Li-Ping Zhang and
Long-Guan Zhu*

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

Correspondence e-mail: chezlg@zju.edu.cn

Key indicators

Single-crystal X-ray study
$T = 295$ K
Mean σ(C–C) = 0.008 Å
Disorder in main residue
R factor = 0.065
wR factor = 0.157
Data-to-parameter ratio = 11.3

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

The cyclic dimer bis(μ2-4-sulfonatobenzoato)-bis[(di-2-pyridylamine)copper(II)] trihydrate

The title complex, $[Cu_2(C_7H_4O_5S)_2(C_{10}H_9N_3)_2]\cdot 3H_2O$, comprises the centrosymmetric cyclic dimeric Cu^{II} complex and uncoordinated water molecules. The Cu^{II} atom displays a distorted square-pyramidal geometry. Within the cyclic dimer, the Cu···Cu separation is 9.5362 (12) Å.

Comment

In recent decades, a great number of dimeric complexes have been synthesized and structurally characterized (Huang *et al.*, 2003; Rochon & Massarweh, 2001; Heinze *et al.*, 1998), among which several are cyclic (Lawrence *et al.*, 2001; Burrows *et al.*, 1997). 4-Sulfobenzoic acid (H₂sb) is a good bridging ligand for the construction of cyclic dimers (Fan *et al.*, 2005, 2004). Here, we present the title new cyclic complex, (I), bridged by sb²⁻ anions.

(I)
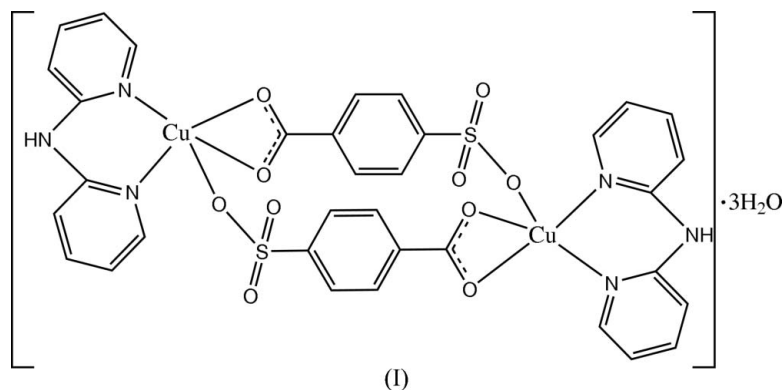
The centrosymmetric dimer of (I) is shown in Fig. 1. The Cu^{II} atom adopts a distorted square-pyramidal geometry (Table 1), formed by two N donors from one 2,2′-dipyr-idylamine and three O atoms, two from a carboxyl group and one from a sulfonyl group of the other sb²⁻ anion. The sulfonyl atom O5ⁱ [symmetry code: (i) $1 - x$, $1 - y$, $1 - z$] occupies the apical site. The bridging mode of the sb²⁻ anion in (I) is similar to that found in [Cd(phen)(sb)(H₂O)₂]₂ (phen is 1,10-phenanthroline; Fan *et al.*, 2005) but different from that found in [Cu(2,2′-bipy)(sb)(H₂O)]₂ (2,2′-bipy is 2,2′-bipyr-idine; Fan *et al.*, 2004). In the cyclic dimer molecule, the Cu···Cu separation of 9.5362 (12) Å is shorter than the value of 9.7495 (8) Å in [Cu(2,2′-bipy)(sb)(H₂O)]₂ (Fan *et al.*, 2004). The benzene ring is coplanar with the carboxyl group, the dihedral angle being 0.6 (8)°. The two pyridine rings of the 2,2′-dipyridylamine subtend a dihedral angle of 11.8 (4)°.

In the crystal structure of (I), extensive hydrogen bonding occurs between uncoordinated water and the complex molecules (Table 2).

Experimental

A mixture of copper(II) acetate hydrate (0.040 g, 0.2 mmol), potassium hydrogen 4-sulfobenzoate (0.048 g, 0.2 mmol), 2,2′-dipyridylamine (0.031 g, 0.2 mmol), NaOH (0.020 g, 0.5 mmol) and water (15 ml) was heated at 423 K for 72 h in a 30 ml Teflon-lined stainless-steel autoclave. After cooling to room temperature, a green solution was obtained. Green block-shaped single crystals of (I) were obtained from the resulting solution after 1 d.

