

Bis[tris(1,2-ethanediamine-*N,N'*)-nickel(II)] tetrathioantimonate(V) nitrate

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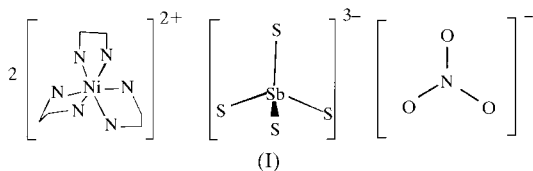
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The title double salt, $[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3]_2(\text{SbS}_4)(\text{NO}_3)$, was crystallized under solvothermal conditions. Hydrogen bonds between the SbS_4^{3-} anions (at four sites) and the $[\text{Ni}(\text{en})_3]^{2+}$ (en = ethylenediamine) cations (at two sites) form a three-dimensional network. The NO_3^- anion is disordered over four sites. The cation lies on a twofold rotation axis and the SbS_4^{3-} anion on a $\bar{4}$ axis.

Comment

This contribution stems from our search for novel thioantimonates linked to transition metals. The use of solvothermal methods and the aid of structure-directing amines enabled us to synthesize molecular complexes (Schur *et al.*, 1998), as well as extended frameworks (Bensch & Schur, 1996), with thioantimonate(III) as building groups. The strongly chelating en ligand, however, often leads to the separation of the transition metals (*M*) as $[\text{M}(\text{en})_3]^{2+}$ complexes and the formation of compounds of the type $[\text{M}(\text{en})_3]\text{Sb}_4\text{S}_7$ (Bensch & Schur, 1997; Stephan & Kanatzidis, 1997). Exploration of the effect of different metal sources, *e.g.* using Ni^{II} nitrate instead of elemental Ni, leads to the



formation of the title compound, (I), with a tetrathioantimonate(V) anion. The compound was obtained as a minor phase in the reaction of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with elemental antimony and sulfur under solvothermal conditions in an aqueous solution of en. The crystal structure is built up from $[\text{Ni}(\text{en})_3]^{2+}$ cations, tetrahedral SbS_4^{3-} anions and nitrate anions. The geometries of the $[\text{Ni}(\text{en})_3]^{2+}$ complex, as well as of the SbS_4^{3-} anion, show the expected interatomic distances and angles (Fig. 1). The NO_3^- anion is disordered (see refinement section) and its presence has been confirmed by a strong

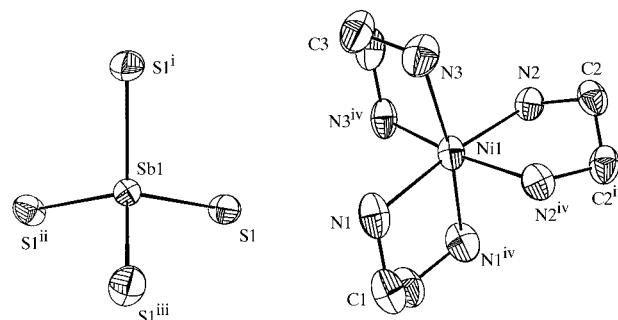


Figure 1

The SbS_4^{3-} anion and the $[\text{Ni}(\text{en})_3]^{2+}$ cation with labelling and displacement ellipsoids drawn at the 50% probability level. The disordered NO_3^- anion has been omitted (symmetry codes are as in Table 1).

Raman resonance at 1045 cm^{-1} . The arrangement of the ions in the crystal structure is best considered as being composed of layers stacked along the *z* axis (Fig. 2). In each layer, the cations are surrounded by two SbS_4^{3-} and two NO_3^- anions, respectively, with equal anions lying diametrically, resulting in a chessboard-like arrangement. Four such layers are stacked along the *z* axis. Each S atom of the SbS_4^{3-} anion is involved in hydrogen bonding to the amino groups from the surrounding cations, indicated by short $\text{H} \cdots \text{S}$ separations. Within a layer, these amount to $2.523(5) \text{ \AA}$ [$\text{H1A} \cdots \text{S1}(-x, -y, z), \text{N1}-\text{H1A}-\text{S} 165^\circ$] and 2.656 \AA [$\text{H2A} \cdots \text{S1}(y, 1-x, -z), \text{N}-\text{H}-\text{S} 150^\circ$]. A weaker hydrogen bond of 2.757 \AA [$\text{H1B} \cdots \text{S1}(-x, \frac{1}{2} + y, \frac{1}{4} - z), \text{N}-\text{H}-\text{S} 138^\circ$] is found to link the layers. This hydrogen-bonding pattern is in accordance with the tabular habit of the crystals. [For a discussion of hydrogen bonding in tetrathio-

