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Bis(μ-4-sulfobenzoato-κ^2O:O')bis[aqua(2,2′-bipyridine-κ^2N,N')copper(II)]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.032
wR factor = 0.089
Data-to-parameter ratio = 12.0

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

The title compound, $[Cu_2(C_7H_4O_5S)_2(C_{10}H_8N_2)_2(H_2O)_2]$, crystallizes as a centrosymmetrically dimer containing two Cu^{II} atoms bridged by two 4-sulfobenzoate ligands. Each Cu^{II} atom displays a square-pyramidal coordination geometry completed by three O atoms from one water molecule and two 4-sulfobenzoate ligands and two N atoms from one 2,2′-bipyridine ligand. The dimers are linked into pairs by hydrogen bonds.

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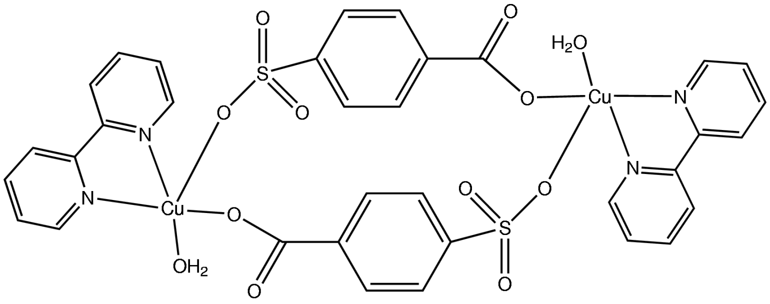
Comment

It is well known that the sulfonate group exhibits different coordination behavior compared to the carboxyl group (Zheng *et al.*, 2003; Wang *et al.*, 2004; Starynowicz, 2000). Numerous 1,4-benzenedicarboxylate (bdc) complexes have been extensively studied in the past decade due to their potential applications as functional materials and to the considerable interest arising from the variety of framework topologies they adopt (Yaghi *et al.*, 2003; Eddaoudi *et al.*, 2002; Zhu *et al.*, 2004). However, complexes with 4-sulfobenzoate (sb), a ligand with a combination of sulfonate and carboxyl groups, remain few (Yuan *et al.*, 2001; Xiong *et al.*, 2001). In dimeric bdc compounds, the structures are constructed and controlled by additional anions to compensate charge and/or complete the coordination (Sun *et al.*, 2000; Cano *et al.*, 1997; Huang *et al.*, 2003; Xiao, Li *et al.*, 2004; Xiao, Hu & Li, 2004). We report here the first cyclic dimer with the sb ligand, $[Cu(sb)(2,2'\text{-bipy})(H_2O)]_2$, (I).



(I)

The molecular structure is a centrosymmetric dimer loop (Fig. 1), in which each Cu atom has a five-coordinate geometry defined by one O-atom donor from one water molecule, two N atoms from one 2,2′-bipyridine, and two O atoms from two sb ligands. Atoms N1, N2, O1 and O6 occupy the basal plane, while atom O3* [symmetry code: (*) $-x$, $2-y$, $-z$] occupies the apical site (Table 1). The Cu—O(carboxylato) distance in (I) is similar to those in dimeric bdc compounds, such as

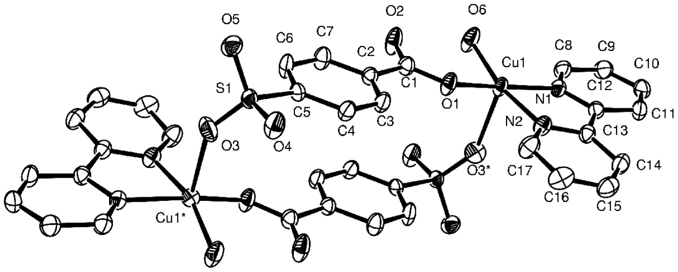


Figure 1
ORTEP-3 diagram (Farrugia, 1997) of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (*) $-x$, $2 - y$, $-z$.]

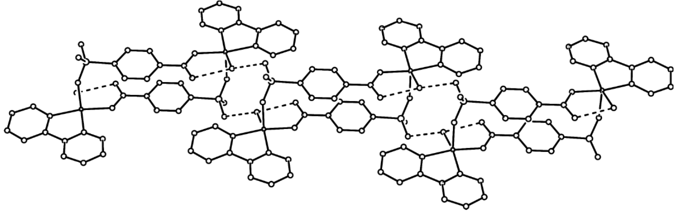


Figure 2
View of the one-dimensional hydrogen-bonded chain of (I). Hydrogen bonds are shown by dashed lines and the H atoms have been omitted for clarity.

