

A mixed-valence Cu^{II}/Cu^I anion–cation complex: bis[μ -5-sulfosalicylato(3–)]bis[(di-2-pyridylamine)copper(II)] bis[bis(di-2-pyridylamine)copper(I)] dihydrate

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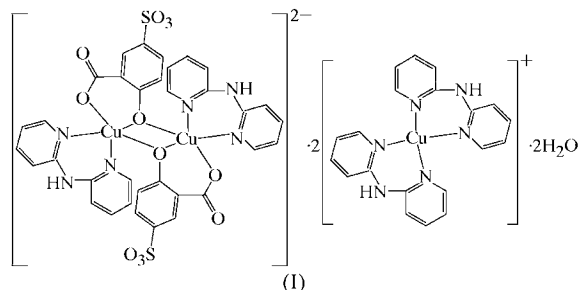
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The title compound, [Cu^{II}(C₇H₃O₆S)₂(C₁₀H₉N₃)₂][Cu^I(C₁₀H₉N₃)₂]₂·2H₂O, consists of anionic Cu^{II} moieties, cationic Cu^I species and uncoordinated water molecules. The anionic dimeric unit consists of one crystallographically independent fully deprotonated 5-sulfosalicylate (2-oxido-5-sulfonato-benzoate) anion, a di-2-pyridylamine group and a Cu^{II} atom. Each Cu^{II} atom is five-coordinate within a square-pyramidal geometry. The anion lies on a special position of $\bar{1}$ site symmetry. In the cationic monomer, the Cu^I atom adopts tetrahedral geometry. The cations and anions are connected by O–H...O and N–H...O hydrogen bonds.

Comment

It is well known that Cu^{II} ions can be reduced to Cu^I by nitrogen-heterocyclic ligands, such as 4,4'-bipyridine or pyridine derivatives, under hydrothermal conditions (Wen *et al.*, 2004). Interesting reactions and novel structures can be achieved when Cu^{II} is reduced. Mixed-valence Cu^{I,II} complexes are of great importance in the fields of structural topology and functional materials (Zhang & Chen, 2003). In



general, mixed-valence copper complexes exist as polynuclear species or ion pairs (Pawlowski *et al.*, 2004). Although

numerous complexes with cationic Cu^{II} and anionic Cu^I components have been prepared, complexes containing cationic Cu^I and anionic Cu^{II} motifs have been apparently ignored. In our recent report on metal 5-sulfosalicylates, a copper salt was reacted with 5-sulfosalicylic acid (H₃ssal) and di-2-pyridylamine (dpa), and [Cu₃(ssal)₂(dpa)₃]₃·3H₂O was obtained (Fan & Zhu, 2005). Without an abstracting reagent, a similar synthesis, but with the addition of NaOH, yielded the

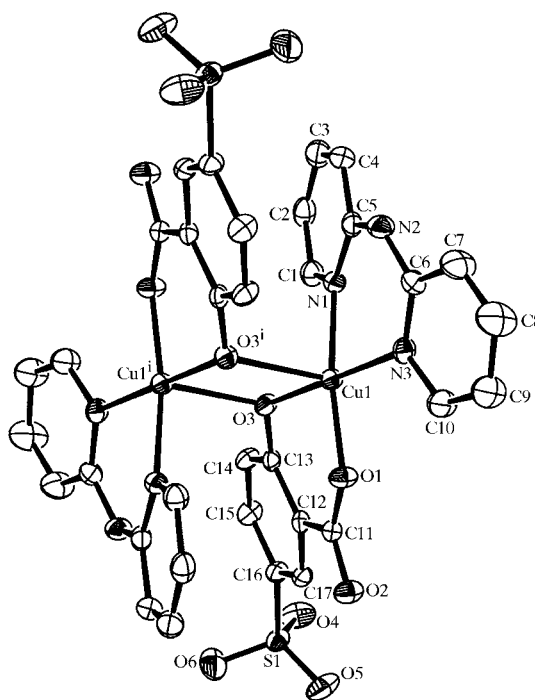


Figure 1
An ORTEP-3 view (Farrugia, 1997) of the anionic dimer. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1, -y + 1, -z + 2$.]

