Siemens (1995). *SMART* and *SAINT. Area-Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sinn, H., Kaminsky, W., Vollmer, H. J. & Woldt, R. (1980). *Angew. Chem. Int. Ed. Engl.* **19**, 390–393.

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$H_2N(CH_2)_2NH_3^+.[Mn\{H_2N(CH_2)_2NH_2\}_3]^{2+}.[SbSe_4]^{3-}$

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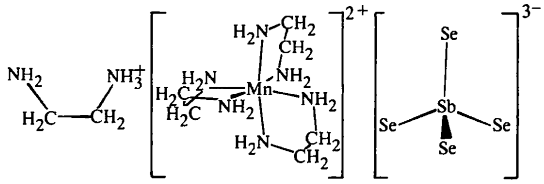
Abstract

The reaction of elemental manganese, antimony and selenium with 1,2-ethanediamine (en) in an aqueous ethaneamine solution under hydrothermal conditions yields orange crystals of 2-aminoethylammonium tris(1,2-ethanediamine)manganese tetraselenoantimonate, enH.Mn(en)$_3$.SbSe$_4$. The structure contains tetrahedral $SbSe_4^{3-}$ anions and octahedral $Mn(en)_3^{2+}$ cations, as well as monoprotonated ethanediamine molecules.

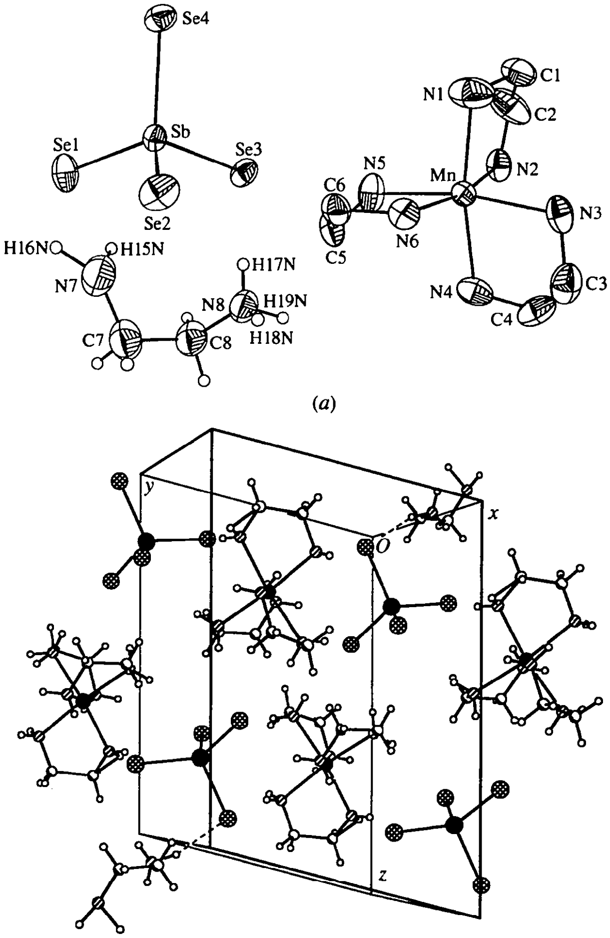
Comment

Applications of mild solvothermal processes have led to a wealth of novel chalcogenides, ranging from unique thiometallate clusters to three-dimensional frameworks (Sheldrick & Kaub, 1986; Sheldrick & Wachhold, 1997; Krebs, 1983). Despite expectations of new and unusual electronic properties, the chemistry of the heavier chalcogenides is less developed. This might be in part due to the ease of hydrolysis of seleno- and tellurometallates. Consequently, non-aqueous reaction media are preferred for their syntheses. In our recent investigations, we have isolated the novel transition metal complex $[Mn(en)_3]_2[Mn_4(en)_9(SbSe_4)_4].2H_2O$ by reacting elemental manganese, antimony and selenium in an aqueous amine solution using high amine concentrations (Bensch *et al.*, 1997). Since it is well known that temperature has an enormous effect on product formation (Sheldrick & Wachhold, 1997), we have investigated the aforementioned system under different synthesis conditions. By using higher temperatures, we have obtained enH.Mn(en)$_3$.SbSe$_4$, (I), as a pure phase forming orange needles.



(I)

The crystal structure of the title compound contains isolated $Mn(en)_3^{2+}$ cations and $SbSe_4^{3-}$ anions. Monoprotonated ethanediamine solvent molecules complete the crystal structure and balance the charge of the $SbSe_4^{3-}$ anions. Each Mn cation is sixfold coordinated by the six N atoms of the chelating en ligands within a distorted octahedron. The Mn—N distances are between 2.235 (6) and 2.286 (5) Å. The Sb—Se distances of the tetrahedral $SbSe_4^{3-}$ anion are between 2.470 (1) and 2.478 (1) Å,



(*a*)

(*b*)

Fig. 1. The crystal structure of the title compound. (*a*) View of the SbSe$_4$ anion, the Mn(en)$_3$ cation and the enH cation with labelling and displacement ellipsoids drawn at the 50% probability level (disorder has been omitted for clarity). (*b*) Packing diagram viewed along [100] with the shortest intermolecular Se—H distances (2.35 Å) indicated by dotted lines.

and are in good agreement with those found in other selenoantimonate(V) compounds (Eisenmann & Zagler, 1989; Sheldrick & Wachhold, 1996). The anions are aligned in the direction of the *b* axis. Two $SbSe_4^{3-}$ anions and two solvent molecules are arranged to fill the voids between the $Mn(en)_3^{2+}$ cations (see Fig. 1*b*). One H atom bound to the protonated N atom of enH exhibits a short contact to the Se3 atom of the $SbSe_4^{3-}$ anion. The distance Se3···H19N of 2.35 (8) Å and the angle N8—H19N···Se3 of 161 (6)° indicate hydrogen bonding. There are additional short Se···H distances of 2.695 (6), 2.610 (6) and 2.725 (8) Å which are significantly shorter than the sum of the van der Waals radii.

