Solvothermal synthesis and characterization of tris(ethylenediamine)nickel(II) hexaseleno-distannate(IV)

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The title compound, $[Ni(C_2H_8N_2)_3]_2[Sn_2Se_6]$, was synthesized under solvothermal conditions in an ethylenediamine/water solution at 453 K. The compound contains discrete centro-symmetric $[Sn_2Se_6]^{4-}$ anions, which are dimers of two tetrahedral $SnSe_4$ groups sharing a common edge. The transition metal cation is six-coordinated by three ethylenediamine molecules in an octahedral geometry.

Comment

Chalcogenides possess a very diverse and interesting structural chemistry, and exhibit useful physical and chemical properties that are promising for applications in modern technologies (Assoud *et al.*, 2004; Manos *et al.*, 2005). Up to now most known selenostannates were prepared using the molten alkali-metal polychalcogenide flux and high-temperature solid state techniques in the absence of oxygen (Palchik *et al.*, 2002). Low-temperature solvo(hydro)thermal reactions have produced a limited number of selenostannates (Loose & Sheldrick, 2001). Among these selenostannates, the counterions to the $[Sn_xSe_y]^{n-}$ anions can be classified as metal cations (Zimmermann & Dehnen, 1999), organic amine cations (Fehlker & Blachnik, 2001) and transition metal complex cations. The study of selenostannates combining with transition metal complex cations as counter-ions is still a fairly unexplored area. Transition metal complex cations may serve as structure-directing agents in growing selenostannate crystals.

(I)
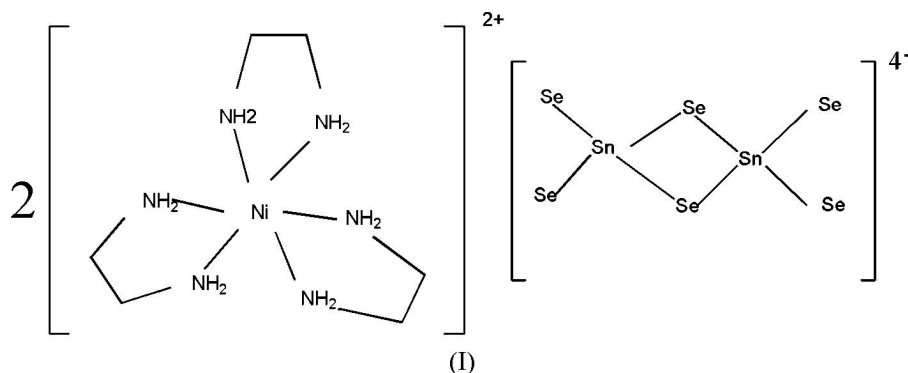
In this paper, we report the structure of the title compound, (I), prepared under solvothermal conditions (Fig. 1). Selected bond lengths and angles are listed in Table 1. The discrete centrosymmetric $[Sn_2Se_6]^{4-}$ anions are formed by two edge-sharing $SnSe_4$ tetrahedra. The terminal Sn—Se distances range from 2.4603 (5) Å to 2.4717 (4) Å and are shorter than the bridging Sn—Se bond lengths, which are between
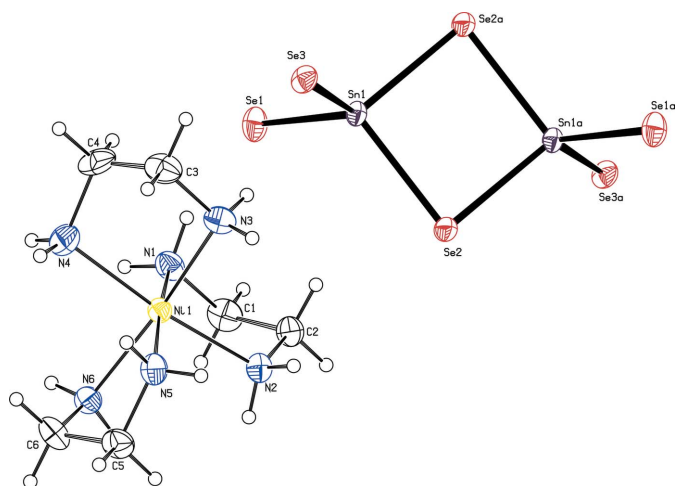
Figure 1
View of the molecular structure of (I) with the atom-labelling scheme and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (a) $1 - x, -y, -z$..

