Sn1—O1—Si1—O2	4.3 (3)	Sn1—N1—C5—C4	38.7 (4)
O1—Si1—O2—Si2	8.1 (4)	C1—Sn1—N1—C5	−10.7 (3)
Si1—O2—Si2—O3	−14.0 (4)	N1—Sn1—C1—C4	−18.5 (3)
O2—Si2—O3—Sn1	9.1 (3)	Sn1—C11—C14—C15	53.3 (5)
Si2—O3—Sn1—O1	−1.3 (2)	C11—C14—C15—N2	−67.5 (5)
O3—Sn1—O1—Si1	−6.4 (2)	C11—Sn1—N2—C15	−10.5 (3)
Sn1—C1—C4—C5	51.7 (5)	Sn1—N2—C15—C14	39.1 (4)
C1—C4—C5—N1	−65.9 (5)	N2—Sn1—C11—C14	−19.8 (3)

The data collection covered almost the whole sphere of reciprocal space with a completeness of 98.4% up to θ_{max}. The crystal-to-detector distance was 2.6 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analysing the duplicate reflections, there was no indication of any decay. The structure was solved by direct methods and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods. The H atoms were placed in geometrically calculated positions and refined with a common isotropic displacement parameter [C—H(methylene) 0.97 Å, C—H(methyl) 0.95 Å and U_{iso} 0.118 (3) Å^2].

Data collection: Nonius Kappa-CCD software. Cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997). Data reduction: *DENZO* and *SCALEPACK*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1276). Services for accessing these data are described at the back of the journal.

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Aqua(1,10-phenanthroline-N,N')(μ3-thio-sulfato-S:S:O)cadmium(II) Hydrate

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Abstract

The structure of [Cd(S$_2$O$_3$)(C$_{12}$H$_8$N$_2$)(H$_2$O)].H$_2$O is reported. It consists of polymeric chains evolving along the 2$_1$ symmetry axis, interconnected by hydrogen bonds. The Cd^{2+} environment is a distorted octahedron which presents a rather long Cd—O distance [2.549 (4) Å]. The thiosulfate ion binds to three different cationic sites, through one singly coordinated O atom and one S atom acting in a bridging mode.
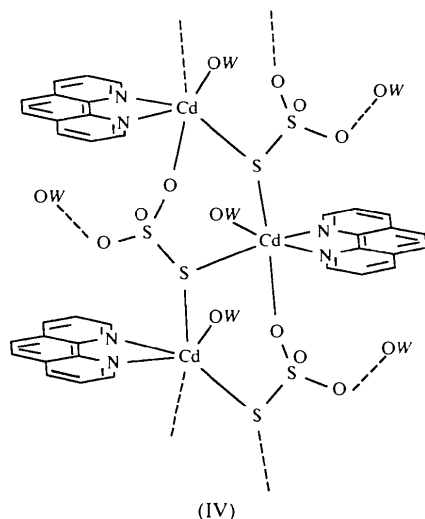
Comment

Cadmium thiosulfates have been the subject of our interest in the last few years and as a result three related crystal structures have been reported, all of which display the thiosulfate group acting as a polydentate ligand, *viz* [Cd$_2$(S$_2$O$_3$)$_2$(C$_{14}$H$_{12}$N$_2$)$_2$] [(I); Baggio *et al.*, 1996], [Cd(S$_2$O$_3$)(C$_{10}$H$_8$N$_2$)] [(II); Baggio, Pardo, Baggio & Garland, 1997] and Cd(S$_2$O$_3$).2H$_2$O [(III); Baggio, Pardo, Baggio & González, 1997].

As usual in complexes of d^{10} ions, the size of the accompanying ligands [2,9-dimethyl-1,10-phenanthroline (dmph) in (I), 2,2'-bipyridine (bpy) in (II) and H$_2$O in (III)] leads to different environments around the cadmium center which affect the way in which the thiosulfate bonds to the metal. These different types of coordination, in turn, influence the

geometry of the anion, with a lengthening of the S—S bond compared with that in free thiosulfate, and a clear differentiation between those S—O bonds involving coordinated O atoms from those involving non-coordinated O atoms. In (I), the anion acts both as a bridging and as a bidentate ligand, linking two pentacoordinated metal centers into a dimeric moiety. In (II), a somewhat more complicated bonding scheme is presented, joining three pentacoordinated cadmium centers together through the two S and one O atom. Finally, in (III), the most complex coordination scheme reported so far is displayed, where a bridging S and two O atoms link four metal centers.

In order to gather additional information regarding ligand-size effects in cadmium–thiosulfate complexes, we report here the structure of $[Cd(S_2O_3)(C_{12}H_8N_2)-(H_2O)].H_2O$, (IV), a case where the organic ligand, 1,10-phenanthroline (phen), presents an intermediate size between those of its dmph, (I), and bpy, (II), analogs.

