

Siemens (1990). *SHELXTL/PC. Program Package for the Solution, Refinement and Graphical Presentation of Crystal Structures.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stoe & Cie (1991a). *DIF4. Data Collection Program.* Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1991b). *REDU4. Data Reduction Program.* Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1998). **C54**, 319–321

Triethylammonium Tris(thiobenzoato-*O,S*)-cadmate(II)

JAGADESE J. VITTAL^a AND PHILIP A. W. DEAN^b

^aDepartment of Chemistry, National University of Singapore, Singapore 119 260, and ^bDepartment of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7. E-mail: chmjv@leonis.nus.sg

(Received 8 July 1997; accepted 23 October 1997)

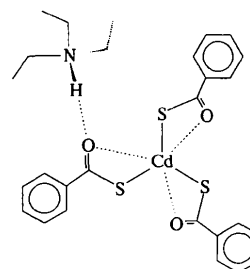
Abstract

The synthesis and structure of the title compound, (C₆H₁₆N)[Cd(C₇H₅OS)₃], are reported. There are two independent formula units in the asymmetric unit. In each [Cd{S(O)CPh}₃][−] anion, the Cd^{II} atom is located in the plane of the three S atoms. The Cd—S distances are 2.489 (1), 2.496 (1) and 2.547 (1) Å in ion-pair (1), and 2.505 (1), 2.515 (1) and 2.592 (1) Å in ion-pair (2). In addition, there are weak intramolecular interactions between the Cd and carbonyl O atoms [Cd⋯O 2.537 (2), 2.663 (2) and 3.111 (2) Å in (1), and 2.464 (2), 2.677 (2) and 2.718 (2) Å in (2)]. Each cation–anion pair is linked by a strong N—H⋯O hydrogen bond, with respective O⋯H and O⋯N distances of 1.925 (3) and 2.834 (3) Å in (1), and 1.886 (2) and 2.789 (2) Å in (2).

Comment

We have been interested in the chemistry and structures of thiobenzoate complexes and have described previously the structures of (*R*₄*E*)[*M*{S(O)CPh}₃] [*R* = Ph, *E* = As or P, *M* = Zn, Cd, Hg (Vittal & Dean, 1996a) or Pb (Burnett *et al.*, 1994); *R* = Me, *E* = N, *M* = Sn (Vittal & Dean, 1996b) or Hg (Vittal & Dean, 1997)], as well as (Me₄N)[Na{Cd[S(O)CPh]₃}₂] (Vittal & Dean, 1993). In the case of the complexes containing the zinc-group metals, the MS₃ cores were found to adopt a planar

geometry. What influences lead to this relatively uncommon geometry remain to be understood. The compound (Et₃NH)[Cd{S(O)CPh}₃] was synthesized during an attempt to prepare Ba[Cd{S(O)CPh}₃]₂. The structure of the new salt, (I), allows an investigation of the influence of the counterion and hydrogen bonding on the configuration of the [Cd{S(O)CPh}₃][−] anion. The synthesis and structural findings are reported in this paper.



(I)

The single-crystal X-ray diffraction analysis of (I) shows that there are two independent formula units in the asymmetric unit. No crystallographically imposed symmetry is present. There are close hydrogen-bonding interactions between the anions and cations. However, an extended hydrogen-bonded network appears to be absent. Views of the ion pairs (1) and (2) are shown in Figs. 1(a) and (1b), respectively. Selected bond distances and angles are given in Table 1, and the hydrogen-bonding parameters are shown in Table 2. In each ion pair, the three S(O)CPh[−] ligands are bonded to the Cd^{II} atom primarily through their S atoms. Neglecting the weak interactions with the O atoms, the coordination kernels approximate planar CdS₃. The sum of the S—Cd—S angles are 358.53 (5) and 355.80 (5)° for (1) and (2), respectively. For comparison, this sum is 359.99 (10)° in [Ph₄As][Cd{S(O)CPh}₃] (Vittal & Dean, 1996a). The deviations of the Cd atoms from the S₃ planes are 0.176 (1) and 0.298 (1) Å, respectively, for ion-pairs (1) and (2). In a similar manner, the metal atoms are 0.403 (1) and 0.226 (1) Å away from the O₃ planes in (1) and (2), respectively. The phenyl rings are twisted from the C, O, S planes; the angles vary from 13.4 (3) to 21.4 (2)° in (1) and from 14.0 (3) to 32.6 (1)° in (2).