2.5786 (4) Å and 2.5763 (4) Å. The Se2—Sn1—Se2^i angle in the four-membered ring is larger than the Sn1—Se2—Sn1^i angle [symmetry code: (i) $1 - x, -y, -z$]. All Se—Sn—Se angles deviate significantly from the ideal value of 109.5° for a tetrahedron, indicating that the two SnSe$_4$ tetrahedra in the $[Sn_2Se_6]^{4-}$ anion are distorted.

In the $[Ni(en)_3]^{2+}$ ion the transition metal is coordinated by six N atoms from three bidentate ethylenediamine ligands forming a distorted octahedron. The slight distortion of the NiN$_6$ octahedron is reflected in the *trans* N—Ni—N angles of 170.13 (15)° to 172.29 (16)°.

Experimental

The title compound was obtained by placing a mixture of NiCl$_2$·6H$_2$O, tin, powdered selenium, H$_2$O and ethylenediamine with a molar ratio of 1:1.4:3:246:61 into a glass tube and sealing it in a Teflon-lined stainless steel bomb. This was then heated at 453 K for 7 d, and then cooled slowly to ambient temperature. The product was washed with ethanol and water, yielding red block-shaped crystals suitable for X-ray diffraction analysis.

Crystal data

$[Ni(C_2H_8N_2)_3]_2[Sn_2Se_6]$	$Z = 4$
$M_r = 1189.18$	$D_x = 2.250$ Mg m^{-3}
Orthorhombic, *Pbca*	Mo $K\alpha$ radiation
$a = 15.2885$ (13) Å	$\mu = 8.71$ mm^{-1}
$b = 11.9367$ (10) Å	$T = 293$ (2) K
$c = 19.2389$ (16) Å	Block, red
$V = 3511.0$ (5) Å^3	$0.20 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	20244 measured reflections
φ and ω scans	4188 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	3352 reflections with $I > 2\sigma(I)$
$T_{min} = 0.275$, $T_{max} = 0.476$	$R_{int} = 0.038$
(expected range = 0.242–0.419)	$\theta_{max} = 28.0°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.030$	$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2]$
$wR(F^2) = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
4188 reflections	$\Delta\rho_{max} = 0.88$ e Å^{-3}
199 parameters	$\Delta\rho_{min} = -0.50$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.491 (5)	Ni1—N4	2.128 (4)
C2—N2	1.475 (4)	Ni1—N1	2.134 (4)
C3—N3	1.487 (5)	Ni1—N5	2.140 (4)
C4—N4	1.503 (5)	Se1—Sn1	2.4603 (5)
C5—N5	1.478 (4)	Se2—Sn1^i	2.5763 (4)
C6—N6	1.493 (4)	Se2—Sn1	2.5786 (4)
Ni1—N2	2.108 (4)	Se3—Sn1	2.4717 (4)
Ni1—N6	2.109 (4)	Sn1—Se2^i	2.5763 (4)
Ni1—N3	2.110 (4)		
N6—Ni1—N3	170.13 (15)	Se3—Sn1—Se2^i	113.341 (15)
N2—Ni1—N4	172.29 (16)	Se1—Sn1—Se2	114.734 (15)
Sn1^i—Se2—Sn1	87.120 (13)	Se3—Sn1—Se2	112.042 (16)
Se1—Sn1—Se3	110.887 (16)	Se2^i—Sn1—Se2	92.881 (13)
Se1—Sn1—Se2^i	111.923 (16)		

Symmetry code: (i) $-x + 1, -y, -z$.

The three coordinated ethylenediamine molecules are disordered over two positions, which were identified from difference Fourier maps. Disordered atoms were refined anisotropically with appropriate restraints for approximate isotropic behaviour and similarity of displacement parameters. Each N atom in every ethylenediamine group takes up two positions; the site occupancy factors were refined and then fixed at 0.83 and 0.17, respectively. H atoms were positioned geometrically, with the C—H and N—H distances fixed at 0.97 and 0.90 Å, respectively, and refined using a riding model with the isotropic displacement parameters fixed at 1.2 times U_{eq} of the parent atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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