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Solvothermal synthesis of $[Ni(C_4H_{13}N_3)_2]_2Sb_4S_8$: the first compound with a cyclic $[Sb_4S_8]^{4-}$ anion

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Under mild hydrothermal conditions the novel thioantimonate(III) $[Ni(C_4H_{13}N_3)_2]_2Sb_4S_8$ was synthesised using elemental nickel, antimony and sulfur; the structure is composed of cyclic isolated $[Sb_4S_8]^{4-}$ anions and $[Ni(C_4H_{13}N_3)_2]^{2+}$ cations.

Open framework structures based on interconnected chalcogenometallates are of great interest as possible 'zeolite' similar phases, for which highly interesting properties could be expected. Condensation of maingroup-thioanions in the presence of large organic cations[1–3] acting as structure directing agents was achieved under solvothermal conditions. The incorporation of transition metals (tm) into the thiometallate network should lead to new connections and to changed physical properties. Our main goals are the investigation of the synthetic conditions necessary to connect tmS_x fragments with main group thiometallates and to study the influence of the 'template' on the dimensionality of the products. Thioantimonates(III) exhibit a variable coordination behaviour caused by the stereochemically active lone pair.[4–6] However, until now large isolated Sb_xS_y anions were observed in only very few compounds. Recently, we and other groups reported the first examples of transition metal containing thioantimonates(III).[7,8] During our continuing work in this field the new thioantimonate(III), $[Ni(DETA)_2]_2Sb_4S_8$† [DETA = diethylenetriamine], containing the new and unusual isolated ring anion $[Sb_4S_8]^{4-}$ was obtained. The present contribution reports the synthesis and crystal structure of this new compound.

In the crystal structure of $[Ni(DETA)_2]_2Sb_4S_8$‡ two crystallographically independent $[Sb_4S_8]^{4-}$ ring anions [Fig. 1(a) and (b)] and two crystallographically independent $[Ni(DETA)_2]^{2+}$ cations are found. Four pyramidal SbS_3 units sharing common corners build a Sb_4S_4 hetero ring. Each Sb atom is bounded to a terminal S atom thus forming the final $[Sb_4S_8]^{4-}$ anion. The cyclo-octathiotetraantimonate anion belongs to the class of the medium-sized rings that preferably adopt the bent flexible chair conformation. Charge balancing is achieved by the two isolated $[Ni(DETA)_2]^{2+}$ cations.

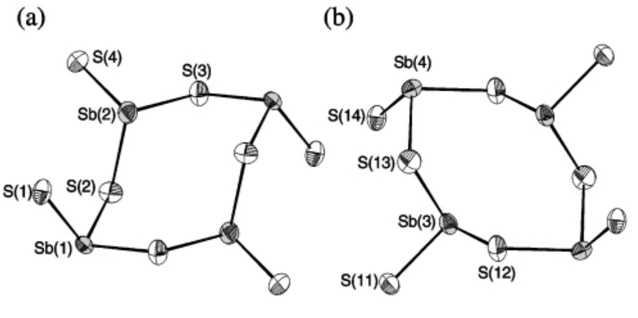

Fig. 1 (a) and (b): The two $[Sb_4S_8]^{4-}$ anions in $[Ni(DETA)_2]_2Sb_4S_8$ with labelling and displacement ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): Sb(1)–S(1) 2.337(2), Sb(1)–S(2) 2.429(2), Sb(1)–S(3) 2.453(2), Sb(2)–S(4) 2.315(3), Sb(2)–S(3) 2.471(2), Sb(3)–S(11) 2.328(2), Sb(3)–S(13) 2.492(2), Sb(3)–S(12) 2.497(2), Sb(4)–S(14) 2.326(2), Sb(4)–S(13) 2.426(2); S(1)–Sb(1)–S(2) 104.32(7), S(2)–Sb(1)–S(3) 101.62(7), Sb(1)–S(3)–Sb(2) 110.88(7), S(11)–Sb(2)–S(12) 101.48(7), S(14)–Sb(4)–S(13) 100.38(8), Sb(4)–S(13)–Sb(3) 102.60(8).

The Sb–S distances within the Sb_4S_4 rings are between 2.426(2) and 2.497(2) Å and the S–Sb–S angles vary from 87.92(7) to 107.53(8)°, both being in good agreement with data found in the literature.[9] As expected, the terminal Sb-S distances [Sb(1)–S(1), Sb(2)–S(4), Sb(3)–S(11) and Sb(4)–S(14)] are shorter ranging from 2.315(3) to 2.337(2) Å. They are significantly shorter than the Sb–μ_2-S links [Sb(1)–S(2), Sb(2)–S(2), Sb(2)–S(3), Sb(3)–S(12), Sb(3)–S(13), Sb(4)–S(13)], which are often observed in literature.[10] The pertinent angles vary between 93.90(9) and 104.32(7)°. If the lone pair of Sb(III) is considered, the coordination of the SbS_3 pyramids can be viewed as distorted ψ-SbS_3 tetrahedra.[11] The two independent $[Sb_4S_8]^{4-}$ anions have a similar geometry. The Sb_4S_8 rings are stacked onto each other forming rods parallel to the *a*-axis (Fig. 2). We note that the shortest intramolecular Sb–S contacts are above 3.9 Å and no intermolecular Sb–S separations shorter than 4 Å are observed.

