$[Ni(C_4H_{13}N_3)_2]_3(Sb_3S_6)_2$: The First Structure Containing Isolated Heterocyclic $[Sb_3S_6]^{3-}$ Anions

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The novel thioantimonate(III) compound $[Ni(dien)_2]_3(Sb_3S_6)_2$, which was synthesised under solvothermal conditions, contains isolated $[Sb_3S_6]^{3-}$ anions. In the X-ray crystal structure, isolated cyclic $[Sb_3S_6]^{3-}$ anions occupy a boat-like conformation and two different isomeric $[Ni(dien)_2]^{2+}$ cations are arranged in separate stacks.

Introduction

In the structures of thioantimonates(III), the primary building units (PBU's) SbS_3, SbS_4 and the less common SbS_5 [1] or SbS_6 [1,2] PBU's are interconnected to form secondary building units (SBU's) such as the heterorings Sb_xS_x, with x ranging from 2 to 32. Rings with small values of x are very common in thioantimonate(III) structures whereas the larger rings are quite rare.[3,4] Very little is known about the processes occurring in the heterogeneous reaction mixtures, which result in the crystallisation of distinct thioantimonates(III). A few years ago, we isolated and characterised several antimony polysulfides such as $[Ph_4P]_2[Sb_2S_{15}]$,[5] $[Ph_4P]_3Sb_3S_{25}$ [6] and $[Ph_4P]_2[Sb_2S_{17}]$[7] which may play important roles as precursors in the syntheses. More recently, we synthesised and characterised $[Ni(dien)_2]_2Sb_4S_8$ [8] as well as $[Mn(C_3H_{10}N_2)_3]_2(Sb_4S_8)\cdot 2H_2O$[9] with the cyclic Sb_4S_4 heteroring as the main structural motif. The successful isolation of these compounds suggests that even these small heterocycles exist in solution. Using an upper limit of 3 Å for Sb−S bonds, the Sb_2S_2 ring can be found in $Ca_2Sb_2S_5$.[10] However, the Sb atoms of this ring have two additional S atoms at a distance less than 3.2 Å, in contrast to the Sb atoms of the Sb_4S_4 ring where no Sb···S contacts were observed below 4 Å. The small Sb_xS_x heteroring with $x = 3$ is commonly observed in extended thioantimonate(III) structures and two different conformations have been identified. In such structures, the Sb_3S_3 rings mostly occupy a chair-like conformation.[4,11−13] A special case of this chair-like conformation is an arrangement in which one endo-cyclic terminal sulfur atom is rotated by nearly 180° thus forming long bonds to the two other antimony atoms.[14,15] This arrangement has been classified as an Sb_3S_4 "semicube". We note that some authors also denote an Sb_3S_6 unit as a "semicube".[12] The boat-like conformation has also been identified in several thioantimonates.[16−18] During our continuing efforts in this area, we obtained the new compound $[Ni(dien)_2]_3(Sb_3S_6)_2$ which contains an isolated Sb_3S_3 heteroring as the main structural feature. This is the first compound containing this isolated Sb_3S_3 ring and it is only the third thioantimonate(III) compound reported with a small isolated thioantimonate(III) heteroring.

Results and Discussion

Crystal Structure

$[Ni(dien)_2]_3(Sb_3S_6)_2$ (dien = diethylenetriamine) crystallises in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. In the crystal structure, there are two crystallographically independent $[Ni(dien)_2]^{2+}$ cations and one isolated heterocyclic $[Sb_3S_6]^{3-}$ anion (Figures 1−3). The $[Sb_3S_6]^{3-}$ anion and one of the two crystallographically independent $[Ni(dien)_2]^{2+}$ cations are located in general position whereas the second cation is located on a centre of inversion.

