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Thioantimonate(III) anions acting as bridging ligands in neutral transition metal complexes: solvothermal synthesis and characterisation of the two novel compounds $[Co(C_6H_{18}N_4)]_2Sb_4S_8$ and $[Co(C_6H_{18}N_4)]_2Sb_2S_5$ containing $[Sb_4S_8]^{4-}$ and $[Sb_2S_5]^{4-}$ anions

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The two novel thioantimonate(III) compounds $[Co(C_6H_{18}N_4)]_2Sb_4S_8$ **1** and $[Co(C_6H_{18}N_4)]_2Sb_2S_5$ **2** were synthesised under solvothermal conditions by reacting elemental Co, Sb and S in a 95% solution of tris(2-aminoethyl)amine (tren). Compound **1** crystallises in the monoclinic space group $P2_1/c$, $a = 17.936(4)$ Å, $b = 13.442(3)$ Å, $c = 14.000(3)$ Å, $\beta = 101.73(3)°$, and compound **2** crystallises in the monoclinic space group $C2/c$, $a = 30.157(6)$ Å, $b = 7.720(2)$ Å, $c = 22.875(8)$ Å, $\beta = 94.68(3)°$. The $[Sb_4S_8]^{4-}$ anion in compound **1** is composed of two SbS_3 and two SbS_4 units. The two SbS_4 moieties share a common edge and each SbS_4 has a common edge with a SbS_3 pyramid. This interconnection leads to the formation of three Sb_2S_2 heterorings. The two remaining terminal S atoms of the anion are bound in a monodentate fashion to the $[Co(C_6H_{18}N_4)]^{2+}$ cation. The $[Sb_2S_5]^{4-}$ anion in **2** is formed by two corner linked SbS_3 units. Two terminal S atoms are bound to the $[Co(C_6H_{18}N_4)]^{2+}$ cation in a monodentate manner. Compounds **1** and **2** are the first compounds that contain thioantimonate(III) anions acting as bridging ligands. Both compounds start to decompose at about 240 °C due to the removal of the organic ligands. In the X-ray powder patterns of the decomposition products Sb_2S_3, CoSbS and CoS could be identified.

Introduction

Since the pioneering work of Schäfer and co-workers on the solvothermal syntheses of thioantimonates(III)[1–10] a large number of new and exciting compounds based on $Sb_xS_y^{z-}$ moieties have been prepared and characterised over the last few years. It is well documented that thioantimonates(III) exhibit a rich structural diversity due to the high flexibility of the coordination behaviour of the Sb(III) atom with coordination numbers between 3 and 6.[11,12] It is believed that the flexibility of the Sb(III) atom is due to the stereochemically active lone pair.[13,14]

The dimensionality of the thioantimonate(III) anions is determined by the size of the cations when alkali or alkaline earth cations are used. Nice examples are compounds with the $[Sb_4S_7]^{2-}$ anion. For $K_2Sb_4S_7$ a three dimensional network is formed,[1] in $Rb_2Sb_4S_7$ the anion is layered,[15] and for the thioantimonate(III) with the large $Sr(H_2O)_6^{2+}$ cation only one dimensional anionic chains are observed.[7]

With organic cations no well pronounced relationship between the size of the cation and the resulting dimensionality of the thioantimonate(III) anion is observed. The four recently prepared and characterised compounds $[Ni(dien)_2]_2Sb_4S_8$,[16] $[Ni(dien)_2]_3(SbS_4)_2$,[17] $[Ni(dien)_2]Sb_6S_{10}{\cdot}0.5H_2O$ and $[Fe(dien)_2]Sb_6S_{10}{\cdot}0.5H_2O$[18] should serve as an example. In these compounds the cations have the same shape and charge. In the first and second compound isolated $[Sb_4S_8]^{4-}$ and $[SbS_4]^{3-}$ anions are observed, whereas the third and fourth compound contain a two dimensional layered $[Sb_6S_{10}]^{2-}$ anion. Hence it could be concluded that other factors like actual synthesis conditions and/or intermolecular hydrogen bonding determine the dimensionality of the resulting anionic framework.

Several groups have investigated thioantimonates(III) with the aim of preparing open-framework or microporous compounds. According to the syntheses of zeolites and other porous oxidic materials organic molecules like amines were used as structure directing agents.[19–25] A few years ago we started to investigate whether transition metal cations could be incorporated into the thioantimonate(III) network and synthesised a series of isostructural manganese thioantimonates(III), $Mn_2Sb_2S_5{\cdot}L$ (L = methylamine (ma), ethylamine (ea), 1,3-diaminopropane (dap), *N*-methyl-1,3-diaminopropane (mdap), diethylenetriamine (dien)).[26,27] To the best of our knowledge there are only a few additional thioantimonate(III) compounds in which a transition metal is part of the anionic network.[23,28–32] Most of these compounds contain Cu as transition metal and were prepared at elevated temperatures.

