Cs2—S4^{iii}	3.530 (2)	Mo2—Mo2^{xi}	2.6673 (8)
Cs2—S3^{iv}	3.7223 (13)	Mo2—Mo3	2.6699 (6)
Cs3—S2^{iii}	3.4950 (13)	Mo2—Mo3^{xi}	2.6907 (6)
Cs3—S1^{v}	3.5603 (13)	Mo3—S3^{iii}	2.4775 (14)
Cs3—S3^{vi}	3.8623 (15)	Mo3—S3	2.5017 (14)
Mo1—S5	2.407 (2)	Mo3—S4^{xii}	2.5789 (11)
Mo1—S1^{vii}	2.4634 (13)	Mo3—S2^{x}	2.5805 (14)
Mo1—S1^{viii}	2.4634 (13)	Mo3—Mo3^{iii}	2.6688 (8)
Mo1—S1^{ix}	2.4847 (13)	Mo3—Mo4^{iii}	2.6877 (6)
Mo1—S2^{x}	2.6012 (14)	Mo3—Mo4	2.6916 (6)
Mo1—Mo1^{xi}	2.6621 (8)	Mo4—S4^{xii}	2.480 (2)
Mo1—Mo2	2.7398 (7)	Mo4—S4^{xiv}	2.504 (2)
Mo1—Mo2^{iii}	2.7539 (7)	Mo4—S3	2.5781 (13)
Mo1—Mo1^{xii}	3.1687 (9)	Mo4—Mo4^{xi}	2.6587 (11)

Symmetry codes: (i) $1+y, 1-x+y, z-\frac{1}{2}$; (ii) $1-x+y, 1-x, \frac{1}{2}-z$; (iii) $1-x+y, 1-x, z$; (iv) $x-y-1, x-1, z-\frac{1}{2}$; (v) $-y, x-y, \frac{1}{2}-z$; (vi) $y, 1-x+y, z-\frac{1}{2}$; (vii) $1+x-y, x, 1-z$; (viii) $y, -x+y, 1-z$; (ix) $-x+y, -x, z$; (x) $1-x, -y, \frac{1}{2}+z$; (xi) $1-y, x-y, z$; (xii) $1-x, -y, 1-z$; (xiii) $1+y, 1-x+y, \frac{1}{2}+z$; (xiv) $1+y, 1-x+y, 1-z$.

Data were corrected for Lorentz–polarization effects and an empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to isotropically refined data. The structure was solved with *MULTAN*11/82 (Main *et al.*, 1982) and subsequent difference Fourier syntheses. The largest positive peak in the final difference Fourier map was 2.69 Å from Cs3, while the largest negative peak was 1.25 Å from Mo4. Refinement of the occupancy factors for the Cs sites confirmed that they are fully occupied. Calculations were performed on a Digital Pentium Celebris 590 FP for *SHELXL*93 (Sheldrick, 1993) and on a Digital MicroVAX 3100 for the *MolEN* (Fair, 1990) programs.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1146). Services for accessing these data are described at the back of the journal.

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Cadmium Thiosulfate Dihydrate

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Abstract

The polymeric structure of the title compound, $CdS_2O_3.2H_2O$, consists of tightly woven two-dimensional networks interconnected by hydrogen bonds. The Cd^{2+} environment is octahedral and each thiosulfate ion binds to four different cationic sites, in simple as well as in bridging mode.

Comment

So far, few structures of complexes of cadmium(II) with thiosulfate have been reported. Two have been solved only recently, namely $Cd_2(S_2O_3)_2(C_{14}H_{12}N_2)_2$, (1) (Baggio, Baggio, Pardo & Garland, 1996), and $Cd(S_2O_3)(C_{10}H_8N_2)$, (2) (Baggio, Pardo, Baggio & Garland, 1997), and in both these compounds the anions present unusual types of coordination: in (1) the thiosulfate group acts both as a bridging and as a bidentate ligand, binding two metal centers to form a dimeric moiety; in (2) the anion, acting as a bridge, binds to three Cd atoms through S atoms and one O atom.

The interesting results obtained so far have prompted us to attempt the X-ray structural study of cadmium thiosulfate dihydrate, (3), a compound in which the coordination around the metal atom, as well as the type of bonding displayed by the thiosulfate group, could not be predicted by stoichiometric arguments alone; also, no X-ray structural data seemed to be available, except for preliminary spectroscopic work by Gabelica (1973).