The Sb_3S_3 ring is formed by three vertex-linked SbS_3 trigonal pyramids (Figure 1). Each Sb atom of the Sb_3S_3 heteroring has a bond to a terminal S atom thus forming the final anion. The Sb−S distances in the Sb_3S_3 ring are similar to those reported for extended thioanti-

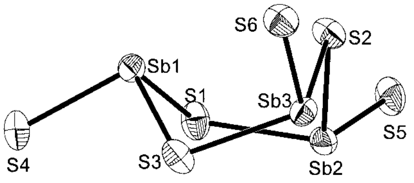

Figure 1. The $[Sb_3S_6]^{3-}$ anion in $[Ni(dien)_2]_3(Sb_3S_6)_2$ with labelling and displacement ellipsoids drawn at the 50% probability level

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monates(III).[19−22] The Sb(1) and Sb(2) atoms each have one long intramolecular contact to an S atom [Sb(1)−S(2) 3.606 Å, Sb(2)−S(3) 3.891 Å]. No intermolecular Sb−S contacts shorter than 4.8 Å are present Table 1).

Table 1. Selected bond lengths (Å) and angles (°) for the $[Sb_3S_6]^{3-}$ anion in $[Ni(dien)_2]_3(Sb_3S_6)_2$

Sb(1)−S(4)	2.3310(9)	Sb(1)−S(3)	2.4756(10)
Sb(1)−S(1)	2.4838(9)	Sb(2)−S(5)	2.3333(9)
Sb(2)−S(2)	2.4617(9)	Sb(2)−S(1)	2.4623(9)
Sb(3)−S(6)	2.3216(9)	Sb(3)−S(3)	2.4702(9)
Sb(3)−S(2)	2.4774(9)		
S(4)−Sb(1)−S(3)	93.47(3)	S(4)−Sb(1)−S(1)	98.40(3)
S(3)−Sb(1)−S(1)	99.56(3)	S(5)−Sb(2)−S(2)	102.22(3)
S(5)−Sb(2)−S(1)	99.00(3)	S(2)−Sb(2)−S(1)	98.00(3)
S(6)−Sb(3)−S(3)	104.70(3)	S(6)−Sb(3)−S(2)	101.46(3)
S(3)−Sb(3)−S(2)	97.68(3)	Sb(2)−S(1)−Sb(1)	102.03(3)
Sb(2)−S(2)−Sb(3)	93.44(3)	Sb(3)−S(3)−Sb(1)	106.65(3)

The Ni^{2+} cations are in a distorted octahedral environment formed by six N atoms of two dien ligands with one unique $[Ni(dien)_2]^{2+}$ cation in the *u-fac* conformation [Ni(1)] and the other in the *s-fac* conformation (Figure 2). The Ni−N distances range between 2.100(3) and 2.145(3) Å, with N−Ni−N angles varying from 81.04(2) to 180.00(2)°. Angles and distances are similar to the corresponding literature values for $[Ni(dien)_2]^{2+}$ complexes (Table 2).[8,19,20]

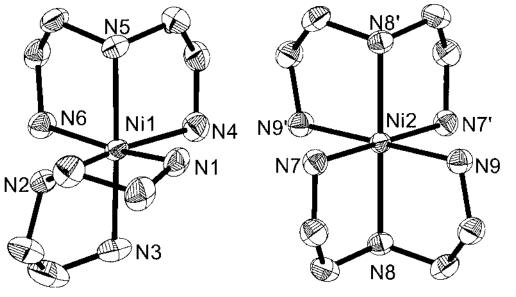

Figure 2. Coordination of the Ni cations in $[Ni(dien)_2]_3(Sb_3S_6)_2$ with labelling and displacement ellipsoids drawn at the 50% probability level (hydrogen atoms are omitted for clarity)

Cations and anions are packed in such a way that both form individual stacks parallel to the *a* axis (Figure 3). Four cations and two anions are arranged around a channel which is directed along the *a* axis. Disordered solvent molecules are located in this channel (see Exp. Sect.). A similar arrangement of cations and anions is also found in $[Ni(dien)_2]_3[SbS_4]_2$[20] and $[Ni(dien)_2]_2Sb_4S_8$.[8]

The three-dimensional arrangement of cations and anions is caused by N−H···S contacts. Every $[Sb_3S_6]^{3-}$ anion has fifteen such contacts with H···S distances between 2.440 and 2.903 Å and N−H···S angles ranging from 138.2 to 166.7°. The terminal S atoms have significantly more S···H contacts than the μ-S atoms (ratio: 2:1). The N−H atoms of the $[Ni(1)(dien)_2]^{2+}$ cation are involved in 10 and those of the second $[Ni(2)(dien)_2]^{2+}$ cation, in 5 H···S contacts.

