

2-Aminoethylammonium tris(1,2-ethylene-diamine)nickel(II) tetraselenoantimonate(V)

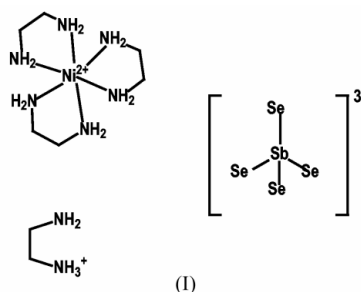
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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
R factor = 0.054
wR factor = 0.088
Data-to-parameter ratio = 24.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The new molecular metal chalcogenide, $(\text{enH})[\text{Ni}(\text{en})_3]\text{SbSe}_4$ or $(\text{C}_2\text{H}_9\text{N}_2)[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3][\text{SbSe}_4]$, has been synthesized by a solvothermal reaction in an ethylenediamine/methanol solution at 443 K. The structure contains tetrahedral SbSe_4^{3-} anions and octahedral $[\text{Ni}(\text{en})_3]^{2+}$ cations, as well as the monoprotonated ethylenediamine cation $[\text{enH}]^+$.

Comment

Chalcogenidometallates with open frameworks have attracted considerable interest as possible zeolite-like materials, for which highly interesting properties could be expected. In recent decades, a large number of thioantimonates exhibiting different degrees of fused Sb_xS_y anionic fragments have been reported (Sheldrick & Wachhold, 1997, 1998). These compounds contain a variety of polymeric complex anions. Compounds with one-, two-, and three-dimensional structures have been isolated and characterized. In contrast to the thioantimonates, the chemistry of heavier chalcogenoantimonates is less developed, probably due to the ease of hydrolysis of seleno- and telluroantimonates. Following solvothermal synthesis, the structures of $[\text{Mn}(\text{en})_3]_2 \cdot [\text{Mn}_4(\text{en})_9(\text{SbSe}_4)_4] \cdot 2\text{H}_2\text{O}$ (en is 1,2-ethylenediamine; Bensch *et al.*, 1997), $[\text{enH}][\text{Mn}(\text{en})_3][\text{SbSe}_4]$ (Wendland & Bensch, 1998), $\text{Cu}_2\text{SbSe}_3 \cdot 0.5\text{en}$ and $\text{Cu}_2\text{SbSe}_3 \cdot \text{en}$ (Chen *et al.*, 1998), $[\text{Fe}(\text{en})_3]_2(\text{Sb}_2\text{Se}_5)$ (Chen *et al.*, 2000) and $[\text{enH}][\text{Fe}(\text{en})_3][\text{SbSe}_4]$ (Girard & Li, 1998) have been reported. In our recent investigations, we have obtained a new complex, namely $(\text{enH})[\text{Ni}(\text{en})_3][\text{SbSe}_4]$, (I), which, to the best of our knowledge, is the first selenoantimonate containing $[\text{Ni}(\text{en})_3]^{2+}$ as a structure-directing agent. Here we report the synthesis and crystal structure of (I).The asymmetric unit of (I) comprises an isolated $[\text{Ni}(\text{en})_3]^{2+}$, monoprotonated ethylenediamine cation, and an SbSe_4^{3-} anion (Fig. 1). In the complex cation, the Ni atom is surrounded by six N atoms from three neutral ethylenediamine (en) ligands, which function as bidentate ligands, forming five-membered chelate rings, with Ni–N bond lengths ranging from 2.108 (3) to 2.130 (3) Å, giving a distorted

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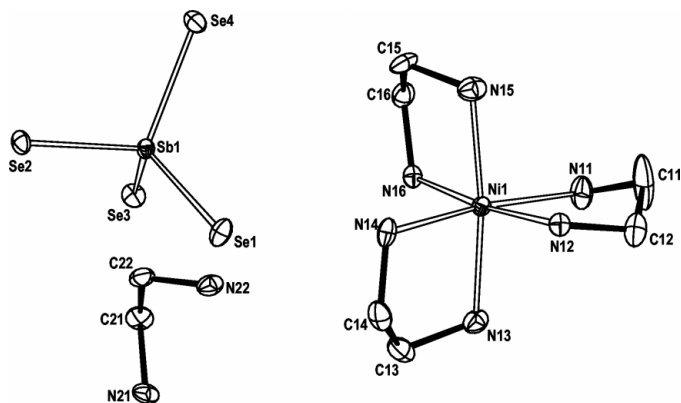


Figure 1
The molecular structure of the title compound, with ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted.

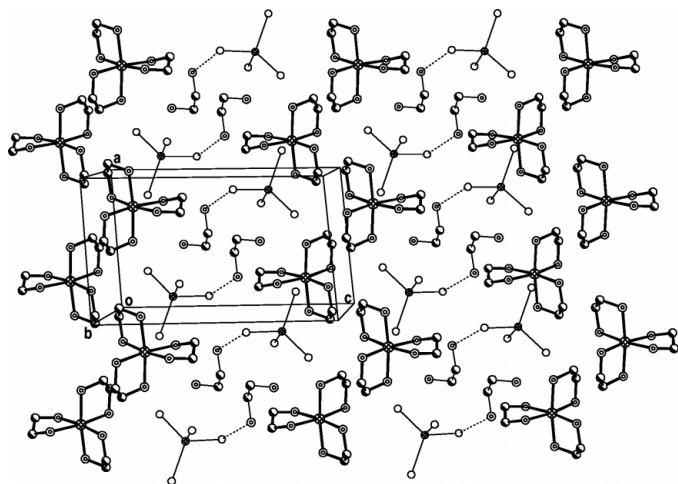


Figure 2
The crystal structure of the title compound, with intermolecular hydrogen bonds shown as dotted lines.

