

Solvothermal synthesis of $[\text{Mn}(\text{en})_3]_2[\text{Mn}_4(\text{en})_9(\text{SbSe}_4)_4] \cdot 2\text{H}_2\text{O}$: the first example of a selenoantimonate(v) acting as a ligand in a transition-metal complex

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Reaction of elemental manganese, antimony and selenium under mild solvothermal conditions yields the complex anion $[\text{Mn}_4(\text{en})_9(\text{SbSe}_4)_4]^{4-}$, the first example of a transition-metal complex with SbSe_4^{3-} anions acting as ligands; the anions are coordinated in a terminal position as well as a bridging ligand.

During recent years an increasing interest in new chalcogenide framework structures has been observed owing to their promising combination of 'zeotype' structures with new properties.¹ Application of mild solvothermal processes has led to a wealth of novel chalcogenides extending from unique thiometallate clusters to three-dimensional frameworks.^{2,3} A special interest is focussed onto the combination of main-group and transition-metal chalcogenides, especially with respect to the incorporation of the latter into the 'open' frameworks of thio-germanates, -stannates or -antimonates.^{4,5} Under mild solvothermal conditions we obtained new thioantimonate framework types,^{6,7} thioantimonate polysulfides⁸ and manganese-containing Sb_xS_y frameworks.⁹ Despite the expected new and unusual electronic properties the chemistry of the heavier chalcogenides is less developed. It is well documented that in aqueous solutions seleno- and telluro-metallates³ undergo hydrolysis reactions and consequently non-aqueous reaction media are preferred for their syntheses. Nevertheless, the reaction of elemental antimony, selenium and manganese in an aqueous amine solution with addition of ethylenediamine (en) yielded the remarkable transition-metal complex $[\text{Mn}(\text{en})_3]_2[\text{Mn}_4(\text{en})_9(\text{SbSe}_4)_4]$.[†] The use of pure metals in the synthesis has attracted some attention in recent years including the insertion of transition metals into R–X bonds of alkyl- or phosphoryl-halogens¹⁰ or the donor solvent mediated reaction of metals with sulfur to give polysulfido complexes.¹¹ The observation that the SbSe_4^{3-} ligands in the title compound are formed using the elements as starting materials raises the question about the mechanism involved.

The crystal structure[‡] of the title compound consists of isolated $\text{Mn}(\text{en})_3^{2+}$ cations and the $[\text{Mn}_4(\text{en})_9(\text{SbSe}_4)_4]^{4-}$ anions are probably stabilized by the large $\text{Mn}(\text{en})_3^{2+}$ ions [Fig. 1(a) and (b)]. The anion is built up from two SbSe_4 – $\text{Mn}(\text{en})_2$ – SbSe_4 – $\text{Mn}(\text{en})_2$ subunits, connected *via* a bridging ethylenediamine ligand, which is located around a center of inversion. The subunits contain two crystallographically independent manganese centers in distorted octahedral coordinations. The two different SbSe_4^{3-} groups exhibit different binding modes. The $\text{Se}(1)_{\text{br}}$ (br = bridging) center of the $\text{Sb}(1)\text{Se}_4^{3-}$ unit joins the $\text{Mn}(1)$ and $\text{Mn}(2)$ atoms. Each Mn is chelated by two en ligands. The coordination sphere of $\text{Mn}(2)$ is completed by $\text{Se}(5)_t$ (t = terminal) of the terminal $\text{Sb}(2)\text{Se}_4^{3-}$ ligand, leading to a *cis*-configuration of the distorted octahedral environment [Fig. 1(a)]. The $\text{Mn}(1)$ centers are bridged by an en ligand, and therefore the $\text{Mn}(1)$ is coordinated by five N atoms and one Se center.