Table 2. Selected bond lengths (Å) and angles (°) for the $[Ni(dien)_2]^{2+}$ cations in $[Ni(dien)_2]_3(Sb_3S_6)_2$

Ni(1)−N(4)	2.114(3)	Ni(1)−N(3)	2.114(3)
Ni(1)−N(1)	2.117(3)	Ni(1)−N(2)	2.127(3)
Ni(1)−N(5)	2.134(3)	Ni(1)−N(6)	2.145(3)
N(1)−C(1)	1.467(6)	C(1)−C(2)	1.522(6)
N(4)−Ni(1)−N(3)	94.70(14)	N(4)−Ni(1)−N(1)	93.88(13)
N(3)−Ni(1)−N(1)	95.88(13)	N(4)−Ni(1)−N(2)	173.65(12)
N(3)−Ni(1)−N(2)	81.48(13)	N(1)−Ni(1)−N(2)	81.52(12)
N(4)−Ni(1)−N(5)	82.52(12)	N(3)−Ni(1)−N(5)	172.95(12)
N(1)−Ni(1)−N(5)	90.79(11)	N(2)−Ni(1)−N(5)	101.85(11)
N(4)−Ni(1)−N(6)	94.99(13)	N(3)−Ni(1)−N(6)	92.79(12)
N(1)−Ni(1)−N(6)	167.04(12)	N(2)−Ni(1)−N(6)	90.28(12)
N(5)−Ni(1)−N(6)	81.04(11)		
Ni(2)−N(8)	2.100(3)	Ni(2)−N(9)	2.121(3)
Ni(2)−N(7)	2.130(3)		
N(8)−Ni(2)−N(9)	82.9(1)	N(8)−Ni(2)−N(9A)	97.2(1)
N(8A)−Ni(2)−N(7)	97.1(1)	N(8)−Ni(2)−N(7)	82.9(1)
N(9)−Ni(2)−N(7)	90.1(1)	N(9A)−Ni(2)−N(7)	89.9(1)

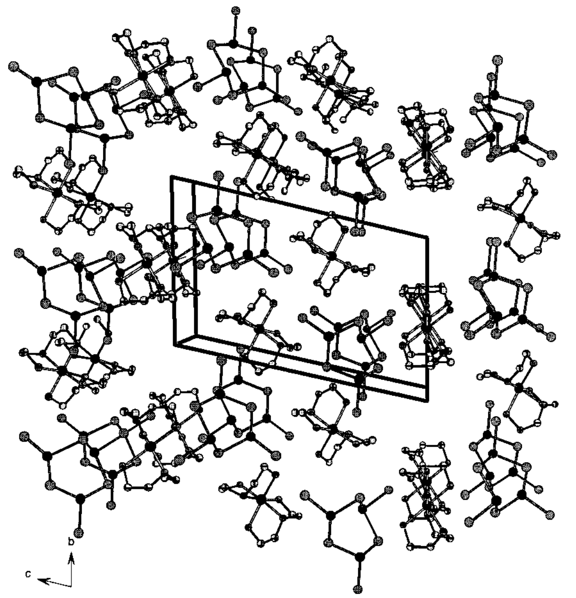

Figure 3. Crystal structure of $[Ni(dien)_2]_3(Sb_3S_6)_2$ viewed along the *a* axis (hydrogen atoms are omitted for clarity)

As mentioned above, the Sb_3S_3 unit usually occurs in a chair- or boat-like conformation, as in $[C_4H_{12}N_2]_{0.5}$-$[CuSb_6S_{10}]$[18] or $[(CH_3NH_2)_{1.0}K_{2.97}][Sb_{12}S_{20}]\cdot 1.34H_2O$.[22] The latter is a rare example of the coexistence of two different conformations in one crystal. Interestingly, the Sb_3S_3 unit in the title compound also has a boat-like conformation. The geometry of this anion was optimised using GAUSSIAN98 indicating that the boat-like conformation is about 2 kcal/mol more stable than the chair-like conformation.

