

Sai-Rong Fan,<sup>a</sup> Hong-Ping Xiao<sup>b</sup>  
and Long-Guan Zhu<sup>a\*</sup><sup>a</sup>Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China, and <sup>b</sup>School of Chemistry and Materials Science, Wenzhou Normal College, Wenzhou 325027, People's Republic of China

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

## Key indicators

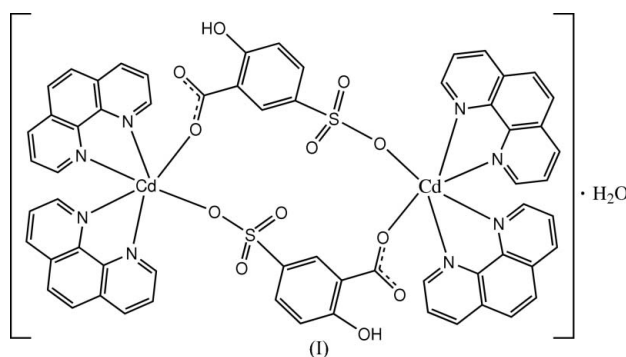
Single-crystal X-ray study  
T = 296 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
Disorder in solvent or counterion  
R factor = 0.031  
wR factor = 0.072  
Data-to-parameter ratio = 12.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis( $\mu$ -5-sulfonatosalicylato)bis[bis(1,10-phenanthroline)cadmium(II)] monohydrate

In the title compound,  $[\text{Cd}_2(\text{C}_7\text{H}_4\text{O}_6\text{S})_2(\text{C}_{12}\text{H}_8\text{N}_2)_4] \cdot \text{H}_2\text{O}$ , the  $\text{Cd}^{\text{II}}$  atoms are bridged by two 5-sulfonatosalicylate dianions, forming a centrosymmetric dinuclear complex. Each Cd atom is coordinated by four N atoms from two 1,10-phenanthroline molecules and two O atoms from two 5-sulfonatosalicylate ligands in a distorted octahedral environment. A strong  $\pi$ - $\pi$  stacking interaction occurs between 1,10-phenanthroline ligands from neighboring dimers. Extensive hydrogen bonds give rise to a two-dimensional network and enhance the stability of the crystal packing.

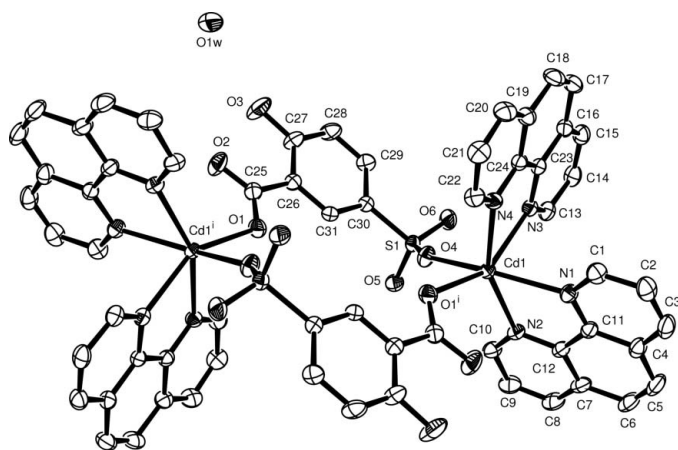
Received 7 November 2005  
Accepted 28 November 2005  
Online 7 December 2005

## Comment

5-Sulfosalicylic acid (5-H<sub>3</sub>ssal) has three functional groups, viz. hydroxy, carboxylic acid and sulfonic acid groups, and can be partly or fully deprotonated in the formation of metal complexes. Therefore, 5-sulfonatosalicylate metal complexes can exhibit interesting assembly structures (Fan, Cai *et al.*, 2005; Fan & Zhu, 2005*a,b*), among which only one cyclic dimer has been reported (Li *et al.*, 2004). We present here the second 5-sulfonatosalicylate cyclic dimer, (I).



