

## A novel three-dimensional supra-molecular coordination polymer: poly[[diaquadicadmium(II)-di- $\mu_2$ -4,4'-bipyridyl-di- $\mu_2$ -2-sulfonatobenzoato] dihydrate]

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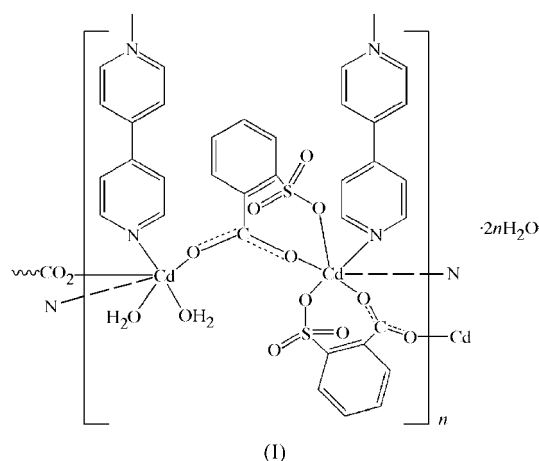
The hydrothermal reaction of  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , 4,4'-bipyridyl and 2-sulfobenzoic acid produced the title compound,  $\{[\text{Cd}_2(\text{C}_7\text{H}_4\text{O}_5\text{S})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$ , which forms a two-dimensional coordination polymer, the sheets of which are linked *via* hydrogen bonds. Two different types of Cd atoms are present, one lying on a twofold rotation axis and the other on a centre of inversion. Similarly, there are two types of bipyridyl ligand present, one lying across a twofold rotation axis and the other across a centre of inversion.

### Comment

Recently, the design and synthesis of novel inorganic–organic supramolecular complexes have attracted considerable attention (Robson *et al.*, 1992; Subramanian & Zaworotko, 1995), due to the potential applications of these complexes in many areas (Zheng *et al.*, 2003). Many cadmium(II)–carboxylate complexes (Shi *et al.*, 2001; Eringathodi *et al.*, 2001) have been synthesized, exhibiting a variety of coordination modes for the carboxylate group (Vaidhyanathan *et al.*, 2000). On the other hand, few cadmium(II)–sulfonate complexes have been reported. Because organosulfonates,  $(\text{RSO}_3)^-$ , are poor ligands, they have typically been employed as ‘non-coordinating’ anions. This has prompted us to search for such complexes. We report here the hydrothermal synthesis and characterization of the title compound, (I), a new cadmium(II)–sulfonatobenzoate coordination compound.

Fig. 1 depicts the different coordination spheres and atom-numbering schemes of the two  $\text{Cd}^{\text{II}}$  atoms in the structure of (I). Atom Cd1 is six-coordinated by two N atoms [N1 and N2<sup>i</sup>; symmetry code: (i)  $x, 1 + y, z$ ] from two 4,4'-bipyridine (4,4'-bipy) ligands which occupy the axial positions, two O atoms [O7 and O7<sup>iii</sup>; symmetry code: (iii)  $-x, y, \frac{1}{2} - z$ ] from two different water molecules and two O atoms (O1 and O1<sup>iii</sup>)