Thermal Investigations

Thermal stability of the complex was investigated using simultaneous differential thermal analysis and thermogravimetry (DTA-TG). Heating single crystals of the title compound under helium in a thermobalance lead to decomposition in four steps with a total mass loss of 37.3% with all steps accompanied by endothermic peaks in the DTA curve ($T1_{peak}$ = 246 °C, Δm = 4.1%; $T2_{peak}$ = 260 °C, Δm = 24.4%; $T3_{peak}$ = 277 °C, Δm = 6.0%; and $T4_{peak}$ = 331 °C, Δm = 2.8%) (Figure 4).

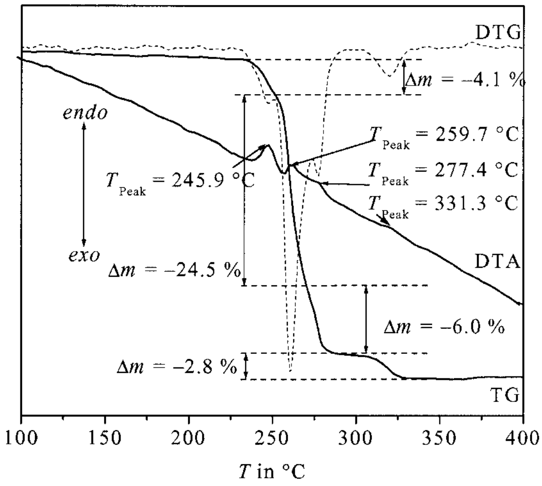

Figure 4. DTA, TG and DTG curves for $[Ni(dien)_2]_3(Sb_3S_6)_2$

Taking only the dien ligands into account, the expected mass loss is 31.4%, which is about 5.9% lower than the experimentally obtained value. This discrepancy may be due, in part, to the emission of H_2S and of solvent molecules (CH_3OH) which are located in the channels of the structure. Elemental analysis and mass spectroscopic investigations are in agreement with this. The elemental analysis gave a C,H and N content of 33.4% (C 16.2, H 4.4, N 12.8%), which is 2% larger than the theoretical content for the dien ligands alone. Mass spectra recorded simultaneously during decomposition showed a very intense signal for H_2S in the last step. Unfortunately, the content of CH_3OH could not be determined using mass spectrometry because of a substantial overlap of the different thermal processes and because of the experimental set-up of our instrument. The grey residue remaining after the thermal decomposition contained NiSbS (Ullmanit) and Sb_2S_3, both of which are frequently found after the thermal decomposition of thioantimonates containing nickel.[4,8,19−21]

Conclusion

The synthesis of thioantimonates was performed in basic solutions under solvothermal conditions. Little is known about the processes occurring in the heterogeneous reaction mixtures and which precursors determine the final structures that are formed under particular conditions. As mentioned above, in the extended structures of thioantimonates(III) many different secondary building units may be identified, which are formed by the condensation of the primary SbS_x (x = 3−6) units. After the successful isolation and characterisation of different antimony polysulfides and the $[Sb_4S_8]^{4-}$ anion containing the Sb_4S_4 heteroring, we were able to obtain the smallest known isolated thioantimonate anion $[Sb_3S_6]^{3-}$ containing the Sb_3S_3 ring as the main structural motif. However, the crystallisation of $[Sb_4S_8]^{4-}$ and $[Sb_3S_6]^{3-}$ does not necessarily mean that these species exist under solvothermal conditions. Further studies are necessary for a better understanding of the factors influencing product formation.