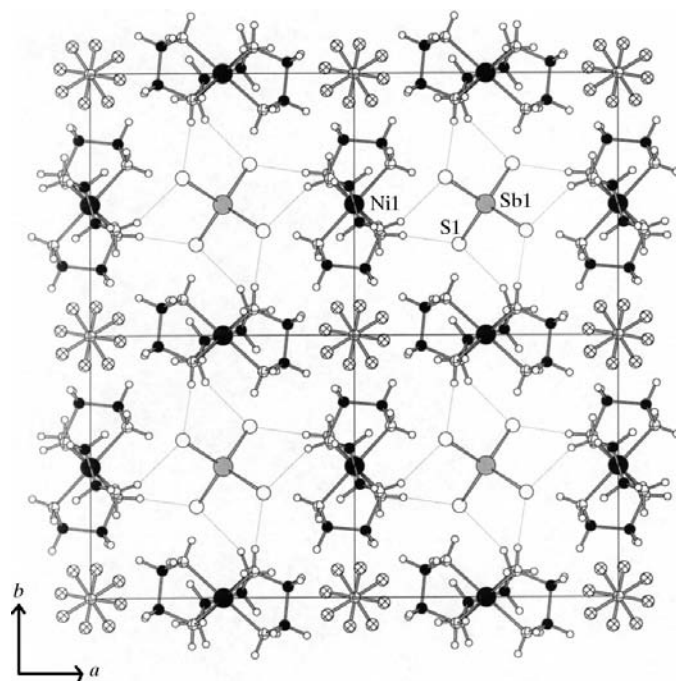


Figure 2

The chessboard-like arrangement of the ions $[\text{Ni}(\text{en})_3]^{2+}$, SbS_4^{3-} and NO_3^- within the unit cell viewed down the *c* axis. Short intermolecular $\text{S} \cdots \text{H}$ distances are indicated by dotted lines.

antimonates, see Mereiter *et al.* (1979).] The presence of hydrogen bonding has been assumed to play a vital role in the stabilization and structure-forming process of thioantimonates synthesized with alkylamines.

The formation of SbS_4^{3-} using en under solvothermal conditions has been reported in several cases. However, it has so far not been observed with other alkylamine solutions under similar conditions. It remains unclear whether special synthetic conditions or the stabilization of the SbS_4^{3-} anions in the crystal structure are mainly responsible for their isolation. However, it is likely that the nitrate acts as an oxidizing agent. The differential thermal analysis and thermogravimetric curves obtained while heating 10 mg of the title compound *in vacuo* at 2 K min^{-1} to 673 K indicate a complex decomposition process. Three exothermic events are observed with peak temperatures at 493, 527 and 563 K, and an endothermic event occurs at 534 K. Two distinguishable mass losses coincide with the two first exothermic events. The sum of the weight losses of 52.3% is in good agreement with the expected value of 53.5% for the total removal of the en ligands and NO_3^- . The result of the decomposition forms a mixture of NiS , NiS_2 and Sb_2S_3 , as evidenced by powder diffractometry.