The title  $\text{Cd}^{\text{II}}$  complex is a centrosymmetric cyclic dimer, in which each Cd atom adopts a distorted octahedral geometry defined by four N atoms from two 1,10-phenanthroline ligands and two O atoms from one sulfonate and one carboxylate group of two 5-Hssal<sup>2-</sup> ligands (Fig. 1 and Table 1). The Cd—O(SO<sub>3</sub>) and Cd—N bond distances are similar to those in the cyclic dimer of bis[ $\mu$ -diaqua(1,10-phenanthroline)( $\mu$ -4-sulfonatobenzoato)cadmium(II)], (II) (Fan, Zhang *et al.*, 2005). 5-Sulfosalicylic acid is doubly deprotonated and acts as a bridging ligand through its sulfonate and carboxylate groups. The Cd···Cd separation in the dimer is 8.1153 (5) Å, which is significantly shorter than 9.931 (1) Å in (II). In neighboring dimers, there is a strong  $\pi$ - $\pi$  stacking interaction between symmetry-related N3/N4/C13—C24 1,10-phenanthroline groups (symmetry code: 1 - x, 1 - y, 2 - z), with an inter-



**Figure 1**  
ORTEP-3 (Farrugia, 1997) view of (I). Displacement ellipsoids are drawn at the 40% probability level. H atoms are not shown for clarity [symmetry code (i):  $1 - x, -y, 2 - z$ ].

planar distance of 3.29 (2) Å. Moreover, intra- and intermolecular hydrogen bonds generate a two-dimensional extended network (Fig. 2 and Table 2) and stabilize the crystal packing.

## Experimental

A mixture of  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.053 g, 0.2 mmol), 5-sulfosalicylic acid dihydrate (0.050 g, 0.2 mmol) and 1,10-phenanthroline hydrate (0.040 g, 0.2 mmol) in an aqueous solution (10 ml) was stirred for 2 h, and then sealed in a 20 ml stainless steel reactor with a Teflon liner. The mixture was heated for 72 h at 423 K. Colorless block-shaped crystals of (I) were obtained after cooling to room temperature and these were separated by suction filtration. Thermogravimetric measurement showed 1.35% weight loss between 377 and 441 K, which corresponds to one water molecule per Cd complex.

### Crystal data

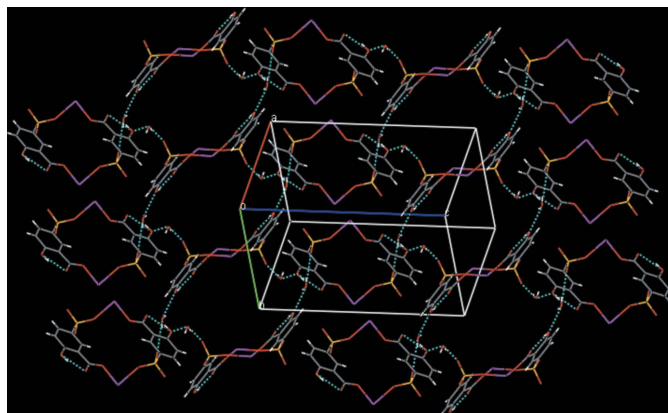
$[\text{Cd}_2(\text{C}_7\text{H}_4\text{O}_6\text{S})_2(\text{C}_{12}\text{H}_8\text{N}_2)_4] \cdot \text{H}_2\text{O}$	$D_x = 1.663 \text{ Mg m}^{-3}$
$M_r = 1395.96$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 7178 reflections
$a = 15.1984$ (7) Å	$\theta = 2.3\text{--}27.9^\circ$
$b = 9.8340$ (4) Å	$\mu = 0.91 \text{ mm}^{-1}$
$c = 18.9902$ (8) Å	$T = 296$ (2) K
$\beta = 100.778$ (1) $^\circ$	Block, colorless
$V = 2788.2$ (2) Å $^3$	$0.31 \times 0.21 \times 0.15 \text{ mm}$
$Z = 2$	

### Data collection

Bruker APEX area-detector diffractometer	4905 independent reflections
$\varphi$ and $\omega$ scans	4600 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$R_{\text{int}} = 0.021$
$T_{\text{min}} = 0.765$ , $T_{\text{max}} = 0.875$	$\theta_{\text{max}} = 25.0^\circ$
14180 measured reflections	$h = -18 \rightarrow 17$
	$k = -11 \rightarrow 11$
	$l = -22 \rightarrow 19$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 2.1742P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.072$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
4905 reflections	$\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$
406 parameters	
H-atom parameters constrained	



**Figure 2**  
A view of the two-dimensional hydrogen-bonding network in (I). Hydrogen bonds are shown as dashed lines. 1,10-Phenanthroline ligands and H atoms not involved in hydrogen bonds have been omitted for clarity.

