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Poly[[aqua(2,2′-bipyridine-*N*,*N*′)cadmium(II)]-μ_3-sulfito-*O*:*O*:*O*′] hydrate]

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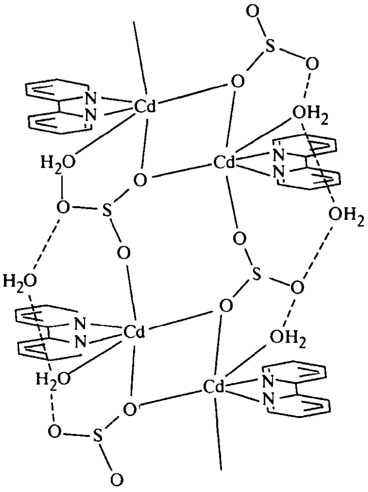
Abstract

The title compound, $\{[Cd(SO_3)(C_{10}H_8N_2)(H_2O)]\cdot H_2O\}_n$, consists of ladder-type chains formed by distorted CdN_2O_4 octahedra replicated by two different types of embedded symmetry centres. The sulfite anion displays a regular geometry and coordinates through two O atoms, the third O atom only being involved in hydrogen bonding.

Comment

The sulfite ion has been extensively studied as a component of many coordination compounds [34 entries in the 1998 version of the Cambridge Structural Database (CSD; Allen & Kennard, 1993)]. As demonstrated therein, the anion is able to adopt different modes of coordination depending on the characteristics of the metal present, due to its being composed both of soft (S) and hard (O) bases, according to Pearson's classification (Pearson, 1973).

However, and in spite of the great number of sulfite-containing organometallic compounds described in the literature, not a single crystallographic study has been reported on sulfite–cadmium complexes, the only structurally related studies being those performed on cadmium sulfite salts by Kiers & Vos (1978) and Engelen *et al.* (1987). Pursuant of our interest in cadmium sulfur oxoanion complexes, we report herein the crystal structure of the title compound, (I).



(I)

The cadmium ion interacts with the bidentate bipyridine, three symmetry-related sulfite groups and a coordination water molecule, all of which provide a heavily distorted octahedral environment, with N1, N2, $O3^{ii}$ and O1*W* occupying the equatorial positions, and O3 and $O1^{i}$ occupying the apical sites [symmetry codes: (i) $x, y, z-1$; (ii) $1-x, -y, 1-z$] (Fig. 1). The degree of deformation achieved by the polyhedron can be assessed by the maximum deviations from ideal geometry: N1 deviates by 0.111 (2) Å from the equatorial plane and Cd—$O1^{i}$ is 17.6(1)° from the normal to the plane. Even the (in principle equivalent) Cd—N bonds display a striking difference of *ca* 5% in length as a result of the overall strain developed. A search in the CSD showed this difference to be in the upper 20% of the distribution for *ca* 3000 cases explored.

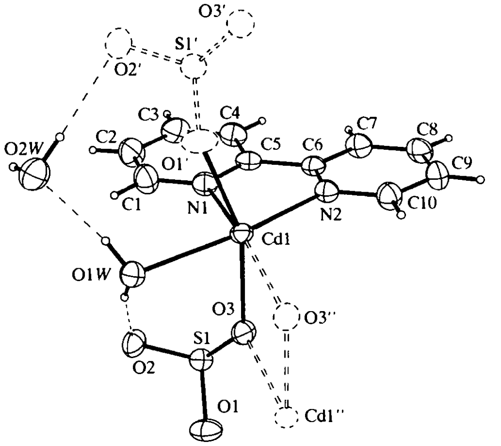


Fig. 1. Molecular diagram showing the numbering scheme used, as well as details of the cation coordination environment and some interchain hydrogen-bonding interactions. Displacement ellipsoids are drawn at the 50% probability level.

The anion shows an interesting mode of coordination that differs both from those reported for the related cadmium salts (in which all three O atoms are engaged in covalent bonding), as well as from those in other metal complexes (where it shows a slight preference for coordination through sulfur). In the present complex, the anion makes use of only two O atoms to coordinate cadmium, namely O1 and O3, the latter being in an unprecedented bridging mode between two metal atoms (see below).