The Cd—S distances in Table 1 are comparable to the values of 2.453 (2), 2.514 (2) and 2.545 (2) Å found for the Ph₄As⁺ salt (Vittal & Dean, 1996a). It is obvious that two of the S—Cd—S angles are similar but significantly different from the third. All the Cd⋯O distances, with the exception of Cd1—O3, are within the limits of the sum of the van der Waals radii (3.1 Å; Bondi, 1964). If we take into account these weak Cd—O interactions, then the coordination geometry of the Cd^{II} atom is best described as a distorted trigonal bipyramid for (1) and a distorted octahedron for (2). The total bond valence

(Brown & Altermatt, 1985) of cadmium in the ion pairs is 2.01 in both (1) and (2), with the interaction with oxygen providing 17 and 23% of the total. For comparison, values of 2.18 and 20% were found for the corresponding Ph_4As^+ salt (Vittal & Dean, 1996a). It is noted that the $\text{PhC}(\text{O})\text{S}^-$ anion that has the shortest $\text{Cd}-\text{O}$ distance has the longest $\text{Cd}-\text{S}$ distance. The O atom that has the longest $\text{Cd}\cdots\text{O}$ distance in (1) and (2) participates in hydrogen bonding to an Et_3NH^+ ion as indicated by the $\text{N}\cdots\text{O}$ distances [2.834 (3) Å for (1) and 2.789 (2) Å for (2)]. As shown in Table 2, the $\text{N}-\text{H}\cdots\text{O}$

angles are close to linearity. The presence of strong hydrogen bonding did not affect the planarity of the CdS_3 skeleton, but instead led to different orientations of the carbonyl groups around the Cd atom. Two such conformations were 'trapped' in the present study. It appears that the intriguing CdS_3 planar conformation in the $[\text{Cd}\{\text{S}(\text{O})\text{CPh}\}_3]^-$ ion is independent of the nature of the counterion or hydrogen bonding as established in this work.

The packing of the two ion pairs in the crystal lattice is shown in Fig. 2. When viewed down the c axis, the structure appears to be pseudo-trigonal.

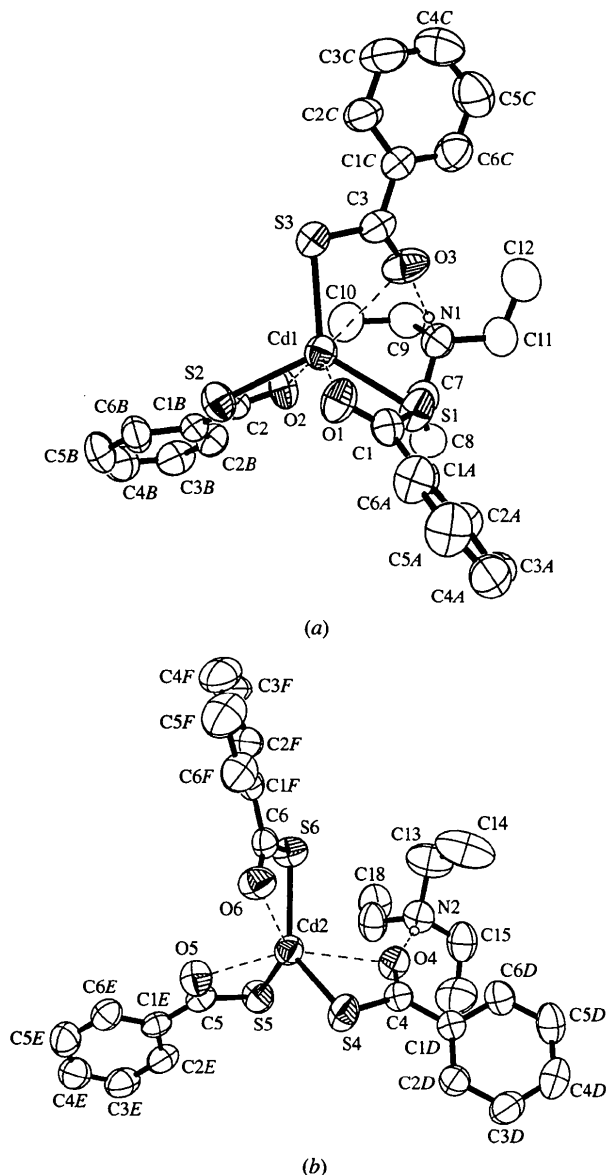


Fig. 1. Views of the two ion pairs (a) ion-pair (1) and (b) ion-pair (2) of $\text{Et}_3\text{NH}^+[\text{Cd}\{\text{S}(\text{O})\text{CPh}\}_3]^-$ showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms attached to C atoms have been omitted for clarity.