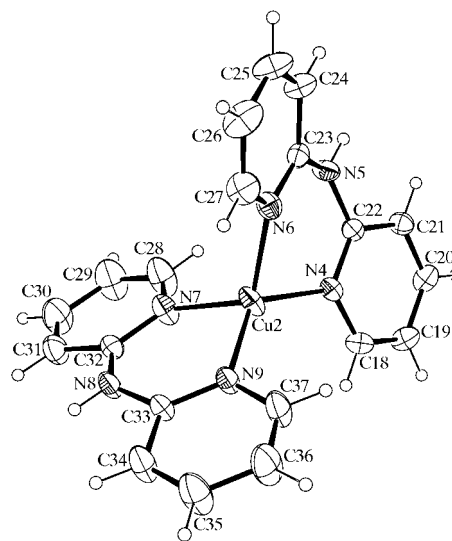


Figure 2
An ORTEP-3 view (Farrugia, 1997) of the cationic monomer. Displacement ellipsoids are drawn at the 50% probability level.

mixed-valence title compound with cationic Cu^{I} components, $[\text{Cu}_2^{\text{II}}(\text{ssal})_2(\text{dpa})_2] \cdot [\text{Cu}^{\text{I}}(\text{dpa})_2]_2 \cdot 2\text{H}_2\text{O}$, (I) (Figs. 1 and 2, and Table 1).

The anionic dimer $[\text{Cu}_2(\text{ssal})_2(\text{dpa})_2]^{2-}$ consists of two centrosymmetrically related five-coordinate Cu^{II} centers, with a $\text{Cu} \cdots \text{Cu}^{\text{I}}$ distance of 3.225 (1) Å [symmetry code: (i) $-x + 1, -y + 1, -z + 2$]. The basal plane of the square-pyramidal geometry of the Cu^{II} center is occupied by two N atoms of a dpa ligand and two O atoms of the fully deprotonated ssal^{3-} ligand, while the apical position is taken by the phenoxo O atom of a second centrosymmetrically imposed ssal^{3-} ligand. A four-membered bridging unit, Cu_2O_2 , is formed between the Cu^{II} atoms *via* phenoxo atoms O3 and O3ⁱ. Only one carboxylate O atom from the ssal^{3-} ligand is directly bonded to the Cu^{II} atom, and the coordination mode of the carboxylate moiety is obviously *anti* monodentate. As expected, in the anion, the C11—O1 bond is significantly

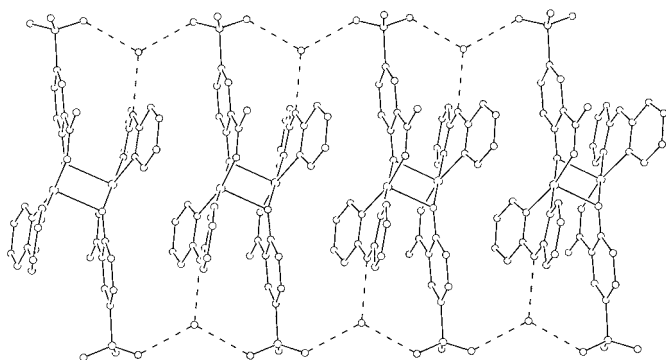


Figure 3
A view of the one-dimensional hydrogen-bonded chain constructed from anions and water molecules. Hydrogen bonds are shown as dashed lines and H atoms have been omitted for clarity.

