# metal-organic compounds

## Tris{bis[N-(2-aminoethyl)-1,2-ethanediamine-$\kappa^3N$]nickel(II)} bis(tetrathioantimonate)

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Yellow crystals of [Ni(deta)$_2$]$_3$[SbS$_4$]$_2$ (deta is diethylenetriamine, C$_4$H$_{13}$N$_3$) were synthesized under solvothermal conditions by reacting elemental Ni, Sb and S in a solution of diethylenetriamine. The structure is composed of tetrahedral [SbS$_4$]$^{3-}$ anions in general positions and octahedral [Ni(deta)$_2$]$^{2+}$ cations located at centres of inversion. In the crystal structure, the anions and cations are stacked in the direction of the $a$ axis in a pseudo-hexagonal arrangement.

## Comment

During our systematic study of syntheses of transition metal thioantimonates in different amine solutions under solvothermal conditions, the novel title thioantimonate(V) [Ni(deta)$_2$]$_3$[SbS$_4$]$_2$, (I), was obtained as yellow plates.



(I)
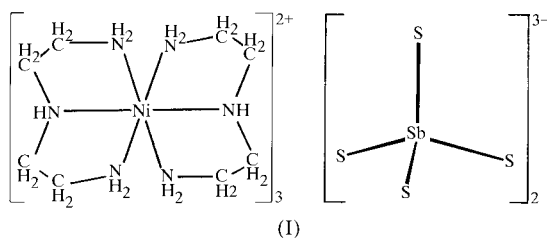
The structure is composed of [Ni(deta)$_2$]$^{2+}$ cations and [SbS$_4$]$^{3-}$ anions (Fig. 1). The Sb—S distances in the tetrahedral thioantimonate(V) anion vary between 2.3205 (8) and 2.3389 (11) Å, and are typical for Sb$^V$—S distances (Schur et al., 1998). The S—Sb—S angles, which vary between 107.49 (3) and 110.80 (4)°, deviate only slightly from ideal tetrahedral geometry and are in the normal range for [SbS$_4$]$^{3-}$ anions. In the crystal structure, three crystallographically independent Ni cations are located on special positions. They are in a distorted octahedral environment of six N atoms of two chelating deta molecules (Fig. 2). The Ni—N distances range between 2.097 (2) and 2.143 (2) Å, with N—Ni—N angles ranging between 81.01 (10) and 98.99 (10)°. In the crystal structure, the cations and anions form separate stacks parallel to the $a$

axis in a pseudo-hexagonal arrangement (Fig. 2). Each anion stack is surrounded by three cation stacks and each cation stack has two next-neighbour anion stacks. This arrangement leads to the formation of large channels running parallel to the $a$ axis, which coincides with the pseudo-sixfold axis. The three-dimensional interconnection of the cations and anions is achieved via intermolecular N—H⋯S hydrogen bonds. The N—H⋯S distances range from 2.57 to 2.87 Å and the



