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The new thioantimonate(V) $(C_3H_{10}N)[NiSbS_4(C_6H_{18}N_4)]$

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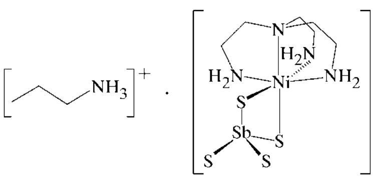
Turquoise crystals of the title salt, propylammonium di-μ-thio-1:2κ^4*S*-dithio-2κ^2*S*-tris(2-aminoethyl)amine-1κ^4*N*-antimony(V)nickel(II), $(C_3H_{10}N)[NiSbS_4(C_6H_{18}N_4)]$ or [PAH]-[Ni(tren)SbS$_4$] [where tren is tris(2-aminoethyl)amine and PA is propylamine], were synthesized under solvothermal conditions by reacting [Ni(tren)$_2$]Cl$_2$, Sb and S in a solution of PA. The Ni$^{\rm II}$ ion is octahedrally surrounded by four N atoms of the tetradentate tren molecule and by two S atoms of the tetrahedral [Sb$^{\rm V}$S$_4$]$^{3-}$ anion, thus forming the anionic [Ni(tren)SbS$_4$]$^-$ part of the compound. Charge balance is achieved through the PAH$^+$ cation. An extended intermolecular hydrogen-bonding network is observed between the anion and the cation.

Comment

Thioantimonates(III) exhibit a rich structural diversity, due to the very flexible coordination behaviour of the Sb$^{\rm III}$ ion, with coordination numbers ranging from 3 to 6 (Sheldrick & Wachhold, 1997; Wang & Liebau, 1996). Thioantimonate(III) anions occur as isolated units, chains, layers or three-dimensional frameworks (Sheldrick & Wachhold, 1998). On the other hand, thioantimonates(V) are often isolated (Graf & Schäfer, 1976; Schur *et al.*, 1998). Compounds in which the Sb$^{\rm V}$S$_4$ tetrahedron is interconnected to transition metal cations are A_2AuSbS$_4$ (A is Rb or Cs; Hanko & Kanatzidis, 1998), MAg$_2$SbS$_4$ and M_2AgSbS$_4$ (M is K or Rb; Schimek *et al.*, 1996), and $[(H_2O)_9Mo_3S_4SbS_4Mo_3(H_2O)_9](CH_3C_6H_4SO_3)_8\cdot 24H_2O$ (Sakane *et al.*, 1998).

A way of connecting Sb$^{\rm V}$S$_4$ tetrahedra to transition metal cations, based on our recent results obtained with thioantimonates(III), has been established. Using the tetradentate ligand tren [tris(2-aminoethyl)amine], together with Co and Ni, we have prepared neutral compounds such as [Co(tren)]Sb$_2$S$_5$ and [Co(tren)]Sb$_4$S$_8$ (Stähler & Bensch, 2001*a*), the chain-like [Sb$_2$S$_4$]$^{2-}$ anion in [Ni(tren)]Sb$_2$S$_4$ (Stähler & Bensch, 2001*a*), and a layered compound, [Co(tren)]Sb$_2$S$_4$ (Stähler & Bensch, 2001*b*). In these compounds, the tetradentate ligand leaves one or two sites free at the transition metal cation, and these sites are used to form bonds to the S atoms of the thioantimonate(III) anions. Applying the very successful method presented for thioantimonates(III), we synthesized the new and unusual title thioantimonate(V) compound, [PAH][Ni(tren)SbS$_4$], (I), with an [Sb$^{\rm V}$S$_4$]$^{3-}$ anion acting as a bidentate ligand.