**Table 1**  
Selected geometric parameters (Å,  $^\circ$ ).

Cd1—O1 <sup>i</sup>	2.2177 (19)	Cd1—N4	2.366 (2)
Cd1—O4	2.3407 (19)	S1—O4	1.469 (2)
Cd1—N1	2.395 (2)	S1—O5	1.451 (2)
Cd1—N2	2.330 (2)	S1—O6	1.437 (2)
Cd1—N3	2.379 (2)		
O1 <sup>i</sup> —Cd1—O4	86.23 (8)	N1—Cd1—N2	71.08 (8)
O1 <sup>i</sup> —Cd1—N1	112.96 (8)	N1—Cd1—N3	82.87 (8)
O1 <sup>i</sup> —Cd1—N2	113.91 (8)	N1—Cd1—N4	87.20 (8)
O1 <sup>i</sup> —Cd1—N3	149.14 (8)	N2—Cd1—N3	96.01 (8)
O1 <sup>i</sup> —Cd1—N4	83.50 (8)	N2—Cd1—N4	155.99 (8)
O4—Cd1—N1	156.97 (8)	N3—Cd1—N4	70.53 (8)
O4—Cd1—N2	89.91 (8)	O5—S1—O4	110.67 (13)
O4—Cd1—N3	86.47 (8)	O6—S1—O4	113.57 (14)
O4—Cd1—N4	108.38 (8)	O6—S1—O5	113.74 (13)

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

**Table 2**  
Hydrogen-bond geometry (Å,  $^\circ$ ).

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
O1w—H1B $\cdots$ O5 <sup>ii</sup>	0.85 (1)	2.10 (2)	2.940 (6)	172 (8)
O1w—H1A $\cdots$ O3	0.85 (1)	2.22 (5)	2.858 (7)	131 (5)
O3—H3A $\cdots$ O2	0.85 (3)	1.75 (2)	2.545 (4)	154 (4)

Symmetry code: (ii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ .

H atoms on C atoms were placed geometrically and refined as riding atoms with  $\text{C—H} = 0.93$  Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The water and hydroxy H atoms were located in a difference Fourier map and were refined with a distance restraint of  $\text{O—H} = 0.85$  (1) Å, and with  $U_{\text{iso}}(\text{H}) = 0.08$  Å $^2$ . The occupancy of the water molecule O1w was initially refined and converged to 0.595 (12), and was then fixed at 0.5 in the final cycles of refinement, corresponding to a monohydrate of the dinuclear complex.

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).

The authors thank Wenzhou Normal College for the diffraction measurements, the National Natural Science Foundation of China (grant No. 50073019) and the Analytical and Measurement Fund of Zhejiang Province.

## References

Bruker (2002). *SADABS*, *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

- Fan, S.-R., Cai, G.-Q., Zhu, L.-G. & Xiao, H.-P. (2005). *Acta Cryst.* **C61**, m177–m178.
- Fan, S.-R., Zhang, L.-P., Xiao, H.-P., Cai, G.-Q. & Zhu, L.-G. (2005). *Z. Kristallogr. New Cryst. Struct.* **220**, 69–70.
- Fan, S.-R. & Zhu, L.-G. (2005a). *Acta Cryst.* **E61**, m174–m176.
- Fan, S.-R. & Zhu, L.-G. (2005b). *Chin. J. Chem.* **23**, 1292–1296.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Li, J.-F., Zhao, Y.-J., Li, X.-H. & Hu, M.-L. (2004). *Acta Cryst.* **E60**, m1210–m1212.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.