

## Di- $\mu_2$ -sulfite- $\kappa^8 O, O': O'', O'''$ -bis- [(2,4,6-tri-2-pyridyl-1,3,5-triazine- $\kappa^3 N^2, N^1, N^6$ )cadmium(II)] octahydrate

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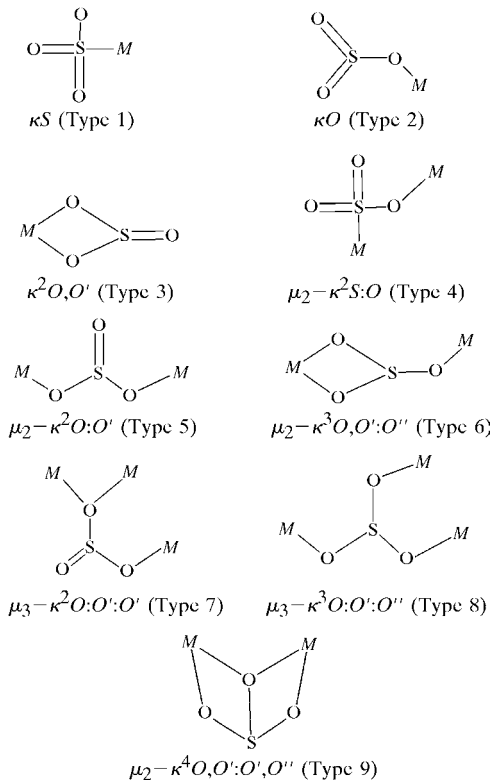
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The title compound,  $[\text{Cd}_2(\text{SO}_3)_2(\text{C}_{18}\text{H}_{12}\text{N}_6)_2] \cdot 8\text{H}_2\text{O}$ , is a dimer built up around a symmetry center, where the sulfite anion displays a so far unreported coordination mode in metal-organic complexes; the anion binds as a  $\mu_2$ -sulfite- $\kappa^4 O, O': O'', O'''$  ligand to two symmetry-related seven-coordinate  $\text{Cd}^{\text{II}}$  cations, binding through its three O atoms by way of two chelate bites with an O atom in common, which acts as a bridge. The cation coordination is completed by a 2,4,6-tri-2-pyridyl-1,3,5-triazine ligand acting in its usual tridentate mode.