Fig. 1 shows the interactions in the unit cell, as well as the labeling scheme. The Cd ion displays a rather distorted octahedral environment, coordinating to O1, O2, O1*W*, O2*W* [range 2.293 (4)–2.340 (4) Å] and to two symmetry-related S1 atoms, arranged in the *cis* mode [2.581 (1) and 2.627 (1) Å]. Cd—O distances in the Cd coordination polyhedron are normal, with no significant differences, irrespective of the source of the O atoms (water or thiosulfate). Furthermore, their mean value [2.32 (4) Å] is surprisingly close to that reported by Bürgi & Dunitz (1994) [2.32 (6) Å] for Cd—O_{water}. The Cd—S distances are similar to those found in related compounds in which S from thiosulfate moieties bridges Cd atoms [2.531 (1) and 2.696 (1) Å in (1), 2.574 (1) and 2.586 (1) Å in (2)]. Following Brown & Altermatt (1985), the distances found in the Cd^{2+} coordination sphere correspond to bond valences ranging between 0.469 and 0.414 for Cd—S, and between 0.346 and 0.304 for Cd—O.

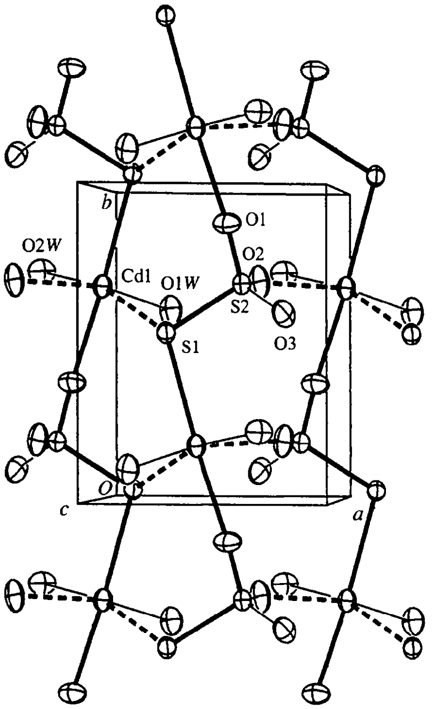

Fig. 1. Unit-cell diagram of the title compound showing the atom-numbering scheme as well as the coordination scheme. Chains running along **b** (heavy lines) can be clearly seen, linked to one another through two different kinds of interchain bonds (heavy dashed). Displacement ellipsoids are drawn at the 50% probability level.

The thiosulfate group binds to four different cationic sites *via* S1 (acting as a bridge), O1 and O2. Bond lengths in the anion are quite compatible with this peculiar type of coordination, with the weakened S—S bond stretching to 2.056 (2) Å and the two S—O bonds to the coordinated O atoms being 2% longer than that to the uncoordinated O3 (Teng, Fuess & Bats, 1984, and references therein).

Comparison of the cation environment in (3) with those found in (1) and (2) reveals that the presence of the bulky N chelates (dimethylphenathroline and bipyridine, respectively) in the Cd coordination sphere of the latter compounds makes the approach of a second O atom from the anion to within bonding distance of the cation difficult (the nearest such approaches are 3.14 and 2.96 Å, respectively). Therefore, Cd is pentacoordinate in (1) and (2), unlike in the present structure.

The resulting highly interconnected structure is rather similar to the structure of (1) and can be best visualized as a set of infinite ···Cd—O1—S2—S1—Cd′··· chains running along **b**. These chains are linked to one another through two different kinds of interchain bonds, S1—Cd and O2—Cd [the latter is not found in (1)] (Fig. 1), defining a compact two-dimensional network parallel to (001). In the process, two types of closed rings appear: a six-membered ring (Cd—S1—S2—O1—Cd′—S1′) and a larger, eight-membered ring (S1—S2—O2—Cd′—O1′—S2′—O2′—Cd″) (primes are used to distinguish symmetry-related atoms). These two-dimensional structures are, in turn, connected along ⟨001⟩ into a three-dimensional array by the hydrogen-bonding interactions of the coordinated water molecules, through two double, bifurcated contacts involving O1*W* and two single contacts involving O2*W* (Table 2).

Experimental

The title compound was obtained according to the method described by Delhez & Gabelica (1969); large crystals were precipitated from an aqueous solution through the addition of a mixture of methanol–ether at *ca* 278 K. When exposed to atmospheric conditions, the crystals were found to deteriorate slowly; thus, they were kept under a Vaseline cover. A robust specimen was selected for data collection.