Fig. 1. The molecular diagram of (IV) showing the numbering of atoms. Displacement ellipsoids are drawn at the 50% probability level.

(IV)

A view of the molecule with the labeling scheme is shown in Fig. 1. The Cd ion displays a rather distorted octahedral environment, coordinating to two symmetry-related S atoms, S1 and $S1(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, as well as N1, N2, O3$(x, 1 + y, z)$ and O1W. The Cd—S1 bridging distances [2.596 (2) and 2.698 (2) Å] resemble those found in related compounds where S atoms from thiosulfate groups bridge Cd atoms [2.531 (1) and 2.696 (1) Å in (I), 2.574 (1) and 2.586 (1) Å in (II), and 2.627 (1) and 2.581 (1) Å in (III)].

The two Cd—O distances are surprisingly different, even considering their diverse nature: while Cd—O1W [2.271 (4) Å] is at the lower end of the range reported in the literature for Cd—O_{water} distances [2.32 (6) Å; Burgi & Dunitz, 1994], the bond to one of the thiosulfate O atoms [Cd—O3$(x, 1 + y, z)$ 2.549 (4) Å] is much longer than those found in other octahedral Cd compounds with similar oxygen-bonded sulfur oxoanions, viz 2.328 (10) in (III), 2.28 (2) (Cavalca et al., 1967) and 2.285 (15) Å

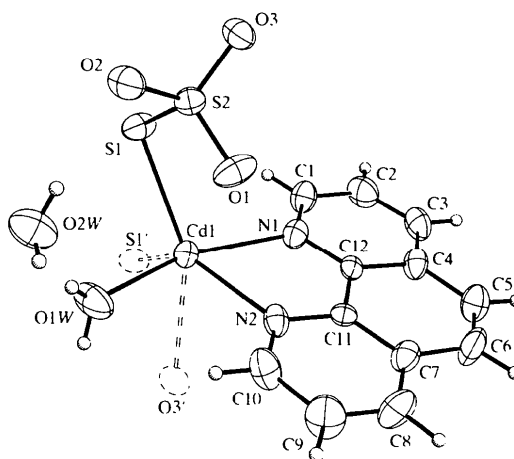(Rodesiler et al., 1987). This latter distance corresponds to a bond valence of 0.18 [after Brown & Altermatt (1985)], a value which corresponds to a rather weak bond, and which justifies the fact that no appreciable difference is observed between those S—O thiosulfate bond lengths involving coordinated and non-coordinated O atoms. The Cd—N bond lengths of 2.351 (4) and 2.346 (4) Å are normal, and within the range reported by Burgi for Cd—N_{phen} distances in octahedral Cd complexes [2.37 (2) Å; Burgi & Dunitz, 1994]. As is frequently observed in phenanthroline complexes, the individual six-membered rings are slightly tilted with respect to each other [0.5 (2) and 1.7 (2)°].

The thiosulfate group binds to three different cationic sites via S1 (acting as a bridge) and O3. Bond lengths in the anion are normal for this specific type of coordination, with a weakened S—S bond stretching up to 2.054 (2) Å (Teng et al., 1984, and references therein) and three quite similar S—O bond lengths (see above).

The crystal structure resembles those found in the other compounds of the series: there are pairs of infinite $\cdots$Cd—S1—S2—O3—Cd$'\cdots$ linear chains running along **b**, linked to each other by a single type of interaction (the S1—Cd bond) into 'bands' broadened along the [101] direction (Fig. 2). The two water molecules, which are disposed at the external edge of these stripes, have all their H atoms engaged in hydrogen bonding (Table 2), providing internal cohesion with three strong interactions [O1W—H1$WA\cdots$O2W, O1W—H1$WB\cdots$O2$(x, 1 + y, z)$ and O2W—H2$WB\cdots$O2] mainly directed along the direction of the chains. The fourth hydrogen bond present in the structure [O2W—H2$WA\cdots$O1$(-x, -y, -z + 1)$] links the bands together into two-dimensional (2D) networks parallel to [101]. The resulting 2D structures present the bulky phen groups protruding out of the planes, in a way which gives them the form of zigzag layers. These, in turn, pack such that the peaks of one

lie approximately in the troughs of the next, with a separation between layers compatible with normal van der Waals interactions.
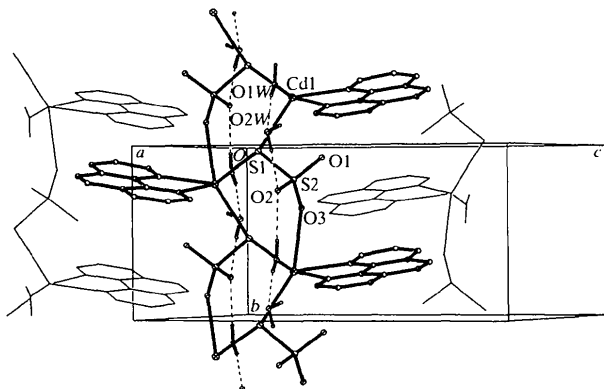