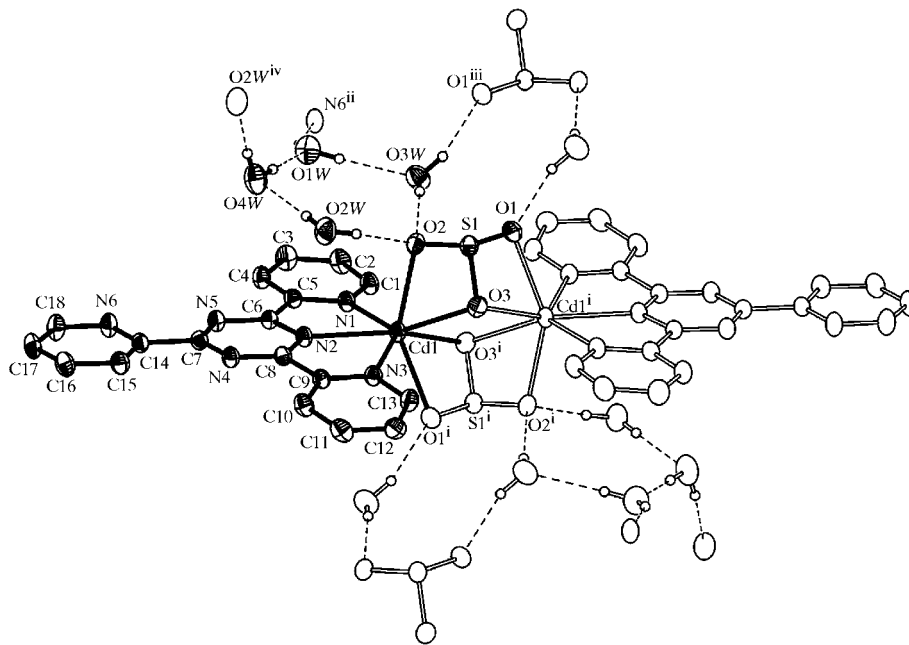
### Comment

The sulfite anion has proved to be a very versatile ligand, both in sulfite salts, where it displays an amazingly complex diversity of coordination modes, and in coordination compounds with organic ligands, where the variety is not so ample but still important. A search of the November 2005 release of the Cambridge Structural Database (CSD; Allen, 2002) shows eight different coordination modes for the anion, presented in the first scheme below. When attached to a single cation the ligand appears to bind through S in a  $\kappa\text{S}$  mode (Type 1), through one O atom (Type 2) or through two O atoms in a  $\kappa^2 O, O'$  mode (Type 3). When two different cationic sites are involved, the anion binds in three alternative modes, *viz.* via its S and one O atom, as  $\mu_2\text{-}\kappa^2\text{S}:O$  (Type 4), through two O atoms, as  $\mu_2\text{-}\kappa^2 O:O'$  (Type 5), or with its three O atoms, in a  $\mu_2\text{-}\kappa^3 O, O': O''$  mode (Type 6). Finally, when binding to three cations, the anion always does so *via* its three O atoms, either in a  $\mu_3\text{-}\kappa^2 O:O': O''$  mode (Type 7) or in a  $\mu_3\text{-}\kappa^3 O:O': O''$  mode (Type 8). Type 1 compounds are the most common (29 entries in the CSD, mostly  $\text{Co}^{\text{III}}$  complexes). The geometry of the sulfite unit in this type of coordination is quite regular, with all angles around  $110^\circ$  and S—O distances not significantly

different [mean value =  $1.467(2) \text{ \AA}$ ], except in the case when the O atom is involved in hydrogen bonds, which seems to lengthen the S—O bonds [mean value =  $1.474(6) \text{ \AA}$ ; CSD refcodes STEDCOI10, VEBJAN, VEBJER, VEBJIV and XUFVEZ). The mean S—O bond length is considerably shorter than those in ionic sulfite salts [ $1.529(7) \text{ \AA}$  (Battelle & Trueblood, 1965) and  $1.536(7) \text{ \AA}$  (Baggio & Becka, 1969)]. In other cases when O atoms are involved in coordination, S—O bonds show a characteristic lengthening for S— $\text{O}_{\text{coord}}$  bonds as compared with S— $\text{O}_{\text{non-coord}}$  ones. This effect can be seen in the following cases, referred to by their CSD refcodes (mean distances are given as S— $\text{O}_{\text{coord}}$ /S— $\text{O}_{\text{non-coord}}$ ): BERXUR [Type 2,  $1.591(1)/1.504(1) \text{ \AA}$ ]; AVAZAY, FIFBAX, KIRBOC and YAPMOR [Type 3,  $1.545(17)/1.364(16) \text{ \AA}$ ]; FEYNUS, KAJCON, LAMBIK, LOQCAV, SOQXUR, YIQFOT and YIQFUZ [Type 4,  $1.519(2)/1.460(3) \text{ \AA}$ ]; and ALELUY, KAVJIA and ZETXEB [Type 5,  $1.548(3)/1.489(1) \text{ \AA}$ ]. The angles are quite regular, all lying around the expected tetrahedral values, except in the case of the constraints introduced by chelation, leading to angles as small as  $90^\circ$  (FIFBAX and YAPMOR) or  $98^\circ$  (IHIWOL and GAKTES, Type 6). There are only two entries showing an O atom acting as a bridge between two metal centers (Type 7, GAKTIW and HOFCEK). In these cases, the S— $\text{O}_{\text{bridge}}$  bond length [mean value =  $1.563(1) \text{ \AA}$ ] is considerably longer than the other S—O bonds [S— $\text{O}_{\text{non-coord}} = 1.507(2) \text{ \AA}$  and S— $\text{O}_{\text{coord}} = 1.521(1) \text{ \AA}$ ].