(I)

The structure of (I) is composed of PAH$^+$ cations and [Ni(tren)SbS$_4$]$^-$ anions (Fig. 1). The Ni^{2+} ion is surrounded by four N atoms of the tren ligand and by two S atoms of the [Sb$^{\rm V}$S$_4$]$^{3-}$ anion, forming a distorted octahedron (NiN$_4$S$_2$). The Ni—N distances range from 2.0876 (19) to 2.116 (2) Å, with N—Ni—N angles of between 82.47 (9) and 162.13 (9)° (Table 1). The two Ni—S distances of 2.4359 (12) and 2.6936 (9) Å are significantly different. It can be assumed that geometrical reasons are responsible for the long Ni—S2 bond. The S1—Ni—N1 [176.65 (5)°] and S2—Ni—N2 [178.31 (6)°] angles deviate slightly from the ideal value of 180°. The Sb$^{\rm V}$S$_4$ tetrahedron is only moderately distorted, with Sb—S distances and S—Sb—S angles in the ranges 2.3071 (10)–2.3467 (8) Å and 98.54 (4)–115.66 (3)°, respectively (Table 1). These values are in the normal range for [Sb$^{\rm V}$S$_4$]$^{3-}$ anions (Mereiter *et al.*, 1979; Hanko & Kanatzidis, 1998; Sakane *et al.*, 1998).

The anionic part of the structure of (I) may be viewed as being composed of an [NiN$_4$]$^{2+}$ cation sharing two S atoms with the [Sb$^{\rm V}$S$_4$]$^{3-}$ anion, thus yielding the final [Ni(tren)SbS$_4$]$^-$ anion. These anions are stacked along the *a* axis (Fig. 2) and the PAH$^+$ cations are located near the [Sb$^{\rm V}$S$_4$]$^{3-}$ anion. The C—N bond distance in PAH$^+$ is in the normal range for a primary amine [C7—N5 = 1.465 (3) Å].

In (I), a hydrogen-bond network (Table 2) is observed which may contribute significantly to the stability of the compound. There are three short intermolecular contacts, involving atoms S1 (H2N2$\cdots$S1$^{\rm ii}$ and H1N4$\cdots$S1$^{\rm ii}$; see Table 2 for symmetry codes) and S4 (H1N2$\cdots$S4$^{\rm i}$) of the [Sb$^{\rm V}$S$_4$]$^{3-}$ tetrahedron and the H atoms of the tren ligand, with H$\cdots$S

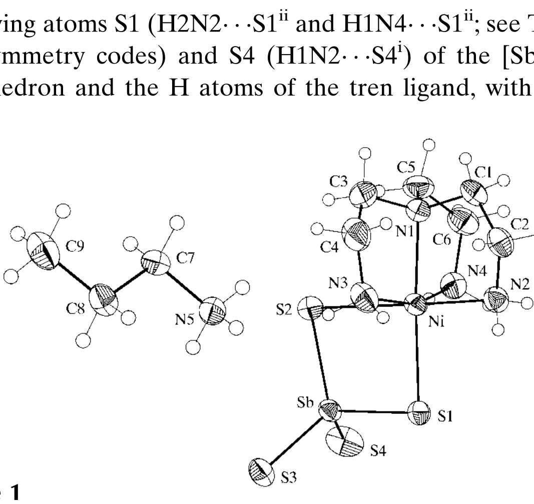


Figure 1
The PAH$^+$ cation and [Ni(tren)SbS$_4$]$^-$ anion in (I), with the atom-labelling scheme. Displacement ellipsoids are at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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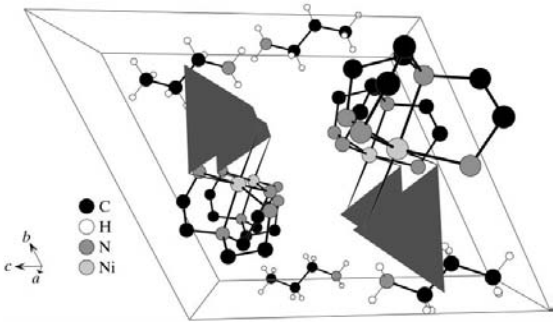

Figure 2
The arrangement of the cations and anions in (I). The H atoms of the tren ligands have been omitted for clarity.

distances in the range 2.54–2.62 Å. Four H⋯S contacts are observed between the PAH^+ cation and atoms S1, S3, $S3^{iii}$ and $S4^{i}$, with H⋯S distances in the range 2.46–2.75 Å; the corresponding angles are in the range 120–173°.