Crystal data

$CdS_2O_3.2H_2O$
$M_r = 260.55$
Monoclinic
$P2_1/n$
$a = 5.720 (1)$ Å
$b = 7.081 (1)$ Å
$c = 14.121 (3)$ Å
$\beta = 101.06 (3)^\circ$
$V = 561.3 (2)$ Å^3
$Z = 4$
$D_x = 3.083$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5–12.5^\circ$
$\mu = 4.57$ mm^{-1}
$T = 293 (2)$ K
Plate
0.70 × 0.30 × 0.20 mm
Colorless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1988)
$T_{min} = 0.08$, $T_{max} = 0.36$
1534 measured reflections
1290 independent reflections

1225 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 27.51^\circ$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 18$
2 standard reflections every 98 reflections intensity decay: < 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.089$
$S = 1.23$

$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 2.4771P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.01$

1290 reflections
91 parameters
H atoms refined with constraints

$\Delta\rho_{max} = 1.11$ e Å^{-3}
$\Delta\rho_{min} = -1.39$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cd1—S1	2.627 (1)	S2—S1	2.056 (2)
S2—O3	1.437 (4)	S1—Cd1^{i}	2.581 (1)
S2—O1	1.460 (4)	O2—Cd1^{ii}	2.316 (4)
S2—O2	1.465 (4)	O1—Cd1^{iii}	2.339 (4)
O3—S2—O1	111.2 (3)	O3—S2—S1	107.2 (2)
O3—S2—O2	113.5 (2)	O1—S2—S1	105.2 (2)
O1—S2—O2	111.1 (2)	O2—S2—S1	108.2 (2)

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

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

D—H···*A*	*D*—H	H···*A*	*D*—H···*A*
O1*W*—H1*WA*···O3^{i}	0.80 (5)	2.41 (6)	156 (4)
O1*W*—H1*WA*···O1^{i}	0.80 (5)	2.32 (5)	141 (4)
O1*W*—H1*WB*···O2*W*^{ii}	0.81 (8)	2.38 (9)	126 (6)
O1*W*—H1*WB*···O2^{iii}	0.81 (8)	2.23 (9)	148 (6)
O2*W*—H2*WA*···O1*W*^{iv}	0.80 (6)	2.29 (7)	135 (5)
O2*W*—H2*WB*···O3	0.81 (5)	2.14 (5)	139 (4)

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

The H atoms of the water molecules were found from successive difference Fourier syntheses. To prevent them drifting during refinement, conditions of similarity were imposed on all O—H and H···H distances. This introduced two extra variables. The final ranges for hydrogen-related parameters were O—H 0.80 (5)–0.81(8) Å, H—*O*W—H 102 (5)–103(6)° and *U* 0.04 (2)–0.10(4) Å^2. The rather large residual electron density observed around the cation position (1.11 e Å^{-3}, 0.89 Å from Cd1; −1.39 e Å^{-3}, 0.85 Å from Cd1) after convergence had been achieved might well be attributed to remaining absorption effects not completely accounted for by the semi-empirical ψ-scan correction performed.

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: *XS* in *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* (Sheldrick, 1993), *PARST* (Nardelli, 1983), *CSD* (Allen, Kennard & Taylor, 1983).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1331). Services for accessing these data are described at the back of the journal.

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Structure d'un Diphosphate Synthétique de Cobalt: $Co_2P_2O_7$

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Abstract

The title compound, a new polymorphic phase of dicobalt diphosphate, $Co_2P_2O_7$, was prepared by hydrothermal methods. The structure contains CoO_6 coordination octahedra and P_2O_7 groups. The CoO_6 octahedra are connected by edge sharing to form six-membered rings, which are further interconnected to form two-dimensional zigzag sheets parallel to (001). The P_2O_7 groups link these sheets to build three-dimensional networks.

Commentaire

Cette étude vise à la compréhension systématique des structures des phosphates. En ce qui concerne les diphosphates de cobalt, $Co_2P_2O_7$, Krishnamachari & Calvo (1972) ont fait la synthèse d'une phase par fusion et déterminé sa structure. Forsyth, Wilkinson, Paster & Wanklyn (1989) ont fait la structure magnétique du même composé. Celui-ci a adopté le groupe spatial de $P2_1/c$, tandis que celui-là $B2_1/c$ qui correspond à la maille doublée de celle de $P2_1/c$. Belghitti, Boukhari