The Ni^{2+} cations are in a distorted octahedral environment of six nitrogen atoms of two DETA ligands. The Ni–N distances vary between 2.080(8) and 2.193(6) Å and are in the normal range.[12] The angles range from 78.0(3) to 174.8(3)°. In one cation the DETA ligands take up an u-facial (Ni1) and in the second a *mer* geometry.[20]

The three-dimensional arrangement of cations and anions (Fig. 2) is achieved by N–H···S close contacts. Every anion shows seven such contacts with distances between 2.513 and 2.837 Å and angles N–H···S ranging from 144.15 to 175.53°. The H atoms of $[Ni(1)(DETA)_2]^{2+}$ are involved in eight and those of the second complex in six S···H contacts. It is well known that S···H hydrogen bond interactions are weak and a definite decision as to whether genuine hydrogen bonding occurs cannot be drawn alone on the basis of crystal structure determination. Nevertheless, the distinct differences of intermolecular cation–anion interactions may be responsible for the above mentioned differences in the conformations of the anions and cations. Raman spectra of pure DETA and of the title

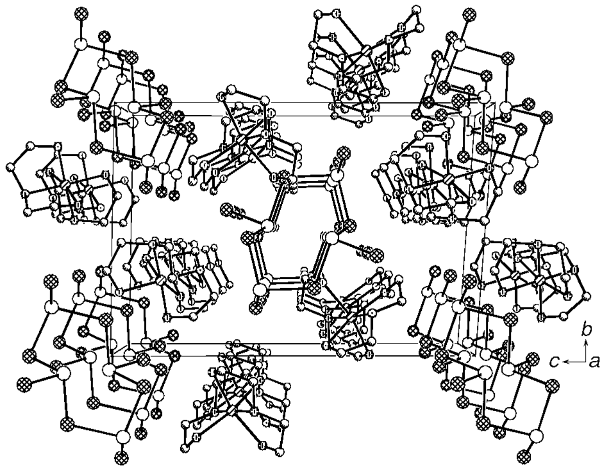

Fig. 2 Crystal structure of $[Ni(DETA)_2]_2Sb_4S_8$ with view along the *a*-axis (hydrogen atoms omitted for clarity).

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compound were recorded to monitor the differences in the νNH_2 and δNH_2 regions. For the free ligand the νNH_2 resonances are between about 3100 and 3400 cm^{-1} with a pronounced peak at 3297 cm^{-1}. The δNH_2 line is located at 1601 cm^{-1}. In the title compound the whole region of νNH_2 modes is broader extending from *ca.* 3030 to 3410 cm^{-1} with a peak at 3232 cm^{-1}. The δNH_2 line is slightly shifted to 1594 cm^{-1}. We note that all modes of the $[Ni(DETA)_2]^{2+}$ complexes are in good agreement with data published in the literature.[20–25] The shift to lower wavenumbers as well as the broadening may be caused by both the N–Ni bonding interactions and possible S···H–N hydrogen bonds.

As can be seen in Fig. 3 the material decomposes in two steps with individual weight changes of 31.1 and 2.7% giving a total weight loss of 33.8% which roughly corresponds to the emission of the four DETA ligands (Δm_{theo} = 32.4%).§ Decomposition starts at T_{onset} = 222 °C and is accompanied by two endothermic peaks at T_p = 260 and 319 °C. The first endothermic signal exhibits a complex shape with two shoulders located at T_p = 251 and 273 °C. In further experiments decomposition of the educt was stopped at 300 and 350 °C. The residues were characterised by CHN analysis, X-ray powder diffraction (XPD), energy dispersive X-ray analysis (EDX) and IR spectroscopy. In the XPD pattern of the grey residue [C, 1.8; H, 0.25; N, 1.15; EDX (atom%): S, 48(1); Sb, 32.2(1.4); Ni, 19.7(2.7)] obtained after the 300 °C treatment, NiS, Sb_2S_3, NiSbS and a small amount of an unknown fourth phase were identified. In the IR spectrum no C–H, C–N, C–C or N–H vibrations could be detected. From the elemental analyses it can be assumed that not only DETA is emitted but also S, and a small amount of C, H, and N remain in the residue. In the XPD pattern of the dark grey sample obtained after heating to 350 °C (C, 1.6%; H, 0%; N, 0.72%; EDX(atom%): S, 47.8(8); Sb, 31.7(1.0); Ni, 20.5(1.9)%] the reflections of the unknown phase disappeared and only NiS, Sb_2S_3 and NiSbS could be identified. The small weight loss between 300 and 350 °C of *ca.* 2.7% may be attributed to the decomposition of the unknown phase accompanied by the emission of C, H and N as well as of sulfur.