octahedral environment. The configuration of the en rings in $[\text{Ni}(\text{en})_3]^{2+}$ is $\Lambda(\delta\delta\lambda)$ or $\Delta(\lambda\lambda\delta)$, according to Saito's description (Saito, 1979). It is noteworthy that the C—C bond distance [C11—C12 = 1.420 (8) Å] in the en ligand with λ configuration is significantly shorter than those [C15—C16 = 1.506 (5) Å and C13—C14 = 1.497 (6) Å] in the other two en ligands with δ configuration. A similar situation was found in the configuration of $[\text{Fe}(\text{en})_3]^{2+}$ in the compound $[\text{enH}][\text{Fe}(\text{en})_3][\text{SbSe}_4]$ (Girard & Li, 1998).

The Sb—Se distances of the tetrahedral SbSe_4^{3-} anion in (I) range from 2.4722 (8) to 2.4810 (11) Å, consistent with those found in analogous compounds (Wendland & Bensch, 1998; Sheldrick & Wachhold, 1996). As shown in Fig. 2, the $[\text{Ni}(\text{en})_3]^{2+}$ cations and their crystallographic inversion center-related species can be considered as forming cationic slabs in the *ab* plane, between which the SbSe_4^{3-} and protonated ethylenediamine species are located. The protonated H atom is assigned to atom N21 rather than to atom N22, due to the closer cation–anion contact (2.54 Å; Pell & Ibers, 1996). Atom Se2 of the isolated SbSe_4^{3-} anion acts as a hydrogen-bond

acceptor, forming an intermolecular hydrogen bond with the N atom of protonated enH⁺; N21...Se2ⁱ = 3.306 (6) Å, H...Se2ⁱ = 2.54 Å and N21—H...Se2 = 145° [symmetry code: (i) 1 - *x*, -*y*, 1 - *z*].

Experimental

Single crystals of (I) were obtained under solvothermal conditions from a solution containing nickel (0.059 g, 1 mmol), antimony (0.122 g, 1 mmol) and selenium (0.237 g, 3 mmol). The reactants were weighed and mixed in a glove-box under a nitrogen atmosphere. The reactants were then loaded into a Teflon-lined steel autoclave and 3 ml of methanol/1,2-ethanediamine (volume ratio = 1:4) was added. The reaction took place at 443 K over a period of 4 d. The product was filtered off and washed with acetone. The title compound is unstable in air, and must be stored under a nitrogen atmosphere.

Crystal data

$(\text{C}_2\text{H}_9\text{N}_2)[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3][\text{SbSe}_4]$
 $M_r = 737.72$
 Triclinic, $P\bar{1}$
 $a = 8.829$ (3) Å
 $b = 9.644$ (4) Å
 $c = 14.283$ (5) Å
 $\alpha = 104.833$ (14)°
 $\beta = 92.357$ (7)°
 $\gamma = 109.866$ (11)°
 $V = 1094.7$ (7) Å³

$Z = 2$
 $D_x = 2.238$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2804 reflections
 $\theta = 3.1$ – 27.5°
 $\mu = 8.75$ mm⁻¹
 $T = 293$ (2) K
 Chip, orange
 0.06 × 0.04 × 0.03 mm

Data collection

Rigaku Mercury CCD diffractometer
 ω scans
 Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)
 $T_{\text{min}} = 0.763$, $T_{\text{max}} = 1.000$
 8993 measured reflections

4908 independent reflections
 3612 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -11 \rightarrow 10$
 $k = -12 \rightarrow 12$
 $l = -18 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.088$
 $S = 1.00$
 4908 reflections
 199 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0138P)^2 + 3.5795P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.90$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.95$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Sb1—Se1	2.4733 (8)	Ni1—N14	2.124 (3)
Sb1—Se2	2.4722 (8)	Ni1—N15	2.124 (3)
Sb1—Se3	2.4810 (11)	Ni1—N16	2.130 (3)
Sb1—Se4	2.4791 (9)	C11—C12	1.420 (8)
Ni1—N11	2.123 (4)	C13—C14	1.497 (6)
Ni1—N12	2.112 (3)	C15—C16	1.506 (5)
Ni1—N13	2.108 (3)		
Se1—Sb1—Se2	106.19 (3)	N12—Ni1—N13	91.47 (13)
Se1—Sb1—Se3	111.96 (3)	N12—Ni1—N14	92.27 (13)
Se1—Sb1—Se4	111.69 (3)	N12—Ni1—N15	93.87 (13)
Se2—Sb1—Se3	109.05 (3)	N12—Ni1—N16	173.05 (13)
Se2—Sb1—Se4	106.54 (2)	N13—Ni1—N14	81.90 (14)
Se3—Sb1—Se4	111.11 (2)	N13—Ni1—N15	172.67 (13)
N11—Ni1—N12	81.69 (14)	N13—Ni1—N16	94.04 (13)
N11—Ni1—N13	93.06 (15)	N14—Ni1—N15	92.86 (14)
N11—Ni1—N14	172.06 (15)	N14—Ni1—N16	92.69 (13)
N11—Ni1—N15	92.68 (15)	N15—Ni1—N16	81.03 (12)
N11—Ni1—N16	93.78 (14)		

H atoms bonded to carbon/nitrogen were inserted at calculated positions with isotropic displacement parameters, riding on their parent atoms.

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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