79 (18)	O5—S1—O4	113.4 (3)
O3—Cu1—O4 ⁱⁱ	97.02 (15)	O5—S1—O6	112.0 (2)
O1—Cu1—O4 ⁱⁱ	97.76 (16)	O4—S1—O6	110.3 (2)
N1—Cu1—O4 ⁱⁱ	95.42 (16)		

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

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...O6 ^{iv}	0.86	2.01	2.836 (6)	161
N4—H4...O2 _w	0.86	1.96	2.822 (8)	178
N6—H6...O3 _w	0.86	2.04	2.894 (10)	172
N6—H6...O1 _w	0.86	2.60	3.099 (8)	118
O1 _w —H1 _B ...O3 ⁱⁱ	0.85 (6)	1.96 (6)	2.798 (6)	170 (7)
O2 _w —H2 _A ...O5 _w ^v	0.86 (7)	1.90 (7)	2.73 (6)	162 (8)
O2 _w —H2 _A ...O5 _w ^v	0.86 (7)	2.31 (6)	3.03 (3)	142 (8)
O2 _w —H2 _B ...O6 ^{vi}	0.85 (5)	1.94 (5)	2.781 (8)	170 (8)
O3 _w —H3 _A ...O5 _w ^{viii}	0.86 (4)	1.78 (7)	2.50 (6)	140 (7)
O3 _w —H3 _A ...O5 _w ^{vii}	0.86 (4)	1.96 (4)	2.81 (3)	169 (9)
O3 _w —H3 _B ...O2 _w ^j	0.86 (3)	2.14 (6)	2.874 (16)	144 (8)
O4 _w —H4 _A ...O5 _w ^v	0.85 (1)	1.98 (9)	2.80 (7)	163 (16)
O4 _w —H4 _B ...O5 _w ^{viii}	0.85 (1)	2.36 (6)	3.20 (4)	169 (16)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$; (ii) $-x, -y + 1, -z + 2$; (iv) $x, y, z + 1$; (v) $-x + 1, -y + 1, -z + 3$; (vi) $x + 1, y, z + 1$; (vii) $-x + 1, -y + 2, -z + 2$; (viii) $x, y - 1, z$.

Table 3
Comparison of bond lengths (Å) in three copper complexes with trinuclear units.

Bond	(I)	(II)	(III)
Cu—N ^a	2.000 (5)		1.973 (2)
Cu—O(COO ⁻) ^a	1.965 (3)	1.960 (4)	1.9447 (19)
Cu—O(COO ⁻) ^a		2.486 (4)	
Cu—N	1.990 (4)	1.991 (5)	1.977 (2)
Cu—N	2.004 (4)	1.996 (5)	1.992 (2)
Cu—O(phenolato)	1.920 (3)	1.881 (4)	1.900 (2)
Cu—O(COO ⁻)	1.935 (4)	1.933 (4)	1.942 (2)
Cu—O(SO ₃ ⁻)	2.330 (4)	2.546 (4)	2.318 (2)

Notes: (a) The distance involving the Cu atom in a special position.

All aromatic H atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and refined as riding atoms, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C,N})$. The occupancies of water molecules O4_w and O5_w were initially refined to 0.60 (3) and 0.54 (2), respectively; they were then fixed at 0.5. At this stage, the O5_w molecule was disordered over two sites with the ratio of 0.341 (17):0.159 (17) for O5_w and O5_w', respectively. The H atoms of these water molecules could not be located. H atoms of other water molecules were located in difference Fourier maps and were refined with a distance restraint of O—H = 0.85 (1) Å and fixed isotropic displacement parameter of $U_{\text{iso}}(\text{H}) = 0.08 \text{ \AA}^2$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; 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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