Experimental Section

Synthesis

$[Ni(dien)_2]_3(Sb_3S_6)_2$ (1): $[Ni(dien)_2]_3(Sb_3S_6)_2$ was synthesised from Sb (0.1217 g; 1 mmol), S (0.0962 g, 3 mmol), and $Ni(CH_3COO)_2{\cdot}4H_2O$ (0.2487 g; 1 mmol) dissolved in a mixture of dien (1 mL) and methanol (1 mL). The mixture was heated at 140 °C for 4 days in a Teflon^R-lined steel autoclave (volume ca. 20 mL) and was subsequently cooled to room temperature over a 3 h period. The brown crystalline product was filtered off, washed with water and acetone, cleaned in an ultrasonic bath and stored under vacuum. The compound is stable in air, water and acetone. The yield was approximately 30% based on Ni. $[Ni(dien)_2]Cl_2$ and $[Ni(dien)_2]_3(SbS_4)_2$ were identified as by-products.

X-ray Crystallography: The X-ray single-crystal data for **1** were collected at 293 K using a STOE Imaging Plate Diffraction System

Table 3. Crystal data and selected results for the structure refinement of $[Ni(dien)_2]_3(Sb_3S_6)_2$

Empirical formula	$C_{24}H_{78}N_{18}Ni_3Sb_6S_{12}$
Crystal colour	brown
Crystal habit	irregular
Molecular mass [g/mol]	1910.39
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	7.1208(5)
b (Å)	12.3254(9)
c (Å)	19.165(2)
α (°)	76.169(8)
β (°)	84.462(9)
γ (°)	85.892(8)
V (Å^3)	1623.6(2)
Z	2
T [K]	293
λ(Mo-K_α) (Å)	0.71073
$d_{calcd.}$ [Mg·cm^{-3}]	1.945
μ(Mo-K_α) [mm^{-1}]	3.73
F(000)	930
2Θ range of data collection (°)	$6° \leq 2\Theta \leq 60°$
Index range	$-10 \leq h \leq 10$ $-15 \leq k \leq 17$ $-27 \leq l \leq 27$
Reflections collected	19706
Independent reflections	9342
Reflections with $F_o > 4\sigma(F_o)$	8114
$wR2$ for all reflections[a]	0.1014
$R1$ for reflections with $F_o > 4\sigma(F_o)$[b]	0.0354
Goodness of fit	1.028
Largest diff. peak/hole [e·Å^{-3}]	0.99/−1.61

[a] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

(IPDS). The intensities were corrected for Lorentz, polarisation and absorption effects. Structure solution was performed using SHELXS-97.[23] Refinement was done against F^2 by using the software SHELXL-97.[24] The non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were positioned with idealised geometry and refined with isotropic displacement parameters using the riding model. The structure contains additional disordered solvent molecules in the channels for which no appropriate structure model could be found. Therefore, the data were treated with the SQUEEZE option for disordered solvent in PLATON.[25] In the first step, this program calculates the space which can be occupied by disordered solvent molecules starting from the refined structure model. In the next step the sum of electrons in this space is calculated and the measured data file is corrected in a way that these electrons are not considered. This calculation gives a volume of 182.2 Å^3/cell which can be used by disordered solvent. Selected crystal data and details of the structure determination are listed in Table 3.

CCDC-21630 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

DTA-TG-MS Investigations: DTA-TG-MS measurements were performed using a Netzsch STA-409. The sample (mass: 11.98 mg) was heated in a dynamic He atmosphere (flow rate 75 ml·min^{-1}) in an Al_2O_3 crucible with a heating rate of 4 K/min to 400 °C).

Density Functional Calculations: Spin-restricted DFT calculations using Becke's three parameter hybrid function with the correlation function of Lee, Yang and Parr (B3LYP)[26−28] were performed for the singlet ground state of $[Sb_3S_6]^{3-}$. The LanL2DZ basis set was used for the calculation. This applies Dunning/Huzinaga full double zeta (D95) basis functions[29] to the first row and Los Alamos effective core potentials plus DZ functions on all other atoms.[30,31] Convergence was reached when the relative change in the density matrix between subsequent iterations was less than $1 \cdot 10^{-8}$. All procedures were used as they are implemented in the GAUSSIAN 98 package.[32]

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