Crystal data

$[Cu_2(C_7H_4O_5S)_2(C_{10}H_9N_3)_2]\cdot 3H_2O$	$Z = 1$
$M_r = 923.86$	$D_x = 1.670$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.2409$ (5) Å	Cell parameters from 3422 reflections
$b = 9.8064$ (6) Å	tions
$c = 11.5670$ (7) Å	$\theta = 2.5$–27.7°
$\alpha = 87.027$ (1)°	$\mu = 1.35$ mm^{-1}
$\beta = 85.507$ (1)°	$T = 295$ (2) K
$\gamma = 80.552$ (1)°	Block, green
$V = 918.5$ (1) Å^3	$0.38 \times 0.19 \times 0.16$ mm

Data collection

Bruker APEX area-detector diffractometer	3218 independent reflections
φ and ω scans	2979 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.019$
(SADABS; Sheldrick, 2002)	$\theta_{max} = 25.0°$
$T_{min} = 0.629$, $T_{max} = 0.813$	$h = -9 \rightarrow 9$
6651 measured reflections	$k = -11 \rightarrow 11$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0638P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.065$	$+ 2.1586P]$
$wR(F^2) = 0.157$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.17$	$(\Delta/\sigma)_{max} < 0.001$
3218 reflections	$\Delta\rho_{max} = 0.98$ e Å^{-3}
284 parameters	$\Delta\rho_{min} = -0.52$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.985 (4)	Cu1—N1	1.956 (4)
Cu1—O2	2.090 (3)	Cu1—N3	1.951 (4)
Cu1—O5^i	2.227 (4)		
O1—Cu1—O2	64.16 (14)	N1—Cu1—O5^i	99.40 (16)
O1—Cu1—O5^i	89.24 (17)	N3—Cu1—N1	94.06 (17)
O2—Cu1—O5^i	95.85 (15)	N3—Cu1—O1	165.98 (17)
N1—Cu1—O1	97.59 (16)	N3—Cu1—O2	102.42 (16)
N1—Cu1—O2	156.07 (17)	N3—Cu1—O5^i	96.54 (17)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$N\cdots$O1W	0.86	1.98	2.817 (11)	165
N2—H2$N\cdots$O1W'	0.86	2.13	2.857 (15)	141
O1W—H1$A\cdots$O4^{ii}	0.81	2.08	2.844 (12)	158
O1W—H1$B\cdots$O2W^{iii}	0.83	1.66	2.349 (15)	139
O1W'—H1$C\cdots$O4^{iv}	0.85	1.66	2.393 (15)	142
O1W'—H1$C\cdots$O4^{iv}	0.85	1.95	2.773 (15)	162
O1W'—H1$D\cdots$O2W^{iii}	0.87	1.91	2.767 (18)	171
O2W—H1$W\cdots$O1	0.85	2.11	2.925 (10)	160
O2W—H2$W\cdots$O4^v	0.85	2.28	3.025 (17)	147
O2W—H2$W\cdots$O3^v	0.85	2.32	3.104 (12)	153

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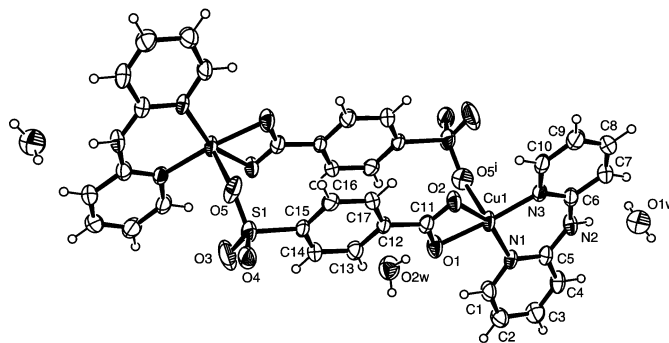

Figure 1
The dimeric structure of (I), with 40% probability displacement ellipsoids (arbitrary spheres for H atoms). Minor disordered components have been omitted for clarity. [Symmetry code (i): $1 - x, 1 - y, 1 - z$.]

The sulfonyl atom O4 is disordered over two positions; two occupancies were initially refined. They converged to 0.503 (4) and 0.497 (4), and then each was fixed at 0.5 in the final cycles of refinement. One uncoordinated water atom (O1W) was also disordered over two positions; the occupancies were initially refined. They converged to 0.532 (4) and 0.468 (4), and were then fixed at 0.57 and 0.43, respectively, in the final cycles of refinement. H atoms on O atoms were located in a difference Fourier map and refined by riding on their as-found positions relative to the O atoms, with U_{iso}(H) = $1.2U_{eq}$(O). Other H atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and were included in the final cycles of refinement in riding mode, with U_{iso}(H) = $1.2U_{eq}$ of the carrier atoms.

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: ORTEP3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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