Experimental

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, antimony and sulfur (molar ratio 1:1:2.5) were reacted in aqueous ethylenediamine solution (5 ml, 50 vol%) in Teflon-lined steel autoclaves at 423 K for 5 d. The solid products were filtered off, yielding $[\text{Ni}(\text{en})_3]\text{Sb}_4\text{S}_7$ as the main product together with approximately 20% of the title phase and trace amounts of $[\text{Ni}(\text{en})_3](\text{SO}_4)$ based on nickel. The light-violet thin quadratic tabular crystals of $[\text{Ni}(\text{en})_3]_2(\text{SbS}_4)(\text{NO}_3)$ decompose within a few days on exposure to air. To date, it has not been possible to synthesize the isomorphous compounds with other transition metals under equivalent synthetic conditions.

Crystal data

$[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3]_2(\text{SbS}_4)(\text{NO}_3)$	Mo $K\alpha$ radiation
$M_r = 790.04$	Cell parameters from 90 reflections
Tetragonal, $I\bar{4}2d$	$\theta = 16\text{--}22^\circ$
$a = 10.276(2) \text{ \AA}$	$\mu = 2.305 \text{ mm}^{-1}$
$c = 30.249(4) \text{ \AA}$	$T = 293(2) \text{ K}$
$V = 3194.3(13) \text{ \AA}^3$	Plate, violet
$Z = 4$	$0.15 \times 0.12 \times 0.1 \text{ mm}$
$D_x = 1.643 \text{ Mg m}^{-3}$	

Data collection

Stoe AED-II four-circle diffractometer	$\theta_{\text{max}} = 27.51^\circ$
ω - θ scans	$h = -1 \rightarrow 13$
2222 measured reflections	$k = 0 \rightarrow 13$
1046 independent reflections (plus 187 Friedel-related reflections)	$l = 0 \rightarrow 39$
934 reflections with $I > 2\sigma(I)$	4 standard reflections
$R_{\text{int}} = 0.036$	frequency: every 120 min
	intensity decay: negligible

Table 1

Selected geometric parameters (\AA , $^\circ$).

Sb1—S1^{i}	2.320 (2)	Ni1—N1	2.113 (4)
$\text{Sb1—S1}^{\text{ii}}$	2.320 (2)	Ni1—N2	2.129 (4)
$\text{Sb1—S1}^{\text{iii}}$	2.320 (2)	$\text{Ni1—N2}^{\text{iv}}$	2.129 (4)
Sb1—S1	2.320 (2)	Ni1—N3	2.139 (5)
$\text{Ni1—N1}^{\text{iv}}$	2.113 (4)	$\text{Ni1—N3}^{\text{iv}}$	2.139 (5)
$\text{S1}^{\text{i}}\text{—Sb1—S1}^{\text{ii}}$	110.12 (4)	$\text{S1}^{\text{ii}}\text{—Sb1—S1}$	110.12 (4)
$\text{S1}^{\text{ii}}\text{—Sb1—S1}^{\text{iii}}$	108.18 (7)		

Symmetry codes: (i) $-x, -y, z$; (ii) $y, -x, -z$; (iii) $-y, x, -z$; (iv) $-x, 1 - y, z$.

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$\Delta\rho_{\text{max}} = 1.08 \text{ e \AA}^{-3}$
$wR(F^2) = 0.070$	$\Delta\rho_{\text{min}} = -0.87 \text{ e \AA}^{-3}$
$S = 1.000$	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
1233 reflections	Extinction coefficient: 0.00055 (10)
92 parameters	Absolute structure: Flack (1983)
H atoms constrained	Flack parameter = $-0.04(5)$
$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

All non-H atoms were refined with anisotropic displacement parameters. The H atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{N—H}, \text{C—H}) = 1.2U_{\text{eq}}(\text{C}_{\text{methylene}}/\text{C}_{\text{amine}})$] using a riding model with the parameters $\text{C—H} = 0.97 \text{ \AA}$ and $\text{N—H} = 0.90 \text{ \AA}$. The absolute structure was determined and is in accordance with the selected setting [Flack parameter $-0.04(5)$]. The N atom of the nitrate ions occupies Wyckoff site *b* and is therefore disordered. The displacement parameters of the O atoms and the N—O separations are reasonable, however.

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990); software used to prepare material for publication: *CIFTAB* in *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1373). Services for accessing these data are described at the back of the journal.

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