Fig. 2. Unit-cell diagram showing a double chain (in heavy full lines), running along **b**, and details of the neighboring chains (in slim full lines) defining a stacking of parallel inverted phenanthroline groups. Intra-chain hydrogen bonds are represented by dashed lines and inter-chain bonds have been omitted for clarity, together with the H atoms of the phenanthroline groups.

Experimental

The title compound was obtained by the reaction of equimolar quantities of cadmium acetate and sodium thiosulfate in aqueous solution, with a methanol solution of phenanthroline. The fine precipitate obtained was discarded and the mother liquors allowed to evaporate slowly. After several weeks, small needles adequate for X-ray diffraction analysis were obtained.

Crystal data

[Cd(S$_2$O$_3$)(C$_{12}$H$_8$N$_2$)(H$_2$O)].-
H$_2$O
M_r = 440.76
Monoclinic
$P2_1/n$
a = 13.558 (4) Å
b = 7.051 (2) Å
c = 15.482 (4) Å
β = 90.42 (2)°
V = 1480.2 (7) Å^3
Z = 4
D_x = 1.978 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25
reflections
θ = 7.5–12.5°
μ = 1.78 mm^{-1}
T = 293 (2) K
Prism
0.30 × 0.22 × 0.12 mm
Colorless

Data collection

Siemens R3m diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scan (SHELXTL/PC;
Sheldrick, 1994)
T_{min} = 0.64, T_{max} = 0.78
2986 measured reflections
2623 independent reflections
1770 reflections with
$I > 2\sigma(I)$

R_{int} = 0.036
θ_{max} = 25.05°
h = $-16 \rightarrow 16$
k = $0 \rightarrow 8$
l = $0 \rightarrow 18$
2 standard reflections
every 98 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.072
S = 0.999
2623 reflections
212 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.019P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = -0.51 e Å^{-3}
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

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

Cd1—O1W	2.271 (4)	Cd1—S1^{ii}	2.6980 (16)
Cd1—N2	2.346 (4)	S1—S2	2.054 (2)
Cd1—N1	2.351 (4)	S2—O1	1.463 (4)
Cd1—O3^i	2.549 (4)	S2—O3	1.466 (4)
Cd1—S1	2.5955 (17)	S2—O2	1.469 (4)
O1W—Cd1—N2	90.5 (2)	N1—Cd1—S1	101.77 (12)
O1W—Cd1—N1	161.50 (19)	O3^i—Cd1—S1	154.74 (10)
N2—Cd1—N1	71.00 (16)	O1W—Cd1—S1^{ii}	103.56 (16)
O1W—Cd1—O3^i	75.63 (15)	N2—Cd1—S1^{ii}	135.60 (11)
N2—Cd1—O3^i	74.16 (14)	N1—Cd1—S1^{ii}	89.69 (12)
N1—Cd1—O3^i	97.68 (15)	O3^i—Cd1—S1^{ii}	69.23 (9)
O1W—Cd1—S1	90.09 (14)	S1—Cd1—S1^{ii}	94.78 (3)
N2—Cd1—S1	127.57 (11)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O2W	0.78 (5)	1.95 (5)	2.736 (7)	167 (5)
O1W—H1WB···O2^i	0.78 (4)	2.00 (4)	2.783 (6)	165 (4)
O2W—H2WB···O2	0.80 (5)	2.18 (6)	2.928 (7)	155 (5)
O2W—H2WA···O1^{ii}	0.80 (6)	2.05 (5)	2.805 (7)	155 (5)

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

Refinement was performed with SHELXL97 (Sheldrick, 1997) on F^2 using the whole data set. H atoms in phen were positioned at their expected positions. Those of the water molecules were found in successive difference Fourier syntheses and refined. To prevent their drifting during refinement, conditions of similarity were imposed on all OW—HW and HW—HW distances. This introduced a couple of extra parameters in the least-squares equations. Final mean values for refined H-atom parameters: OW—HW 0.80 (5) Å and HW—OW—HW 110 (6)°. In all cases, riding isotropic displacement parameters were used, 1.2 times larger than those of the host atoms.