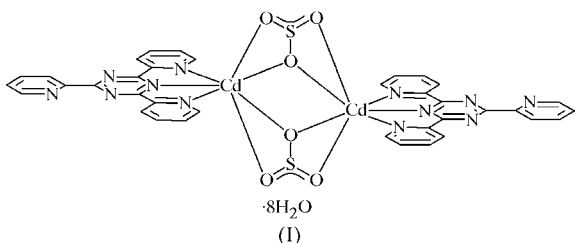


The title complex, (I), is a dimer built up around a symmetry center (Fig. 1), with two symmetry-related seven-coordinate  $\text{Cd}^{\text{II}}$  cations bound to a tridentate 2,4,6-tri-2-pyridyl-1,3,5-triazine (tpt) ligand and a sulfite anion acting in a so far



**Figure 1**  
An ellipsoid plot of the dimeric unit and its environment. Full displacement ellipsoids (for the independent moiety) and open ellipsoids (for the symmetry-related part) are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines. (Symmetry codes are as in Tables 1 and 2.)

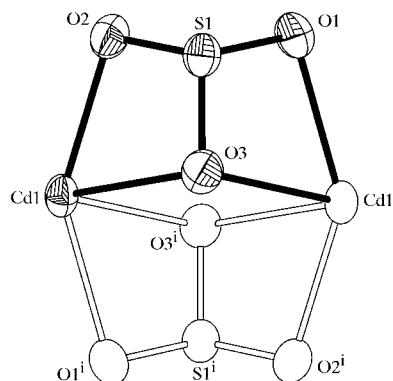
unreported (in metal-organic compounds)  $\mu_2\text{-}\kappa^4\text{O},\text{O}':\text{O}',\text{O}''$  mode (Type 9 in scheme above, and Fig. 2). The two chelating O—S—O angles are almost equal within the determined s.u. values [102.60 (12) and 102.16 (12)°], while the remaining angle is larger [106.54 (12)°]. However, the chelates are not completely symmetrical, their S—O distances differing by some 1.5%.



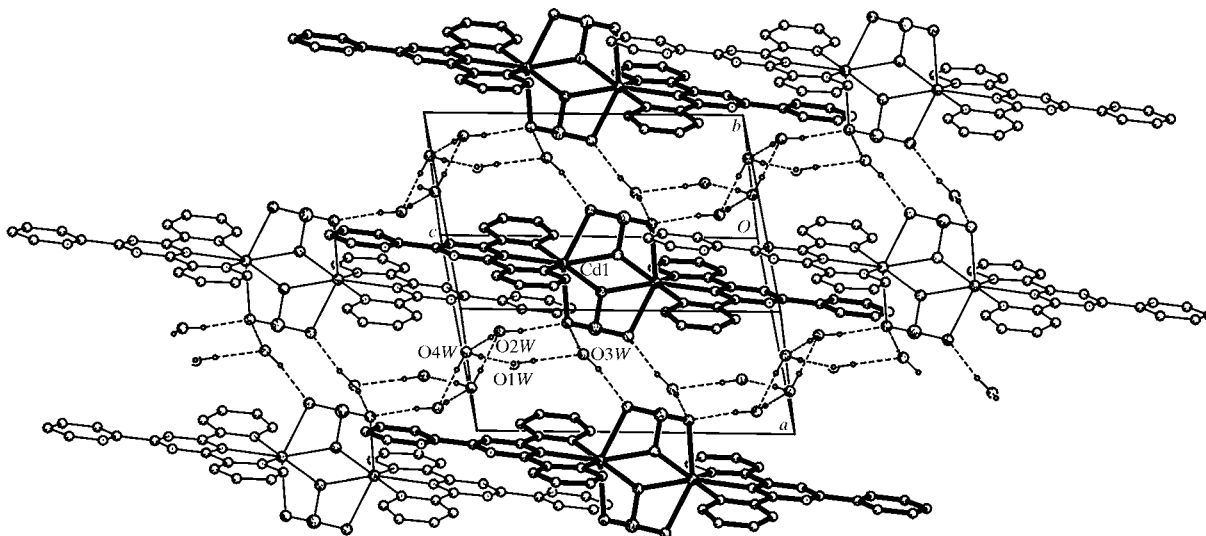
Coordination around the Cd<sup>II</sup> centers generates a dimeric centrosymmetric structure where the two monomers are doubly linked *via* the Cd1—O2—S1—O1—Cd1<sup>i</sup> and Cd1—O3—Cd1<sup>i</sup> loops shown in Fig. 2 (symmetry code as in Table 1). The general disposition of the dimer resembles that of an Mn(tpt) complex that we have recently reported [*viz.* [Mn<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(C<sub>16</sub>H<sub>12</sub>N<sub>6</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].4H<sub>2</sub>O; Diaz de Vivar *et al.*, 2006], where a sulfate group played the role of the actual sulfite. Both structures have dimeric character and they share many other coordination features. The main difference concerns the central O atom, which in the present structure bridges two symmetry-related cations, while in the sulfate analogue it ‘breaks’ one of these bonds, the O atom leaning towards the remaining cation. The vacant site left in the sevenfold Mn coordination polyhedron is occupied by one aqua ligand.