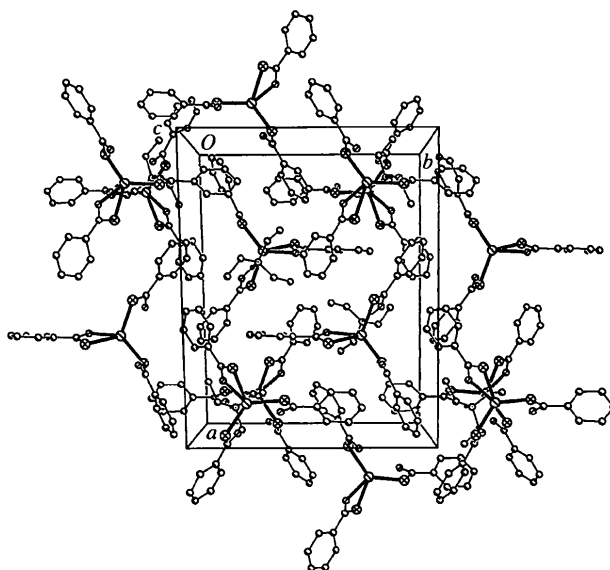


Fig. 2. Packing diagram of $\text{Et}_3\text{NH}^+[\text{Cd}\{\text{S}(\text{O})\text{CPh}\}_3]^-$ viewed down the c axis. H atoms attached to C atoms have been omitted for clarity.

Experimental

All the chemicals were of reagent grade and were used as received. The synthesis was carried out under an argon atmosphere. The product, $(\text{C}_6\text{H}_{16}\text{N})[\text{Cd}(\text{C}_7\text{H}_5\text{OS})_3]$, was obtained in an attempted synthesis of $\text{Ba}[\text{Cd}(\text{C}_7\text{H}_5\text{OS})_3]_2$. Thiobenzoic acid (2.35 g, 17.0 mmol) in 15 ml of methanol was added to Et_3N (1.55 g, 17.0 mmol). The resultant yellow solution of $\text{Et}_3\text{NH}^+.\text{S}(\text{O})\text{CPh}^-$ was added with stirring to a solution of $[\text{Cd}(\text{NO}_3)_2].4\text{H}_2\text{O}$ (1.57 g, 5.1 mmol) dissolved in 10 ml of water to give a milky supernatant and a yellow precipitate. Addition of a solution containing BaCl_2 (0.53 g, 2.55 mmol) in 10 ml of water produced a colorless upper layer and a yellow lower layer. The mixture was stirred for 10 min and then the two layers were separated. About 20 ml of Et_2O was layered onto the yellow fraction and the mixture was allowed to stand in a refrigerator at 278 K. The yellow crystals that formed were decanted, washed with Et_2O and dried in air. A second crop of crystals was obtained from the mixture of mother liquor and washings. Total yield: 2.6 g (81.4%). Single crystals were

formed during the preparation. The stoichiometry of the bulk material was confirmed by analysis of a ^1H NMR spectrum in CDCl_3 .

Crystal data

$(\text{C}_6\text{H}_{16}\text{N})[\text{Cd}(\text{C}_7\text{H}_5\text{OS})_3]$

$M_r = 626.11$

Monoclinic

$P2_1/c$

$a = 19.6219(4) \text{ \AA}$

$b = 15.5067(4) \text{ \AA}$

$c = 19.4399(5) \text{ \AA}$

$\beta = 103.015(1)^\circ$

$V = 5763.0(2) \text{ \AA}^3$

$Z = 8$

$D_x = 1.443 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 8192 reflections

$\theta = 1.69\text{--}29.38^\circ$

$\mu = 1.003 \text{ mm}^{-1}$

$T = 296(2) \text{ K}$

Cut large plate

$0.42 \times 0.35 \times 0.28 \text{ mm}$

Light yellow

Data collection

Siemens SMART CCD diffractometer

ω scans

Absorption correction:

empirical (SADABS;

Sheldrick, 1996)

$T_{\min} = 0.630$, $T_{\max} = 0.755$

35 001 measured reflections

13 914 independent

reflections

10 549 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 29.38^\circ$

$h = -26 \rightarrow 19$

$k = -21 \rightarrow 20$

$l = -22 \rightarrow 26$

Refinement

Refinement on F^2

$R(F) = 0.034$

$wR(F^2) = 0.070$

$S = 1.07$

13 911 reflections

637 parameters

H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 2.6614P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.51 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.46 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

C2—S2—Cd1	83.52 (8)	C4—S4—Cd2	88.32 (8)
C3—S3—Cd1	97.94 (9)	C5—S5—Cd2	80.96 (9)
C1—O1—Cd1	91.02 (14)	C4—O4—Cd2	90.90 (13)
C2—O2—Cd1	94.55 (14)	C5—O5—Cd2	96.4 (2)
C3—O3—Cd1	84.0 (2)	C6—O6—Cd2	91.23 (15)
O1—C1—C1A	120.7 (2)	O4—C4—C1D	120.5 (2)
O1—C1—S1	121.1 (2)	O4—C4—S4	121.3 (2)
C1A—C1—S1	118.2 (2)	C1D—C4—S4	118.1 (2)
O2—C2—C1B	119.5 (2)	O5—C5—S5	120.9 (2)
O2—C2—S2	120.7 (2)	C1E—C5—S5	119.9 (2)
C1B—C2—S2	119.8 (2)	O6—C6—C1F	120.3 (2)
O3—C3—C1C	119.6 (3)	O6—C6—S6	121.4 (2)
O3—C3—S3	123.0 (2)	C1F—C6—S6	118.3 (2)