The overall geometry of the SO_3 group is quite regular, with only a slight lengthening of *ca* 1.3% in the sulfur–oxygen bond involving the bridging O3 atom, compared with the almost equivalent distances for the other two. Compared with the dimensions of the free ion (Larsson & Kierkegaard, 1969), a slight lengthening of the mean S—O distance is observed, which is in accordance with the arguments of Kierkegaard *et al.* (1972).

The bipyridine anion does not present any unusual features; both cycles are planar within experimental error and their rotation around the C5—C6 bond is small [3.3 (1)°].

The cation coordination polyhedra connect to each other through two different types of loops or 'links' arising around the two independent symmetry centres present in the structure (Fig. 2). Both sorts of loops connecting neighbouring cadmium ions are of the type Cd1—*X*—Cd1′—*X*′, *i.e.* a smaller one (four members), where *X* = O3 and which gives rise to the closest Cd· · ·Cd approach of 3.781 (1) Å, and a larger one (eight members), with *X* = O1—S1—O3. The result is the formation of ladder-type chains evolving parallel to the *c* axis, the cohesion of which is helped by an 'inter-chain' link of strong hydrogen bonds [O2· · ·H1*WB*—O1*W*—H1*WA*· · ·O2*W*—H2*WB*· · ·O2(2 − *x*, −*y*, 1 − *z*)]. The non-coordinated water molecule (O2*W*) is engaged in a second type of hydrogen bond [O2*W*—H2*WA*· · ·O2(*x*, *y*, *z* − 1)], connecting chains together in the *a* direction and thus defining bidimensional structures parallel to (010), with the planar bipyridine groups protruding outwards, similar to the teeth in a gear. This enables an 'interlocking' approach between neighbouring layers along the *b* direction, the main interaction being of the van der Waals type.

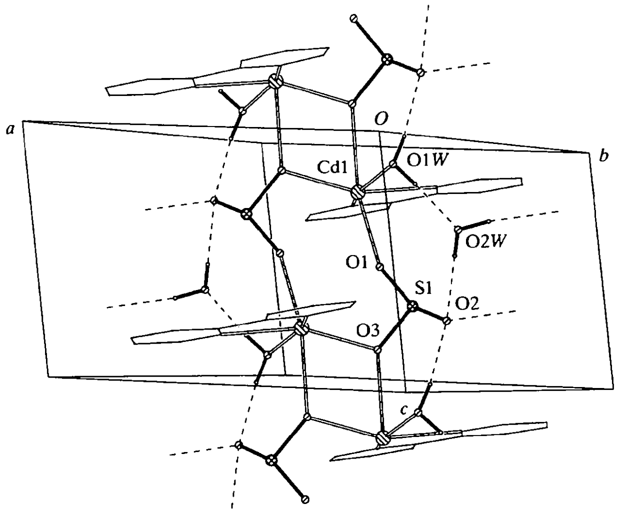


Fig. 2. Packing diagram showing the two different types of closed links building up around the symmetry centres, which give rise to the chains evolving along **c**.

Experimental

The title compound was obtained by diffusion of a water solution of cadmium acetate dihydrate into a water–methanol solution of 2,2′-dipyridyl and sodium sulfite, all the reagents being in equimolar quantities. The original solutions remained separated due to their different densities. When contact was established, very fine and long needles began to develop immediately at the interface. After two weeks, a few crystals suitable for X-ray diffraction were obtained.

Crystal data

$[Cd(SO_3)(C_{10}H_8N_2)(H_2O)]\cdot H_2O$
$M_r = 384.68$
Monoclinic
$P2_1/c$
$a = 10.036\,(2)$ Å
$b = 18.669\,(4)$ Å
$c = 6.7170\,(13)$ Å
$\beta = 98.62\,(3)°$
$V = 1244.3\,(4)$ Å^3
$Z = 4$
$D_x = 2.053$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 7.5$–$15.0°$
$\mu = 1.94$ mm^{-1}
$T = 293\,(2)$ K
Needle
0.48 × 0.22 × 0.20 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1988)
$T_{\min} = 0.52$, $T_{\max} = 0.68$
3094 measured reflections
2856 independent reflections