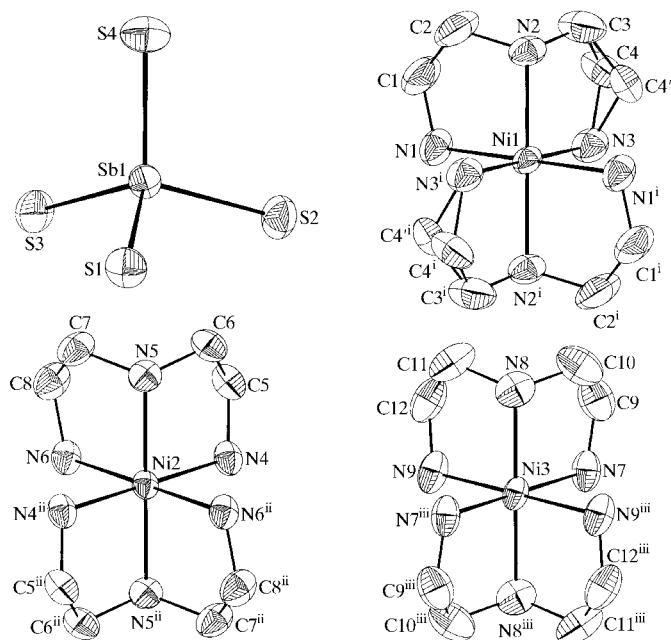**Figure 1**
View of the [SbS$_4$]$^{3-}$ anion and the [Ni(deta)$_2$]$^{2+}$ cations with atom labelling and displacement ellipsoids drawn at the 50% probability level [Symmetry codes: (i) $2 - x$, $2 - y$, $-z$; (ii) $1 - x$, $1 - y$, $-z$; (iii) $1 - x$, $-y$, $1 - z$.]
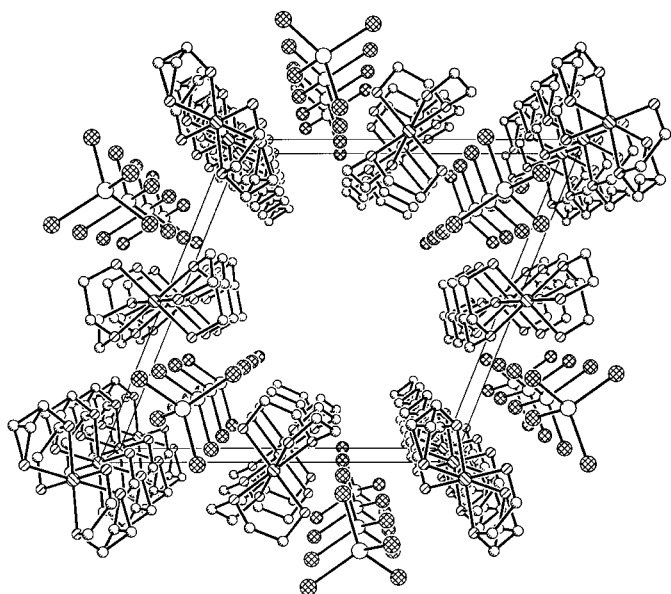


**Figure 2**
The crystal structure of the title compound viewed along the $a$ axis.

N—H···S angles range between 138 and 167°. All four S atoms of the thioantimonate(V) anion are involved in hydrogen bonding. The results of the structure refinement reveal that small amounts of solvent must be located in the channels, as evidenced by several peaks in the difference electron-density map. Because the center of symmetry is located in the middle of the channels and neither deta nor water molecules exhibit inversion symmetry, these molecules must be disordered for symmetry reasons. Therefore, it was impossible to decide whether only deta molecules are within the channels or whether additional water molecules are present. All attempts to find a satisfactory structural model failed. Therefore, the structure was refined using the *SQUEEZE* option (van der Sluis & Spek, 1990) in *PLATON* (Spek, 2000). Applying this procedure, the reliability factors significantly decrease. The thermal stability of the compound was investigated with differential thermal analysis (DTA) combined with thermogravimetry (TG). The decomposition starts at about 520 K and proceeds in at least two steps. The weight loss observed in the TG curve corresponds to the loss of the deta ligands. After decomposition, the binary sulfides $Sb_2S_3$ and NiS are formed, which was evidenced by X-ray powder diffractometry.

## Experimental

The title compound was prepared by hydrothermal treatment of Ni (58.693 mg, 1 mmol), Sb (487.04 mg, 4 mmol) and S (256.528 mg, 8 mmol) at 413 K, in the presence of 50% diethylenetriamine (10 ml) in a Teflon-lined steel autoclave for 8 d. The yield was about 55% based on Ni.

*Crystal data*

| | |
|---|---|
| $[Ni(C_4H_{13}N_3)_2]_3[SbS_4]_2$ | $Z = 1$ |
| $M_r = 1295.19$ | $D_x = 1.483$ Mg m$^{-3}$ |
| Triclinic, $P\bar{1}$ | Mo $K\alpha$ radiation |
| $a = 7.5259\ (15)$ Å | Cell parameters from 128 |
| $b = 14.250\ (3)$ Å | reflections |
| $c = 14.565\ (3)$ Å | $\theta = 10–30°$ |
| $\alpha = 111.79\ (3)°$ | $\mu = 2.199$ mm$^{-1}$ |
| $\beta = 90.72\ (3)°$ | $T = 293\ (2)$ K |
| $\gamma = 90.92\ (3)°$ | Block, yellow |
| $V = 1450.0\ (5)$ Å$^3$ | $0.30 \times 0.02 \times 0.02$ mm |