It is interesting to note that similar synthesis conditions with sulfur led to an oxidation state of only +3 for antimony. Therefore, further studies are under way in order to gain more information about the processes involved in the formation of selenometallates under solvothermal conditions and their effects on product formation.

Experimental

Manganese, antimony and selenium (0.75 mmol, molar ratio 3:2:8) were reacted in 6 ml of an aqueous solution of 35 vol% ethaneamine and 50 vol% 1,2-ethanediamine in Teflon-lined steel autoclaves at 443 K for 7 d. The product was filtered and washed with *n*-hexane. The yield of the phase-pure product was about 65%. Under atmospheric conditions, the crystals readily decompose to form elemental selenium, so they were stored under argon.

Crystal data

$(C_2H_9N_2)[Mn(C_2H_8N_2)_3]$-$[SbSe_4]$
$M_r = 733.95$
Triclinic
$P\bar{1}$
$a = 8.981\ (4)$ Å
$b = 9.720\ (3)$ Å
$c = 14.451\ (4)$ Å
$\alpha = 104.83\ (3)°$
$\beta = 92.42\ (3)°$
$\gamma = 110.62\ (3)°$
$V = 1129.1\ (7)$ Å^3
$Z = 2$
$D_x = 2.159$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 78 reflections
$\theta = 12.5–17.0°$
$\mu = 8.210$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.5 × 0.3 × 0.3 mm
Orange

Data collection

Stoe AED-2 four-circle diffractometer
ω–θ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1990)
$T_{\min} = 0.063$, $T_{\max} = 0.085$
5478 measured reflections
5155 independent reflections

3713 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 11$
$l = -17 \rightarrow 17$
4 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.119$
$S = 0.991$
5155 reflections
228 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0769P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.290$ e Å^{-3}
$\Delta\rho_{\min} = -1.388$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Sb—Se3	2.4701 (10)	Mn—N1	2.237 (7)
Sb—Se1	2.4726 (12)	Mn—N5	2.274 (6)
Sb—Se4	2.4753 (15)	Mn—N4	2.275 (6)
Sb—Se2	2.4775 (13)	Mn—N3	2.278 (6)
Mn—N2	2.235 (6)	Mn—N6	2.286 (5)
Se3—Sb—Se1	106.44 (4)	Se3—Sb—Se2	108.84 (4)
Se3—Sb—Se4	106.93 (4)	Se1—Sb—Se2	112.34 (4)
Se1—Sb—Se4	111.24 (5)	Se4—Sb—Se2	110.77 (5)

All C, N, Se, Sb and Mn atoms were refined with anisotropic displacement parameters. The H atoms, except those of the protonated ethanediamine, were positioned with idealized geometry and refined with fixed isotropic displacement parameters $[U_{\rm iso}(\text{C—H/N—H}) = 1.2U_{\rm eq}(C_{\rm methylene}/C_{\rm amine})]$ using a riding model with C—H = 0.97 and N—H = 0.90 Å. The 2-aminoethylammonium H atoms were refined with free coordinates as well as free isotropic displacement parameters. One C atom of a chelating en ligand of the cation is disordered and was refined using a split model with 50% occupancy for each position.

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1148). Services for accessing these data are described at the back of the journal.

References

Bensch, W., Näther, C. & Schur, M. (1997). *Chem. Commun.* pp. 1773–1774.
Eisenmann, B. & Zagler, R. (1989). *Z. Naturforsch. Teil B*, **44**, 249–256.
Krebs, B. (1983). *Angew. Chem.* **95**, 113–134.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, W. S. & Kaub, J. (1986). *Z. Anorg. Allg. Chem.* **536**, 114–118.
Sheldrick, W. S. & Wachhold, M. (1996). *Z. Naturforsch. Teil B*, **51**, 32–36.
Sheldrick, W. S. & Wachhold, M. (1997). *Angew. Chem.* **109**, 214–234.

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

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

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

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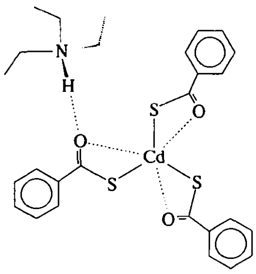
Abstract

The synthesis and structure of the title compound, $(C_6H_{16}N)[Cd(C_7H_5OS)_3]$, 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 $(R_4E)[M\{S(O)CPh\}_3]$ [R = Ph, E = As or P, M = Zn, Cd, Hg (Vittal & Dean, 1996*a*) or Pb (Burnett *et al.*, 1994); R = Me, E = N, M = Sn (Vittal & Dean, 1996*b*) or Hg (Vittal & Dean, 1997)], as well as $(Me_4N)[Na\{Cd[S(O)CPh]_3\}_2]$ (Vittal & Dean, 1993). In the case of the complexes containing the zinc-group metals, the MS_3 cores were found to adopt a planar geometry. What influences lead to this relatively uncommon geometry remain to be understood. The compound $(Et_3NH)[Cd\{S(O)CPh\}_3]$ 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 (1*b*), 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 CdS_3. 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 $[Ph_4As][Cd\{S(O)CPh\}_3]$ (Vittal & Dean, 1996*a*). The deviations of the Cd atoms from the S_3 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 O_3 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 Ph_4As^+ salt (Vittal & Dean, 1996*a*). 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