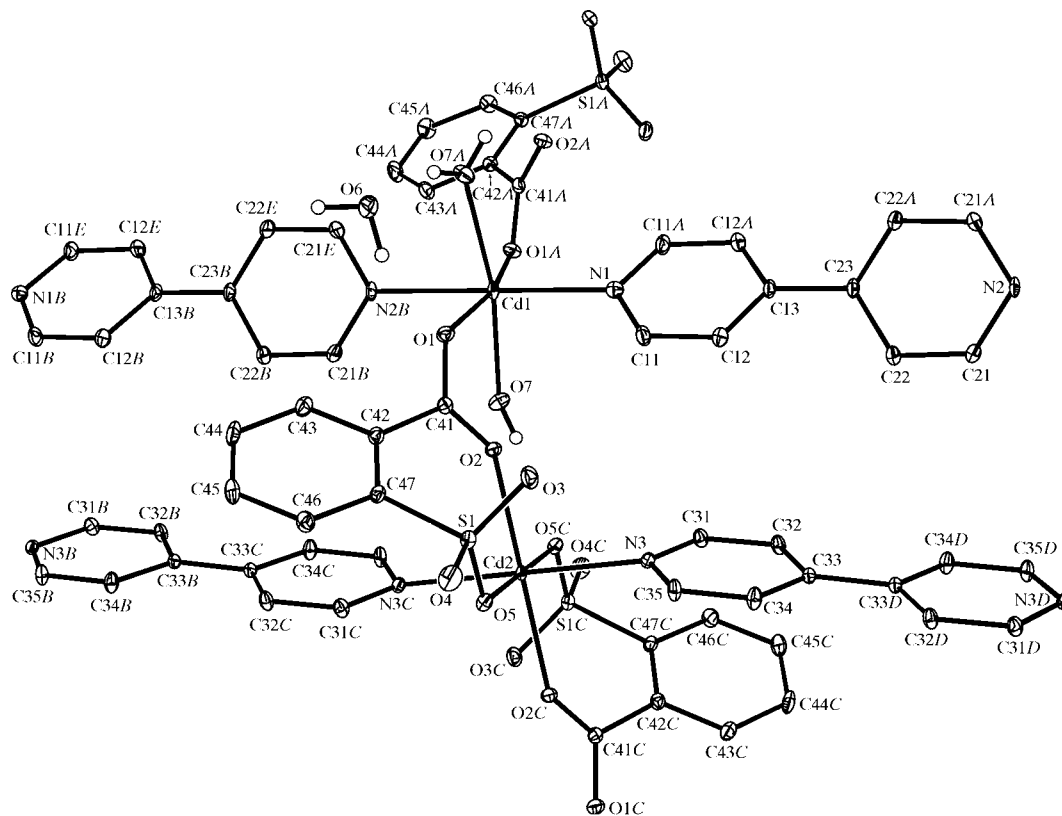
from the carboxylic acid groups of two different 2-sulfonato-benzoate ligands, forming the square base. Another metal centre, atom Cd2, is also six-coordinated, in this case by two N atoms [N3 and N3<sup>iv</sup>; symmetry code: (iv)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ] from two 4,4'-bipy, two O atoms (O2 and O2<sup>iv</sup>) from the carboxylic acid groups of two different 2-sulfonatobenzoate ligands and two O atoms (O5 and O5<sup>iv</sup>) from two different sulfonate groups. In the structure of (I), there are two different coordination spheres of the Cd atoms: atom Cd1 lies on a twofold axis and atom Cd2 lies on an inversion centre. Correspondingly, atoms N1 and N2 lie on a twofold axis by connecting Cd1 atoms, and atom N3 lies across an inversion centre by connecting Cd2 atoms. Therefore, the coordination geometry of both  $\text{Cd}^{\text{II}}$  atoms can be regarded as distorted hexahedral.



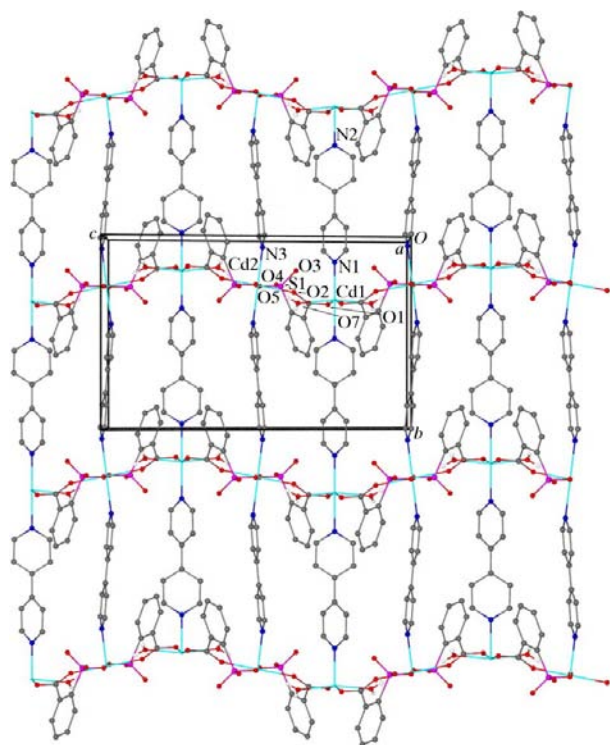
There are two distinct types of chain generated by the  $\text{Cd}^{\text{II}}$  atoms and 4,4'-bipy units alone (Fig. 2). Each  $\text{Cd}^{\text{II}}$  atom is connected by two *trans* 4,4'-bipy ligands, forming [010] chains. One chain type only contains Cd1 and 4,4'-bipy, while the other is composed of Cd2 and 4,4'-bipy units. The carboxylic acid groups act as bridges, connecting the different  $\text{Cd}^{\text{II}}$ –4,4'-bipy chains along [100]. These three types of chain generate a two-dimensional coordination polymer sheet.

The Cd–N distances in (I) are in accord with other bonds found in  $\text{Cd}^{\text{II}}$ –4,4'-bipy complexes. The Cd–O distances involving the anion are slightly shorter than the Cd–O(water) distance and consistent with the average Cd–O bond distance reported for similar compounds (Hagrman *et al.*, 1999). In the coordination polymer, the sulfonate group serves as a monodentate ligand.