Data collection: P3/P4-PC (Siemens, 1991). Cell refinement: P3/P4-PC. Data reduction: XDISK in SHELXTL/PC (Sheldrick, 1994). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Molecular graphics: XP in SHELXTL/PC. Software used to prepare material for publication: SHELXL97, PARST (Nardelli, 1983) and CSD (Allen et al., 1983).

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was characterized by microanalysis and NMR (^{1}H and ^{13}C) spectroscopy.

(I)
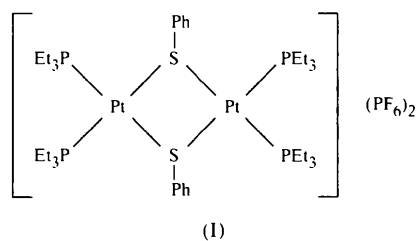
We report here the structure of (I), which crystallizes in space group $P\bar{1}$ with all atoms residing on general positions. The complex crystallizes as discrete cations and anions with no unusual contacts between them. The unit cell contains one formula unit. A view of the dinuclear cation, $[Pt_2(\mu\text{-SPh})_2(PEt_3)_4]^{2+}$, which lies on an inversion centre at $(0,\frac{1}{2},\frac{1}{2})$, is shown in Fig. 1.

Di-μ-phenylthio-bis[bis(triethylphosphine-P)platinum(II)] Bis(hexafluorophosphate), [Pt₂(μ-SPh)₂(PEt₃)₄](PF₆)₂

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Abstract

The structure of $[Pt_2(C_6H_5S)_2(C_6H_{15}P)_4](PF_6)_2$ has been determined by single-crystal X-ray diffraction at room temperature. The cation has C_i symmetry with a square-planar-coordinated Pt atom. The central Pt_2S_2 ring is a rhombus with angles S—Pt—S' 81.34 (5) and Pt—S—Pt' 98.66 (5)°.

Comment

Insertion reactions of alkynes into metal–hydrogen bonds are important elementary steps in homogeneously catalyzed reactions (Cornils & Herrmann, 1996). We found that insertion reactions of the thiosubstituted alkynes RSC≡CR′ (R, R′ = alkyl, aryl) into Pt—H bonds of neutral platinum complexes of the type [PtClH(PR₃)₂] are characterized by unusual regio- and stereoselectivities (Steinborn *et al.*, 1998). Contrary to this, in the reaction of the cationic hydride complex *trans*-[PtH(MeOH)(PEt₃)₂]PF₆ with PhSC≡CSiMe₃, C—S bond cleavage occurs, giving the title complex, [Pt₂(μ-SPh)₂(PEt₃)₄](PF₆)₂, (I), which
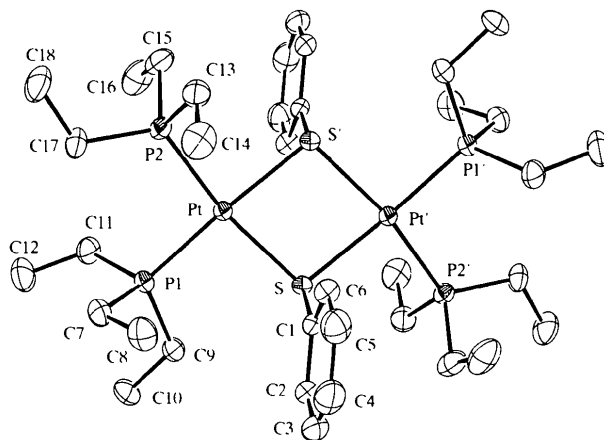

Fig. 1. Perspective view of the cation $[Pt_2(\mu\text{-SPh})_2(PEt_3)_4]^{2+}$. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

The Pt atom is square-planar coordinated (sum of angles 361.15°) by two phosphine ligands and two bridging phenylthio ligands. However, the Pt_2S_2 and PtP_2 planes form a dihedral angle of 11.63 (8)°, indicating a small twist distortion of the square-planar coordination geometry of the Pt^{II} atom. Apparently, to decrease the steric interactions between the phosphine ligands, the P1—Pt—P2 angle is widened to 97.39 (6)°. Also for steric reasons, the complex plane (Pt, Pt^i, P1, P1^i, P2, P2^i, S, S^i; symmetry code as in Table 1) and the planes of the phenyl rings (C1–C6) are almost perpendicular [interplanar angle 89.8 (1)°]. The central Pt_2S_2 ring is planar due to the inversion symmetry and is a rhombus with S—Pt—S^i 81.34 (5) and Pt—S—Pt^i 98.66 (5)°. The Pt—S bond lengths [Pt—S 2.392 (2) and Pt^i—S 2.389 (2) Å] are equal within the 3σ criterion. They are in the range found for other complexes with Pt(μ-SR)Pt moieties (2.274–2.402 Å; Capdevila *et al.*,