Table 2. Hydrogen-bonding geometry ($\text{\AA}$, $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O3	0.91	1.925 (3)	2.834 (3)	177.7 (1)
N2—H2...O4	0.91	1.886 (2)	2.789 (2)	171.6 (1)
C7—H7B...O2	0.97	2.448 (3)	3.416 (3)	174.7 (1)
C8—H8B...O1 ¹	0.97	2.541 (4)	3.474 (4)	164 (1)

Symmetry code: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

The diffraction experiments were carried out on a Siemens SMART CCD diffractometer with an Mo $K\alpha$ sealed tube at 296 K. Preliminary cell constants were obtained from 45 frames (width of 0.3° in ω). Final cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. A frame width of 0.3° in ω and a counting time of 20 s per frame at a crystal-to-detector distance of 4.95 cm were used. The collected frames were integrated using the preliminary cell-orientation matrix. The software *SMART* (Siemens, 1996a) was used for collecting frames of data, indexing reflections and determination of lattice parameters, *SAINT* (Siemens, 1996a) for integration of intensity of reflections and scaling, *SADABS* (Sheldrick, 1996) for absorption correction and *SHELXTL* (Siemens, 1996b) for data reduction, space-group determination, structure determination and refinements, graphics and structure reporting.

Financial support from the National University of Singapore and the Natural Sciences and Engineering Research Council of Canada are gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1365). Services for accessing these data are described at the back of the journal.

References

- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
- Burnett, T. R., Dean, P. A. W. & Vittal, J. J. (1994). *Can. J. Chem.* **72**, 1127–1136.
- Sheldrick, G. M. (1996). *SADABS. Empirical Absorption Correction Program*. University of Göttingen, Germany.
- Siemens (1996a). *SMART and SAINT Software Reference Manuals*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996b). *SHELXTL Reference Manual*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Vittal, J. J. & Dean, P. A. W. (1993). *Inorg. Chem.* **32**, 791–794.
- Vittal, J. J. & Dean, P. A. W. (1996a). *Inorg. Chem.* **35**, 3089–3093.
- Vittal, J. J. & Dean, P. A. W. (1996b). *Acta Cryst.* **C52**, 1180–1182.
- Vittal, J. J. & Dean, P. A. W. (1997). *Acta Cryst.* **C53**, 409–410.

Table 1. Selected geometric parameters ($\text{\AA}$, $^\circ$)

Cd1—S1	2.4958 (7)	Cd2—S4	2.5147 (7)
Cd1—S2	2.5473 (7)	Cd2—S5	2.5920 (8)
Cd1—S3	2.4889 (8)	Cd2—S6	2.5051 (7)
Cd1—O1	2.663 (2)	Cd2—O4	2.718 (2)
Cd1—O2	2.537 (2)	Cd2—O5	2.464 (2)
Cd1—O3	3.111 (2)	Cd2—O6	2.677 (2)
S1—C1	1.743 (2)	S4—C4	1.722 (2)
S2—C2	1.723 (2)	S5—C5	1.728 (3)
S3—C3	1.734 (3)	S6—C6	1.730 (2)
O1—C1	1.232 (3)	O4—C4	1.242 (3)
O2—C2	1.239 (3)	O5—C5	1.243 (3)
O3—C3	1.229 (3)	O6—C6	1.239 (3)
S2—Cd1—S1	123.34 (3)	C1C—C3—S3	117.4 (2)
S3—Cd1—S1	123.43 (3)	S4—Cd2—S5	112.34 (3)
S3—Cd1—S2	111.76 (3)	S4—Cd2—S6	131.11 (3)
S1—Cd1—O1	60.49 (4)	S5—Cd2—S6	112.35 (3)
S2—Cd1—O2	61.12 (4)	S4—Cd2—O4	59.30 (4)
S3—Cd1—O3	54.31 (4)	S5—Cd2—O5	61.71 (4)
O2—Cd1—O1	136.59 (6)	S6—Cd2—O6	60.13 (4)
O3—Cd1—O1	124.28 (6)	O4—Cd2—O5	154.73 (6)
O2—Cd1—O3	92.01 (6)	O4—Cd2—O6	116.43 (6)
C1—S1—Cd1	86.46 (9)	O5—Cd2—O6	85.71 (6)