*Data collection*

| | |
|---|---|
| Stoe AED-II four-circle diffractometer | $R_{int} = 0.020$ |
| | $\theta_{max} = 30.02°$ |
| $\omega/\theta$ scans | $h = 0 \rightarrow 10$ |
| Absorption correction: $\psi$ scan (Stoe & Cie, 1997–1998) | $k = -20 \rightarrow 20$ |
| | $l = -20 \rightarrow 20$ |
| $T_{min} = 0.670$, $T_{max} = 0.777$ | 4 standard reflections |
| 8715 measured reflections | frequency: 120 min |
| 8127 independent reflections | intensity decay: negligible |
| 6737 reflections with $I > 2\sigma(I)$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0402P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.027$ | $+ 0.3047P]$ |
| $wR(F^2) = 0.071$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.047$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 8127 reflections | $\Delta\rho_{max} = 0.56$ e Å$^{-3}$ |
| 263 parameters | $\Delta\rho_{min} = -1.14$ e Å$^{-3}$ |
| H-atom parameters constrained | |

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

| | | | |
|---|---|---|---|
| Sb1—S1 | 2.3389 (11) | Ni2—N4 | 2.138 (2) |
| Sb1—S2 | 2.3206 (8) | Ni2—N5 | 2.107 (2) |
| Sb1—S3 | 2.3218 (11) | Ni2—N6 | 2.143 (2) |
| Sb1—S4 | 2.3205 (8) | Ni3—N7 | 2.129 (2) |
| Ni1—N1 | 2.133 (2) | Ni3—N8 | 2.097 (2) |
| Ni1—N2 | 2.116 (2) | Ni3—N9 | 2.142 (2) |
| Ni1—N3 | 2.130 (3) | | |
| | | | |
| S1—Sb1—S2 | 108.09 (4) | N4—Ni2—N5 | 83.20 (8) |
| S1—Sb1—S3 | 110.80 (4) | N4$^{ii}$—Ni2—N5 | 96.80 (8) |
| S1—Sb1—S4 | 110.24 (3) | N4—Ni2—N6 | 90.48 (8) |
| S2—Sb1—S3 | 107.49 (3) | N4—Ni2—N6$^{ii}$ | 89.52 (8) |
| S2—Sb1—S4 | 109.46 (3) | N5—Ni2—N6 | 82.59 (8) |
| S3—Sb1—S4 | 110.68 (3) | N5—Ni2—N6$^{ii}$ | 97.41 (8) |
| N1—Ni1—N2 | 82.42 (9) | N7—Ni3—N8 | 83.04 (10) |
| N1—Ni1—N2$^i$ | 97.58 (9) | N7—Ni3—N8$^{iii}$ | 96.96 (10) |
| N1—Ni1—N3 | 89.94 (10) | N7—Ni3—N9 | 90.52 (9) |
| N1—Ni1—N3$^i$ | 90.06 (10) | N7$^{iii}$—Ni3—N9 | 89.48 (9) |
| N2—Ni1—N3 | 81.01 (10) | N8$^{iii}$—Ni3—N9 | 97.45 (10) |
| N2$^i$—Ni1—N3 | 98.99 (10) | N8—Ni3—N9 | 82.55 (10) |

Symmetry codes: (i) $2 - x, 2 - y, -z$; (ii) $1 - x, 1 - y, -z$; (iii) $1 - x, -y, 1 - z$.

The H atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters [$U_{iso}$(N—H, C—H) = $1.2U_{eq}$(parent atom)] using a riding model with the parameters C—H = 0.97 Å and N—H = 0.90 Å. The C4 atom of one deta ligand is disordered over two positions (C4 and C4′) and was refined using a split model with anisotropic displacement parameters and varying site-occupation factors. The volume which is accessible for potential solvent molecules was calculated to be 290.4 Å$^3$ and the total electron count per cell was calculated to be 70. Note that the calculated density, the $F(000)$ value, the molecular weight and the formula are given without taking into account the results obtained with the *SQUEEZE* option (van der Sluis & Spek, 1990) in *PLATON* (Spek, 2000).

Data collection: *DIF*4 (Stoe & Cie, 1992); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Crystal Impact, 1999); software used to prepare material for publication: *CIFTAB* in *SHELXL*97.

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