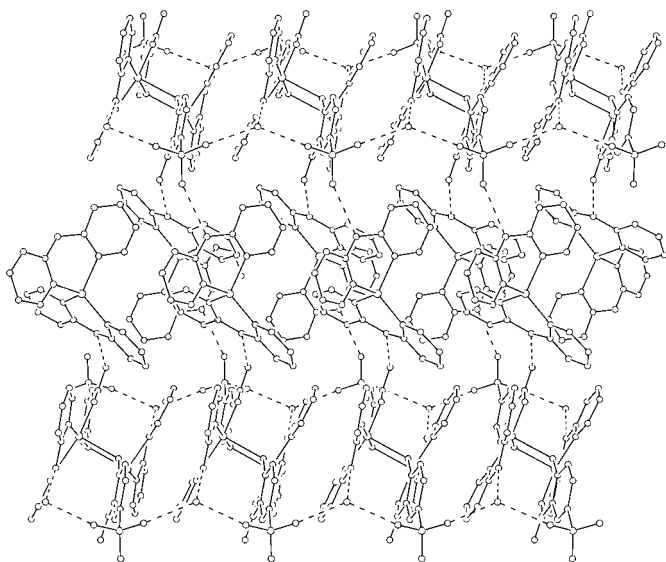


Figure 4
A view of the two-dimensional hydrogen-bonded network of (I) parallel to (010). Hydrogen bonds are shown as dashed lines and H atoms have been omitted for clarity.

longer than the C11—O2 distance, indicating a greater keto character in the latter. The dihedral angle between the planes of the ring (atoms C12—C17) and its carboxyl group is 11.0 (4)°. The structure of the anion is closely related to that of the ternary dimeric compound $[\text{Cu}^{\text{II}}(\text{dpa})(\text{salal})](\text{ClO}_4)_2$ (salal is salicylaldehyde; Garland *et al.*, 1985), in which the Cu^{II} atom is coordinated by an additional O atom from a ClO_4^- anion and the $\text{Cu} \cdots \text{Cu}$ distance is longer than that in the title compound.

The cation consists of a Cu^{I} atom and two dpa ligands (Fig. 2), the Cu^{I} center adopting tetrahedral geometry. The $\text{Cu}^{\text{I}}-\text{N}$ bond lengths are similar to those in the anion, while the conformations of the three dpa ligands in the asymmetric unit differ slightly. The dihedral angle between the two pyridyl rings of the dpa ligand in the anion is 19.2 (2)°, while the corresponding angles in the cation are 23.9 (3) and 15.3 (4)°. The $\text{N}1 \cdots \text{N}3$, $\text{N}4 \cdots \text{N}6$ and $\text{N}7 \cdots \text{N}9$ distances are 2.855 (5), 2.891 (6) and 2.955 (6) Å, respectively.

The anions and water molecules form one-dimensional hydrogen-bonded chains through $\text{N}-\text{H} \cdots \text{O}1\text{W}$ and $\text{O}1\text{W}-\text{H} \cdots \text{O}(\text{SO}_3^-)$ interactions (Fig. 3 and Table 2). These chains are linked into a two-dimensional hydrogen-bonded network by the cations through carboxylate and sulfonate $\text{N}-\text{H} \cdots \text{O}$ interactions (Fig. 4). Therefore, in the solid state, the stability of (I) is enhanced by hydrogen-bonding interactions.

Experimental

A mixture of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.040 g, 0.20 mmol), 5-sulfosalicylic acid dihydrate (0.026 g, 0.10 mmol), di-2-pyridylamine (0.035 g, 0.20 mmol), NaOH (0.019 g, 0.5 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 block-shaped crystals of (I) were obtained by filtration.