Experimental

Compound (I) was obtained in nearly 30% yield by the reaction of $[Ni(tren)_2]Cl_2$ (Ellermeier *et al.*, 2002) (0.211 g, 0.5 mmol), Sb (0.121 g, 1 mmol) and S (0.096 g, 3 mmol) in 5 ml of 99% PA (Merck Chemical). The mixture was heated in a Teflon-lined steel autoclave with an inner volume of 30 ml for 6 d at 413 K, and then cooled to room temperature over a period of 3 h. After washing with water and drying under vacuum, turquoise crystals of (I) were obtained. The compound is stable in both air and water.

Crystal data

$(C_3H_{10}N)[NiSbS_4(C_6H_{18}N_4)]$
$M_r = 515.06$
Triclinic, $P\bar{1}$
$a = 7.5707\ (15)$ Å
$b = 11.303\ (2)$ Å
$c = 12.605\ (3)$ Å
$\alpha = 63.98\ (3)^\circ$
$\beta = 84.49\ (3)^\circ$
$\gamma = 82.26\ (3)^\circ$
$V = 959.7\ (3)$ Å^3
$Z = 2$
$D_x = 1.782$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 20$–29°
$\mu = 2.82$ mm^{-1}
$T = 293\ (2)$ K
Polyhedron, turquoise
0.5 × 0.2 × 0.1 mm

Data collection

Philips PW1100 four-circle diffractometer
ω/θ scans
Absorption correction: ψ scan [*X-SHAPE* (Stoe & Cie, 1998) and *X-RED* (Stoe & Cie, 1998)]
$T_{min} = 0.513$, $T_{max} = 0.720$
4967 measured reflections
4625 independent reflections
3940 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 28^\circ$
$h = 0 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.050$
$S = 1.02$
4625 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0217P)^2 + 0.3866P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

All H atoms were positioned with idealized geometry (C—H = 0.97 Å and N—H = 0.89–0.90 Å) and refined with fixed isotropic displacement parameters using a riding model.

Data collection: *DIF*4 (Stoe & Cie, 1992); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992); structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999).

Table 1
Selected geometric parameters (Å, °).

Sb—S1	2.3467 (8)	S2—Ni	2.6936 (9)
Sb—S2	2.3333 (12)	Ni—N1	2.116 (2)
Sb—S3	2.3150 (8)	Ni—N2	2.0876 (19)
Sb—S4	2.3071 (10)	Ni—N3	2.109 (2)
S1—Ni	2.4359 (12)	Ni—N4	2.110 (2)
S1—Sb—S2	98.54 (4)	N2—Ni—N4	95.54 (8)
S1—Sb—S3	107.58 (3)	N3—Ni—N4	162.13 (9)
S1—Sb—S4	111.90 (3)	N1—Ni—S1	176.65 (5)
S2—Sb—S3	115.66 (3)	N2—Ni—S1	93.94 (6)
S2—Sb—S4	112.23 (4)	N3—Ni—S1	99.24 (7)
S3—Sb—S4	110.31 (4)	N4—Ni—S1	96.23 (6)
Sb—S1—Ni	89.83 (4)	N1—Ni—S2	95.67 (6)
Sb—S2—Ni	84.10 (4)	N2—Ni—S2	178.31 (6)
N1—Ni—N2	83.09 (8)	N3—Ni—S2	86.41 (7)
N1—Ni—N3	82.47 (9)	N4—Ni—S2	85.43 (6)
N1—Ni—N4	82.55 (8)	S1—Ni—S2	87.33 (4)
N2—Ni—N3	92.28 (8)		

Table 2
Hydrogen-bonding and short-contact geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N2—H1N2⋯$S4^{i}$	0.90	2.56	3.445 (2)	170
N2—H2N2⋯$S1^{ii}$	0.90	2.54	3.431 (2)	172
N4—H1N4⋯$S1^{ii}$	0.90	2.62	3.428 (2)	150
N5—H1N5⋯$S3^{iii}$	0.89	2.50	3.347 (3)	159
N5—H2N5⋯$S4^{i}$	0.89	2.46	3.348 (3)	173
N5—H3N5⋯S3	0.89	2.70	3.515 (3)	152
N5—H3N5⋯S1	0.89	2.75	3.284 (3)	120

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1121). Services for accessing these data are described at the back of the journal.

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