The Sb–Se distances for both SbSe_4^{3-} anions are in good agreement with those found in isolated SbSe_4^{3-} anions^{12,13} with the exception that $\text{Sb}(1)–\text{Se}(1)_{\text{br}}$ is elongated by *ca.* 0.04 Å. As

expected the $\text{Mn}(2)–\text{Se}(5)_t$ distance of 2.673(2) Å is shorter than to the bridging $\text{Se}(1)_{\text{br}}$ atom. The Mn–Se distances to $\text{Se}(1)_{\text{br}}$ amount to 2.825(2) Å for $\text{Mn}(1)$ and to 2.757(2) Å for $\text{Mn}(2)$, a significant difference of 0.068(2) Å. This might be due to intramolecular hydrogen bonding between the $\text{Se}(2)_t$ center of the $\text{Sb}(1)\text{Se}_4^{3-}$ anion and an amino hydrogen of a chelate ligand bound to $\text{Mn}(2)$. The $\text{Se}(2) \cdots \text{H}$ distance of 2.614(5) Å is significantly shorter than the sum of their van der Waals radii and the $\text{Se} \cdots \text{H}–\text{N}$ angle of 176.1(2)° is indicative of a hydrogen bond. There is an additional hydrogen bond between one amino hydrogen of a chelate ligand and the oxygen of a water molecule which is located in holes of the structure (Fig. 2). The $\text{O} \cdots \text{H}$ bond length is 2.39(2) Å and the $\text{O} \cdots \text{H}–\text{N}$ angle is 151.4(3)°.

The title compound is the first structurally characterized example of a transition-metal complex containing SbSe_4^{3-} anions as ligands. Chalcogeno–antimonates(III) often crystallize as extended frameworks^{14–16} whereas chalcogeno–antimonates(V) form isolated anions^{12,13} or dense structures.^{17,18} The

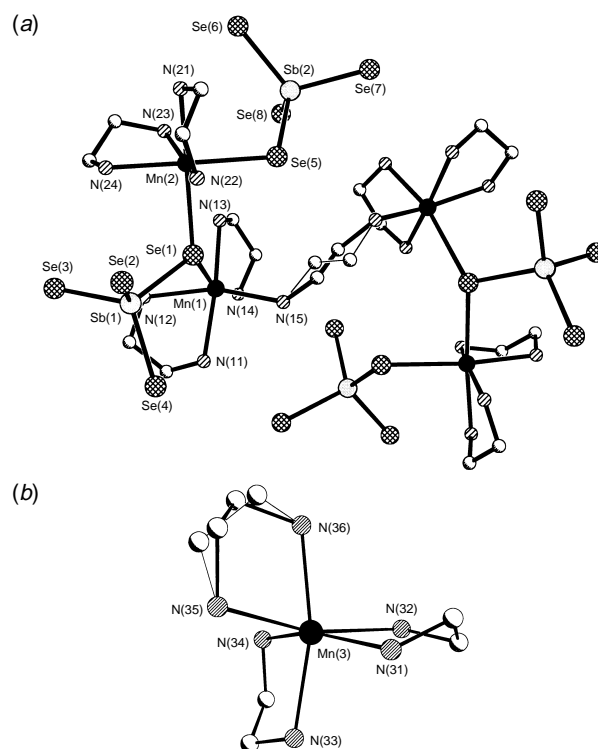


Fig. 1 Crystal structure of $[\text{Mn}(\text{en})_3]_2[\text{Mn}_4(\text{en})_9\text{Sb}_4\text{Se}_{16}]^{2-}$: (a) view of the anion $[\text{Mn}_4(\text{en})_9\text{Sb}_4\text{Se}_{16}]^{2-}$ with numbering. Selected bond lengths (Å) and angles (°): $\text{Sb}(1)–\text{Se}(2)$ 2.4550(8), $\text{Sb}(1)–\text{Se}(4)$ 2.4690(7), $\text{Sb}(1)–\text{Se}(3)$ 2.4713(8), $\text{Sb}(1)–\text{Se}(1)$ 2.5111(7), $\text{Sb}(2)–\text{Se}(8)$ 2.4439(10), $\text{Sb}(2)–\text{Se}(6)$ 2.4738(8), $\text{Sb}(2)–\text{Se}(7)$ 2.4787(8), $\text{Sb}(2)–\text{Se}(5)$ 2.4812(8), $\text{Se}(1)–\text{Mn}(2)$ 2.7573(11), $\text{Se}(1)–\text{Mn}(1)$ 2.8251(12), $\text{Se}(5)–\text{Mn}(2)$ 2.6728(12); $\text{Mn}(2)–\text{Se}(1)–\text{Mn}(1)$ 128.32(4), $\text{Sb}(2)–\text{Se}(5)–\text{Mn}(2)$ 110.88(3), $\text{Se}(5)–\text{Mn}(2)–\text{Se}(1)$ 88.04(3); (b) note the disorder of one chelate ligand in the cation; hydrogen atoms are omitted for clarity