Crystal data

$[\text{Cu}_2(\text{C}_7\text{H}_3\text{O}_6\text{S})_2(\text{C}_{10}\text{H}_9\text{N}_3)_2] \cdot$
 $[\text{Cu}(\text{C}_{10}\text{H}_9\text{N}_3)_2]_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 1747.71$
Triclinic, $P\bar{1}$
 $a = 7.258$ (2) Å
 $b = 14.422$ (4) Å
 $c = 18.312$ (5) Å
 $\alpha = 82.428$ (4)°
 $\beta = 80.697$ (4)°
 $\gamma = 86.409$ (4)°
 $V = 1873.5$ (9) Å³

$Z = 1$
 $D_x = 1.549$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 4694 reflections
 $\theta = 2.5-26.2^\circ$
 $\mu = 1.25$ mm⁻¹
 $T = 295$ (2) K
Block, green
 $0.28 \times 0.19 \times 0.14$ mm

Data collection

Bruker SMART APEX area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\text{min}} = 0.759$, $T_{\text{max}} = 0.844$
13 648 measured reflections

6582 independent reflections
6078 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 25.1^\circ$
 $h = -8 \rightarrow 8$
 $k = -17 \rightarrow 16$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.069$
 $wR(F^2) = 0.148$
 $S = 1.23$
6582 reflections
514 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 3.6691P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.65$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.41$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.926 (3)	Cu2—N9	1.989 (4)
Cu1—O3	1.930 (3)	Cu2—N4	2.013 (4)
Cu1—N1	2.019 (4)	Cu2—N6	2.031 (4)
Cu1—N3	2.033 (4)	Cu2—N7	2.032 (4)
Cu1—O3 ⁱ	2.343 (3)		
O1—Cu1—O3	89.89 (13)	N1—Cu1—O3 ⁱ	93.09 (13)
O1—Cu1—N1	168.73 (15)	N3—Cu1—O3 ⁱ	97.99 (14)
O3—Cu1—N1	90.05 (14)	N9—Cu2—N4	130.02 (18)
O1—Cu1—N3	90.36 (14)	N9—Cu2—N6	116.50 (18)
O3—Cu1—N3	179.45 (16)	N4—Cu2—N6	91.23 (16)
N1—Cu1—N3	89.61 (15)	N9—Cu2—N7	94.58 (17)
O1—Cu1—O3 ⁱ	98.07 (13)	N4—Cu2—N7	110.31 (18)
O3—Cu1—O3 ⁱ	82.45 (12)	N6—Cu2—N7	115.75 (19)

Symmetry code: (i) $-x + 1, -y + 1, -z + 2$.

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—H2A...O7 ⁱ	0.82 (3)	2.00 (3)	2.814 (6)	175 (6)
N5—H5A...O5 ⁱⁱⁱ	0.82 (4)	2.08 (4)	2.896 (5)	178 (5)
N8—H8A...O2 ⁱⁱ	0.82 (5)	1.99 (5)	2.809 (5)	172 (6)
O7—H7A...O4 ⁱⁱⁱ	0.86	1.98	2.813 (6)	162
O7—H7B...O6	0.84	2.00	2.801 (6)	159

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

The aromatic H atoms were generated geometrically and were included in the refinements in the riding-model approximation [$C-H = 0.93$ Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. The water and amine H atoms were located in a difference Fourier map. The N—H distances were refined subject to the restraint $0.82(1)$ Å and, while the O—H distances were initially subjected to a restraint of $0.85(1)$ Å, in the final refinement the water H-atom coordinates were fixed and not refined. H atoms bonded to nitrogen had their U_{iso} values fixed at 0.05 Å², while the values of the water H atoms were fixed at 0.08 Å². The crystals were dried and stored in air, and data collection at room

temperature was carried out directly using such a crystal without a protective oil. *PLATON* analysis (Spek, 2003) suggests that the structure contains a solvent-accessible void, which is able to accommodate an additional water molecule in the region around $(\frac{1}{2}, 0, 0)$; however, the additional water molecule has not been located. Although the crystal was measured to a 2θ limit of 56.7° , only the intensities below 50.1° were used in the refinement; the use of all reflections gave a much lower data completeness (90.5%). In the present refinement, there are 55 reflections missing from the data set.

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1813). Services for accessing these data are described at the back of the journal.

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