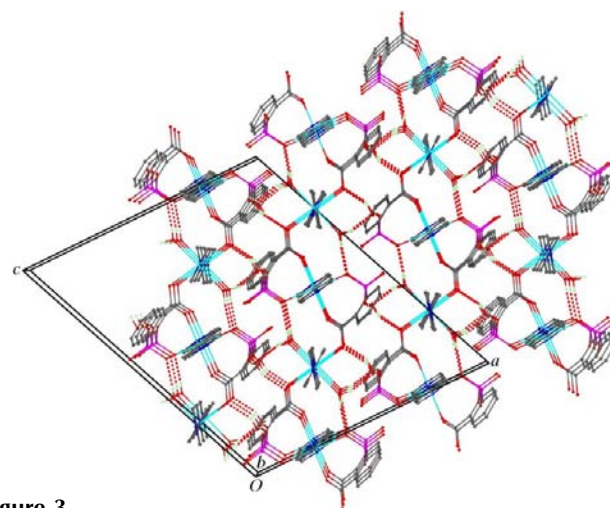
It should be noted that both the carboxylic acid and the sulfonate groups are not only employed as coordinative groups, but also take part in the formation of hydrogen bonds. In the presence of solvent water molecules, coordinated water molecules, carboxylate groups and sulfonate groups, four different kinds of hydrogen bonds are observed in the structure of (I) (Table 2), namely between solvent water molecules and sulfonate O atoms, between coordinated and solvent water molecules, between solvent water molecules and carboxylate acid O atoms, and between coordinated water


**Figure 1**

The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Non-aqua H atoms have been omitted for clarity. [Symmetry codes: (A)  $-x, y, \frac{1}{2} - z$ ; (B)  $x, 1 + y, z$ ; (C)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (D)  $\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z$ ; (E)  $-x, 1 + y, \frac{1}{2} - z$ .]


**Figure 2**

A diagram of the two different Cd-4,4'-bipy chains, viewed along the *a* axis, in which the carboxylate acid group acts as a bridge connecting two Cd-4,4'-bipy chains.


**Figure 3**

A packing diagram for (I), viewed along the *b* axis.

molecules and sulfonate O atoms. The effect of these hydrogen bonds is to link the two-dimensional coordination polymer layers into a three-dimensional framework (Fig. 3).

### Experimental

$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.2 mmol, 0.053 g), 4,4'-bipyridyl (0.2 mmol, 0.031 g) and 2-sulfobenzoic acid (0.2 mmol, 0.040 g) were dissolved in

H<sub>2</sub>O (8 ml). The mixture was then sealed in a 25 ml stainless steel vessel with a Teflon liner and heated to 433 K for 72 h. After cooling to room temperature, the reaction mixture was filtered and colourless crystals of (I) were obtained in 67.3% yield (based on Cd).

## Crystal data

[Cd<sub>2</sub>(C<sub>7</sub>H<sub>4</sub>O<sub>5</sub>S)<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O  
*M<sub>r</sub>* = 1009.6  
 Monoclinic, *C*<sub>2</sub>/*c*  
*a* = 16.888 (5) Å  
*b* = 11.722 (5) Å  
*c* = 20.258 (7) Å  
 $\beta$  = 112.483 (5)°  
*V* = 3706 (2) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.809 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 6223 reflections  
 $\theta$  = 2.2–27.5°  
 $\mu$  = 1.34 mm<sup>-1</sup>  
*T* = 173 (2) K  
 Prism, colourless  
 0.50 × 0.10 × 0.05 mm

## Data collection

Rigaku Mercury70 CCD diffractometer (2 × 2 bin mode) ω–2θ scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.613, *T<sub>max</sub>* = 0.935  
 14 147 measured reflections

4254 independent reflections  
 4059 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.028  
 $\theta_{\max}$  = 27.5°  
*h* = –21 → 19  
*k* = –15 → 15  
*l* = –13 → 26

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.027  
*wR* (*F*<sup>2</sup>) = 0.060  
*S* = 1.10  
 4254 reflections  
 273 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0244P)^2 + 6.0536P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.86 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.61 \text{ e \AA}^{-3}$

All water H atoms were found in difference Fourier maps at an intermediate stage of the refinement and were refined with an O–H restraint of 0.85 (5) Å. H atoms bonded to C atoms were placed in calculated positions and refined using a riding model, with C–H = 0.95 Å and *U<sub>iso</sub>*(H) = 1.2*U<sub>eq</sub>*(C).

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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**Table 1**

Selected bond lengths (Å).

Cd1–N1	2.274 (3)	Cd2–O2	2.2475 (16)
Cd1–O1	2.3182 (16)	Cd2–O5	2.2907 (15)
Cd1–N2 <sup>i</sup>	2.343 (3)	Cd2–N3	2.327 (2)
Cd1–O7	2.352 (2)		

Symmetry code: (i) *x*, 1 + *y*, *z*.

**Table 2**

Hydrogen-bonding 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>
O6–H6A···O1	0.86 (4)	1.97 (4)	2.760 (3)	153 (4)
O6–H6B···O3 <sup>ii</sup>	0.85 (5)	2.02 (5)	2.855 (3)	167 (5)
O7–H7A···O6 <sup>iii</sup>	0.84 (4)	1.91 (4)	2.720 (3)	160 (3)
O7–H7B···O5 <sup>iv</sup>	0.77 (4)	2.14 (4)	2.905 (3)	172 (4)

Symmetry codes: (ii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $-x, y, \frac{1}{2} - z$ ; (iv)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ .

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1351). Services for accessing these data are described at the back of the journal.

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