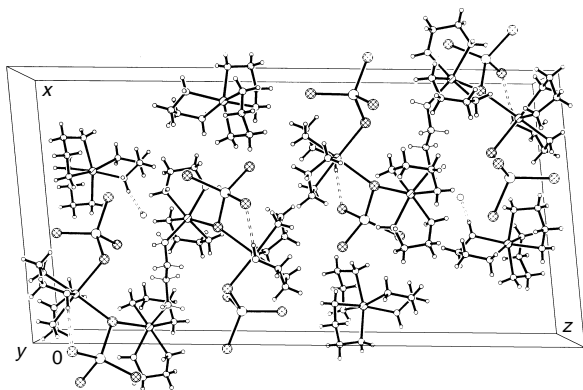


Fig. 2 Packing of the molecules with view along the *b*-axis. For clarity, the disordered atoms of the ligands are omitted; hydrogen bonds are shown as broken lines.

combination of thio- and seleno-arsenates(III) with transition metals resulted in the preparation of a still growing number of low-dimensional structures.¹⁹ However, the only examples of chalcogenopnictide(v) acting as ligands are AsS_4^{3-} groups in nickel complexes as established by spectroscopical methods, but no structural data were reported.²⁰ It is noted that thiometallates of transition metals can be used as ligands.^{21,22}

The complex anion in the crystal structure of the title compound may be regarded as a precursor for polymeric structures. Further studies are under way in order to enlarge the degree of condensation and to prepare extended structures.

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Footnotes and References

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† *Synthesis*: The title compound was obtained by reacting stoichiometric amounts of elemental manganese, antimony and selenium in an aqueous solution of 70 vol% ethylamine and 20 vol% ethylenediamine (en) (yield: ca. 95% based on Mn). The probe was heated to 130 °C for 6 days in a Teflon-lined steel vessel under autogenous pressure. The crystalline product was filtered, washed with dry ethanol and stored under vacuum. The crystals are dark red, moisture-sensitive prisms up to 5 mm long with excellent cleavage perpendicular to the needle axis. The compound could not be prepared in aqueous en solutions, whereas syntheses carried out in amine solutions without addition of en led to the rapid formation of Sb_2Se_3 .

‡ *Crystal structure determination*: $[\text{Mn}(\text{en})_3]_2[\text{Mn}_4(\text{en})_9(\text{SbSe}_4)_4] \cdot 2\text{H}_2\text{O}$, $M = 3017.6$ monoclinic, space group $P2_1/n$ (no. 13), $a = 16.519(2)$, $b = 8.248(1)$, $c = 32.599(3)$ Å, $\beta = 95.76(1)^\circ$, $U = 4419.1(9)$ Å³, $T = 295$ K, $Z = 2$, STOE AED-II four-circle diffractometer (Mo-K α radiation, $\lambda = 0.7107$ Å), $\mu = 8.664$ mm⁻¹. 11 518 reflections collected in the range $3 \leq 2\theta \leq 53^\circ$, 9180 unique reflections. Face-indexed absorption correction; structure solution with SHELXS-86; structure refinement against F^2 using SHELXL-93. 398 parameters, R for 5968 reflections with $I >$

$2\sigma(I) = 0.0359$, wR_2 for all 9180 data = 0.0990, GOF 1.013. Residual electron density: 1.525, -1.088 e Å⁻³. The heavy atoms were refined anisotropically. The hydrogen atoms were positioned with idealized geometry and refined with individual isotropic displacement parameters using a riding model. The highest difference peak in the Fourier map according to a composition of $[\text{Mn}(\text{en})_3]_2[\text{Mn}_4(\text{en})_9(\text{SbSe}_4)_4]$ is located in the small cavity between the bridging and the terminal SbSe_4 ligands. It was assumed that this peak is due to incorporated solvent water molecules which was confirmed by IR spectroscopy showing a broad absorption band between 3600 and 3000 cm⁻¹. In space group $P2_1/n$ the two carbons of the bridging en ligand are around a center of inversion and hence they are disordered. This disorder is not observed in the non-centrosymmetric space group Pn . However, the detailed analysis of the refinements in Pn and $P2_1/n$ clearly revealed the centrosymmetric arrangement of the remaining part of the structure. CCDC 182/557.

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