The organic ligand coordinates *via* three N-atom donors (N1 and N3 from two pyridine rings and N2 from the triazine ring), leaving the third pyridyl group uncoordinated and rotated by 4.6 (2)° to the central core mean plane. The latter is not strictly planar, the deformation being mainly due to the misalignment of the individual pyridyl and triazine components [the range of interplanar angles is 0.2 (2)–10.4 (2)°]. The coordination mode displayed by tpt is its most common one; a search of the CSD showed that 89% of the reported complexes containing the ligand adopt this tridentate bite to the cation.

Only four structures with tpt coordinating to group 12 metals appear in the CSD, *viz.* two with Zn<sup>II</sup> (EYIMUU and PAHTEY), one with Cd<sup>II</sup> (GADLON) and one with



**Figure 2**  
The centrosymmetric cage built up by the sulfite anion around the cadmium centers. (The symmetry code is as in Table 1.)



**Figure 3**

A view of the packing, showing the different hydrogen-bonded columnar units extending vertically along [100]. The central column is shown in heavy lines in order to distinguish it from its neighbors. Hydrogen bonds are shown as broken lines. The planar array, presented here in a slightly slanted fashion for clarity, extends parallel to (010).

Hg<sup>II</sup> (BEJFUR). As in all other reported group 12 tpt complexes, the central metal–N distance [2.353 (2) Å] is shorter than the lateral ones [the mean is 2.434 (20) Å], owing to chelation constraints and the rigid character of the ligand.

The elongated dimer has a prolate profile with principal axes of very different lengths, *viz.* 23.9 (1), 11.2 (1) and 4.8 (1) Å, and dimers stack along their shortest direction, in the form of columns oriented parallel to [100] (shown in heavy lines in Fig. 3). The link between successive units in the column is the water molecule O3W, through two of the hydrogen bonds in which it takes part (entries 5 and 6 in Table 2, and Fig. 3). These chains, in turn, interact laterally with neighboring chains through two different mechanisms, *viz.* a very long hydrogen-bonding chain [8.54 (2) Å between extreme O2 and O2<sup>iv</sup> acceptors; symmetry code as in Table 2] involving all four water molecules and their symmetry-related counterparts (entries 1, 3, 4, 7 and 8 in Table 2, and Fig. 3), and a *Cg* ··· *Cg* interaction between pyridyl groups of the interdigitated tpt ligands (Table 3). The result is a broad two-dimensional structure expanding parallel to the (010) plane. The interaction between these planes is achieved mainly through the strong interaction involving O1W and N6<sup>ii</sup> (entry 2 in Table 2); these are directed straight out of the paper and are therefore not represented in Fig. 3.

## Experimental

2,4,6-Tri-2-pyridyl-1,3,5-triazine and cadmium acetate were dissolved in 95% ethanol and left to diffuse over an aqueous solution of potassium pyrosulfite; the metal–tpt–K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> molar ratio was 1:1:2. After five months, irregular colorless crystals suitable for X-ray analysis were obtained.