The endothermic event at T_p = 556 °C agrees well with the melting point of Sb_2S_3 (literature value: T_m = 550 °C). In the grey reaction product the two phases Sb_2S_3 and NiS could be identified.

In conclusion, we note that the stabilisation of the high negatively charged $[Sb_4S_8]^{4-}$ anion may be achieved by an extended hydrogen bond network as well as by the shape and size of the counterion. There is no simple relationship between cation size and shape and the dimensionality of the anionic thioantimonate network. In addition, hydrothermal crystallisations are multicomponent heterogeneous reactions that are not well understood and we are far from being able to predict structures or physical properties of the products. The successful synthesis and characterisation of new thioantimonates(III) may provide the information that is necessary to lead to more rational syntheses of such compounds.

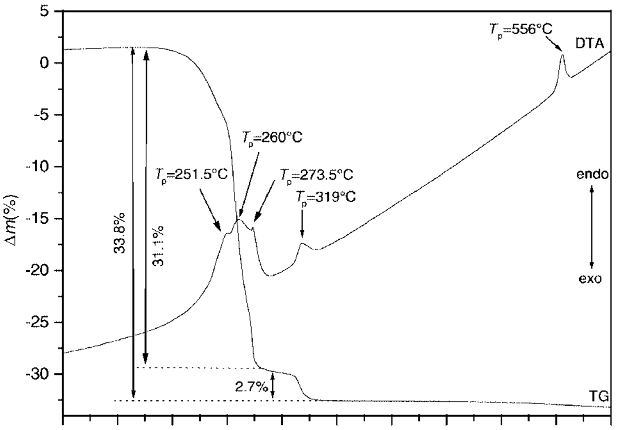

Fig. 3 DTA and TG curves for $[Ni(DETA)_2]_2Sb_4S_8$.

Notes and references

† *Synthesis:* dark yellow platy crystals of $[Ni(DETA)_2]_2Sb_4S_8$ were synthesised from elemental Ni (58.69 mg, 1 mmol), Sb (121.76 mg, 1 mmol) and S (96.19 mg, 3 mmol) in a solution of 100% diethylenetriamine (3 mL, 27 mmol). The mixture was heated to 145 °C for 11 days in a Teflon-lined steel autoclave (*ca.* 20 mL) under autogenous pressure. The crystalline product was filtered off and washed with acetone and stored under vacuum. The yield based on Ni is *ca.* 40%. C, H, N analysis: found: N, 12.0; C, 14.95; H, 4.1; calc.: N, 13.2; C, 15.09; H, 4.12%. EDX analysis (%): found: Ni, 12.7(3); Sb, 29.3(1.4); S, 58(1); calc. Ni, 14.3; Sb, 28.6; S, 57.

‡ *Crystal structure determination*: $[Ni(DETA)_2]_2Sb_4S_8$, M = 1273.6, triclinic, space group $P\bar{1}$ (no. 2), a = 9.0249(6), b = 12.7607(2), c = 18.037(2) Å, α = 92.299(9), β = 91.058(8), γ = 105.735(9)°, U = 1996.6(3) $Å^3$, T = 293 K, Z = 2, Imaging Plate Diffraction System (IPDS) (Mo-Kα; λ = 71.073 pm), μ(Mo-Kα) = 4.04 mm^{-1}, 7843 reflections collected in the range $3 \leqslant 2\theta \leqslant 51.87°$, 3873 unique reflections. Face-indexed absorption correction; structure solution with SHELXS-97: structure refinement against F^2 using SHELXL-97. 380 parameters, $R1$ for 3182 reflections $[F_o > 4\sigma(F_o)]$ = 0.0313, $wR2$ for all 3873 data = 0.0814, GOF 1.049. Residual electron density: 0.73/−0.51 e $Å^{-3}$. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned with idealised geometry and refined with individual isotropic displacement parameters using the riding model. CCDC 154455. See http://www.rsc.org/suppdata/cc/b0/b009583o/ for crystallographic data in .cif or other electronic format.

§ The thermal stability of the compound was investigated using DTA/TG measurements. The sample was heated under argon atmosphere in a Al_2O_3 crucible (heating rate: 3 °C min^{-1}, temperature range: 25–600 °C, mass: 48.6 mg. EDX analysis: EDAX unit attached to an XL 30 ESEM, Philips.

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