$[Cu_2(bdc)(phen)_4](ClO_4)_2$, (II) [1.955 (2) Å; Sun *et al.*, 2000], $[Cu_2(bdc)(2,2'\text{-bipy})_4](NO_3)_2$, (III) [1.995 (4) Å; Huang *et al.*, 2003], $[Cu_2(bdc)(2,2'\text{-bipy})_4](bdc)$, (IV) [1.980 (2) Å; Huang *et al.*, 2003], and $[Cu_2(bdc)(2,2'\text{-bipy})_4](ClO_4)_2$, (V) [1.997 (6) Å; Cano *et al.*, 1997]. The Cu—N bond distances in (I) are nearly equivalent and the average value is 1.994 (2) Å. In contrast, one of the four Cu—N bond distances is significantly longer [2.169 (7)–2.216 (2) Å] in the reported dimeric bdc compounds (II)–(V).

In the cyclic dimer, sb is in a bis-monodentate coordination mode, acting as a linker, and the intradimer Cu···Cu separation is 9.7495 (8) Å, which is significantly shorter than those of reported dimeric bdc complexes (about 11.0 Å). The two rings of the 2,2′-bipyridine subtend a dihedral angle of 8.2 (2)°. The dihedral angle between the planes of the sb ring and its carboxyl group is 4.0 (4)°. The C1—O1 bond length [1.276 (3) Å] is longer than the C1—O2 distance [1.242 (3) Å], indicating more keto character in the latter. The two *cis*-arranged sb ligands in the central ring are exactly parallel. There is an intramolecular hydrogen bond between the water molecule and the uncoordinated carboxyl O atom (Table 2).

The coordinated water molecule forms a hydrogen bond with atom O4 (symmetry code: $x - 1$, $y - 1$, z) of an adjacent dimer, thereby creating a hydrogen-bonded chain (Fig. 2). The shortest Cu···Cu separation between neighboring dimers is 5.7722 (6) Å, which is shorter than those of bdc complexes (6.9 Å). Moreover, sb and 2,2′-bipyridine ligands between the neighboring hydrogen-bonded chains are nearly coplanar [dihedral angle = 3.8 (1)°] and exhibit π–π interactions with a distance of about 3.44 Å. From the above data, it is obvious that in the crystal packing, hydrogen bonds and π–π interactions enhance the stability of the structure.

Experimental

A mixture of $Cu(NO_3)_2\cdot3H_2O$ (0.053 g, 0.22 mmol), potassium hydrogen 4-sulfobenzoate (0.041 g, 0.17 mmol), 2,2′-bipyridine (0.034 g, 0.22 mmol) and water (8 ml) was sealed in a 20 ml stainless steel reactor with a Teflon liner and heated to 423 K for 24 h. After cooling, deep blue block-shaped crystals of (I) were collected by filtration.

Crystal data

$[Cu_2(C_7H_4O_5S)_2(C_{10}H_8N_2)_2(H_2O)_2]$
$M_r = 875.80$
Triclinic, $P\overline{1}$
$a = 8.9013$ (6) Å
$b = 10.2224$ (7) Å
$c = 10.4902$ (7) Å
$\alpha = 92.306$ (1)°
$\beta = 112.334$ (1)°
$\gamma = 103.566$ (1)°
$V = 849.4$ (1) Å^3

$Z = 1$
$D_x = 1.712$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5311 reflections
$\theta = 2.1$–$28.2°$
$\mu = 1.45$ mm^{-1}
$T = 293$ (2) K
Block, blue
0.44 × 0.23 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.568$, $T_{max} = 0.812$
4512 measured reflections
3002 independent reflections

2799 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 25.2°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 11$
$l = -10 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.089$
$S = 1.07$
3002 reflections
250 parameters
H-atom treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.3207P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O6	1.930 (2)	Cu1—N2	1.995 (2)
Cu1—O1	1.949 (2)	Cu1—O3^{i}	2.316 (2)
Cu1—N1	1.992 (2)		
O6—Cu1—O1	91.72 (8)	N1—Cu1—N2	81.23 (8)
O6—Cu1—N1	94.19 (8)	O6—Cu1—O3^{i}	99.13 (9)
O1—Cu1—N1	170.77 (7)	O1—Cu1—O3^{i}	97.93 (7)
O6—Cu1—N2	167.67 (9)	N1—Cu1—O3^{i}	88.13 (7)
O1—Cu1—N2	91.55 (8)	N2—Cu1—O3^{i}	92.18 (8)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*A*···O4^{ii}	0.89 (1)	1.80 (1)	2.688 (3)	172 (3)
O6—H6*B*···O2	0.89 (3)	1.71 (2)	2.538 (3)	153 (4)

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

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H atoms bonded to the C atoms were positioned geometrically and treated as riding, with C—H distances of 0.93 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(parent). The water H atoms were located in difference–Fourier maps and refined with restraints for O—H distances [0.90 (1) Å] and with $U_{\rm iso}$(H) = 0.08 Å^2.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT* and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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