## Crystal data

[Cd<sub>2</sub>(SO<sub>3</sub>)<sub>2</sub>(C<sub>18</sub>H<sub>12</sub>N<sub>6</sub>)<sub>2</sub>]<sub>2</sub>·8H<sub>2</sub>O  
*M<sub>r</sub>* = 1153.72  
 Triclinic, *P* $\bar{1}$   
*a* = 8.5826 (12) Å  
*b* = 10.5117 (14) Å  
*c* = 13.1078 (17) Å  
 $\alpha$  = 103.902 (2)°  
 $\beta$  = 107.988 (2)°  
 $\gamma$  = 91.639 (2)°

*V* = 1085.0 (3) Å<sup>3</sup>  
*Z* = 1  
*D<sub>x</sub>* = 1.766 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 $\mu$  = 1.16 mm<sup>-1</sup>  
*T* = 295 (2) K  
 Block, colorless  
 0.26 × 0.18 × 0.12 mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2001)  
*T<sub>min</sub>* = 0.74, *T<sub>max</sub>* = 0.88

9107 measured reflections  
 4665 independent reflections  
 4289 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.019  
 $\theta_{\max}$  = 28.0°

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.033  
*wR* (*F*<sup>2</sup>) = 0.088  
*S* = 0.84  
 4665 reflections  
 331 parameters  
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 0.6306P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 1.13 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.38 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Cd1—O1 <sup>i</sup>	2.342 (2)	Cd1—N2	2.353 (2)
Cd1—O2	2.302 (2)	Cd1—N3	2.414 (2)
Cd1—O3	2.543 (2)	S1—O1	1.515 (2)
Cd1—O3 <sup>i</sup>	2.395 (2)	S1—O2	1.529 (2)
Cd1—N1	2.455 (2)	S1—O3	1.532 (2)
O1—S1—O2	106.54 (12)	O2—S1—O3	102.16 (12)
O1—S1—O3	102.60 (12)		

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

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA $\cdots$ O3W	0.82 (2)	2.02 (2)	2.838 (4)	174 (3)
O1W—H1WB $\cdots$ N6 <sup>ii</sup>	0.82 (3)	2.19 (3)	2.950 (4)	154 (4)
O2W—H2WA $\cdots$ O4W	0.82 (5)	1.97 (4)	2.785 (4)	175 (5)
O2W—H2WB $\cdots$ O2	0.82 (2)	2.06 (2)	2.827 (3)	156 (4)
O3W—H3WA $\cdots$ O2	0.83 (4)	2.15 (4)	2.958 (3)	166 (4)
O3W—H3WB $\cdots$ O1 <sup>iii</sup>	0.82 (4)	2.11 (4)	2.867 (3)	154 (4)
O4W—H4WA $\cdots$ O1W	0.82 (4)	2.01 (4)	2.817 (4)	173 (4)
O4W—H4WB $\cdots$ O2W <sup>v</sup>	0.82 (5)	2.03 (5)	2.827 (5)	165 (7)

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

**Table 3**
 $\pi$ - $\pi$  contacts (Å, °) in (I).

Ccd is the center-to-center distance, sa is the (mean) slippage angle and ipd is the (mean) interplanar distance; Cg1 is the centroid of the N1/C1–C5 ring, Cg3 that of the N3/C9–C13 ring and Cg4 that of the N6/C14–C18 ring.

$Cg\cdots Cg$	ccd	sa	ipd
$Cg1\cdots Cg4^v$	3.720 (2)	19.54 (2)	3.506 (2)
$Cg3\cdots Cg4^{vi}$	4.035 (2)	36.66 (2)	3.237 (2)

 Symmetry codes: (v)  $-x+1, -y+2, -z+2$ ; (vi)  $-x+1, -y+1, -z+2$ .

H atoms attached to C atoms were included at calculated positions (C–H = 0.93 Å) and allowed to ride on their parent atoms [ $U_{iso}(H) = 1.2U_{eq}(C)$ ]. Water H atoms were found in a difference Fourier synthesis and refined with restrained O–H [0.82 (1) Å] and H $\cdots$ H [1.30 (2) Å] distances but with free  $U_{iso}(H)$  values.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2000); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2005).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3013). Services for accessing these data are described at the back of the journal.

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