2408 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\max} = 27.48°$
$h = -13 \rightarrow 12$
$k = -24 \rightarrow 0$
$l = 0 \rightarrow 8$
3 standard reflections every 150 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.075$
$S = 0.986$
2856 reflections
189 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 0.436P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.94$ e Å^{-3}
$\Delta\rho_{\min} = -0.84$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cd1—O1^{i}	2.272 (2)	Cd1—N1	2.442 (2)
Cd1—O3^{ii}	2.307 (2)	S1—O1	1.521 (2)
Cd1—O1*W*	2.335 (2)	S1—O2	1.525 (2)
Cd1—N2	2.338 (2)	S1—O3	1.543 (2)
Cd1—O3	2.413 (2)		
O1^{i}—Cd1—O3^{ii}	110.50 (8)	N2—Cd1—O3	92.47 (8)
O1^{i}—Cd1—O1*W*	82.18 (9)	O1^{i}—Cd1—N1	88.73 (9)
O3^{ii}—Cd1—O1*W*	90.70 (8)	O3^{ii}—Cd1—N1	160.52 (8)
O1^{i}—Cd1—N2	104.24 (9)	O1*W*—Cd1—N1	88.85 (8)
O3^{ii}—Cd1—N2	107.52 (8)	N2—Cd1—N1	68.99 (8)
O1*W*—Cd1—N2	156.50 (8)	O3—Cd1—N1	87.32 (8)
O1^{i}—Cd1—O3	160.14 (8)	O1—S1—O2	105.08 (14)
O3^{ii}—Cd1—O3	73.54 (8)	O1—S1—O3	101.13 (13)
O1*W*—Cd1—O3	78.29 (8)	O2—S1—O3	105.87 (12)

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 - x, -y, 1 - z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WB*···O2	0.83 (3)	1.93 (3)	2.729 (3)	162 (3)
O1*W*—H1*WA*···O2*W*	0.85 (4)	1.93 (4)	2.761 (4)	166 (3)
O2*W*—H2*WB*···O2^{i}	0.87 (4)	1.94 (4)	2.811 (3)	172 (4)
O2*W*—H2*WA*···O2^{ii}	0.88 (4)	2.12 (4)	2.995 (4)	177 (3)

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

Non-H atoms were refined anisotropically on F^2. Those H atoms which were unequivocally defined by the stereochemistry were placed at their calculated positions, riding on their host atoms (C—H 0.96 Å). Those corresponding to water molecules were found in successive ΔF syntheses and refined with restrained O—H and H—H values.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983) and CSD (Allen & Kennard, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1460). Services for accessing these data are described at the back of the journal.

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Aqua[4-(4-chlorophenyl)-2-phenylthiazole-5-acetato-*O*]trimethyltin(IV)

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Abstract

The crystal structure of the title compound, $[Sn(CH_3)_3(C_{17}H_{11}ClNO_2S)(H_2O)]$, contains hydrogen-bonded infinite planes, wherein each trimethyltin moiety is coordinated to a water molecule and an O atom of the carboxylate ligand. The Sn atom has a distorted trigonal-bipyramidal geometry with three methyl groups in the equatorial plane [mean Sn—C 2.114 (7) Å]. The O atoms bonded to the Sn atom in the axial positions have significantly different Sn—O bond lengths [2.167 (4) and 2.490 (4) Å].

Comment

The structural chemistry of organotin carboxylic acid esters has been extensively explored in recent years because of the rich diversity of structural motifs in the series (Tiekink, 1994). Only a handful of structures have been cited in the literature (Cambridge Structural Database; Allen *et al.*, 1983) in which Sn atoms are bonded to three organic groups defining the trigonal plane and the axial positions are occupied by O atoms of a carboxylate ligand and a coordinated water molecule. In a continuation of our work on the structural chemistry of organotin carboxylates (Danish, Ali, Mazhar, Badshah, Masood & Tiekink, 1995; Danish, Ali, Mazhar, Badshah & Tiekink, 1995; Danish *et al.*, 1996; Parvez *et al.*, 1997; Tahir, Ülkü, Danish *et al.*, 1997; Tahir, Ülkü, Ali *et al.*, 1997; Bhatti *et al.*, 1999), we now report the crystal structure of aqua[4-(4-chlorophenyl)-2-phenylthiazole-5-acetato-*O*]trimethyltin(IV), (I).