A strategy to incorporate transition metal ions into the anionic $Sb_xS_y^{z-}$ moieties requires that not all positions within the $[TML_n]^{x+}$ (TM = transition metal, L = ligand) cations are occupied by the N atoms of the amines applied. Therefore, using a tetradentate ligand together with Co as the TM one could expect that one or two coordination sites at the central Co ion are left to form bonds to S atoms of the anionic part of the structures. According to this consideration we introduced tren as amine and synthesised and characterised the two new and unusual thioantimonate(III) compounds $[Co(C_6H_{18}N_4)]_2Sb_4S_8$ and $[Co(C_6H_{18}N_4)]_2Sb_2S_5$ that contain $[Sb_4S_8]^{4-}$ and $[Sb_2S_5]^{4-}$ anions as bridging ligands, respectively.

Experimental

Crystal structure determination

Single crystal X-ray investigations were performed using a STOE AED-II 4-circle diffractometer and imaging plate diffraction system (Stoe & Cie.) using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The intensities were corrected for Lorentz, polarisation and absorption effects. The structures were solved using SHELXS-97[33] and structure refinements were done against F^2 with SHELXL-97.[34] All

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Table 1 Technical details of data acquisition and selected refinement results for $[Co(tren)]_2Sb_4S_8$ and $[Co(tren)]_2Sb_2S_5$

Formula	$[Co(C_6H_{18}N_4)]_2Sb_4S_8$	$[Co(C_6H_{18}N_4)]_2Sb_2S_5$
Colour, habit	Dark green, squares	Dark green, squares
Molecular weight/g mol^{-1}	1153.83	814.15
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
D_{calc}/g cm^{-3}	2.319	2.038
a/Å	17.936(4)	30.157(6)
b/Å	13.442(3)	7.720(2)
c/Å	14.000(3)	22.875(8)
β/°	101.73(3)	94.68(3)
V/Å^3	3305(1)	5308(28)
Z	4	8
T/K	293	293
Scan range	$3.88° \le 2\theta \le 60.06°$	$4.6° \le 2\theta \le 56.3°$
	$-25 \le h \le 24$	$-39 \le h \le 39$
	$-12 \le k \le 18$	$-9 \le k \le 9$
	$0 \le l \le 19$	$-30 \le l \le 30$
Measured reflections	18205	25642
Independent reflections	9659	6230
Reflections with $F_o > 4\sigma(F_o)$	7932	5248
μ/mm^{-1}	4.729	3.653
R_{int}	0.0198	0.0412
Absorption correction	Face-indexed	Face-indexed
Min./max. trans.	0.2767, 0.4303	0.4622, 0.6846
Extinction coefficient[a]	$x = 0.00076(3)$	$x = 0.00049(4)$
Weight[b]	$y = 0.0235$, $z = 2.0734$	$y = 0.0367$, $z = 0$
$R1$ for all $F_o > 4\sigma(F_o)$	0.0236	0.0235
$R1$ for all reflections	0.039	0.0311
$wR2$ for all $F_o > 4\sigma(F_o)$	0.0521	0.0561
$wR2$ all reflections	0.0550	0.0586
$\Delta\rho$/e Å^{-3}	−0.76/1.25	−0.81/0.59
GOF	1.037	1.013

[a] $F^* = F_c(k[1 + 0.001 \cdot x \cdot F_c^2 \cdot \lambda^3/\sin(2\theta)]^{-0.25})$. [b] $w = 1/[\sigma^2(F_o^2) + (y \cdot P)^2 + z \cdot P]$; $P = (\max(F_o^2,0) + 2 \cdot F_c^2)/3$.

non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were positioned with idealised geometry and refined with fixed isotropic displacement parameters applying a riding model with the parameters $d_{C-H} = 0.97$ Å and $d_{N-H} = 0.90$ Å. Technical details of the data acquisition as well as some selected refinement results are summarised in Table 1.

CCDC reference numbers 161743 and 161744.

See http://www.rsc.org/suppdata/dt/b1/b102273n/ for crystallographic data in CIF or other electronic format.

Thermal investigations

The thermal measurements were performed on a Netzsch STA 429 DTA-TG measurement device. The samples were heated in Al_2O_3 crucibles with a rate of 3 °C min^{-1} up to 400 °C and purged in an argon stream with a flow rate of approximately 50 mL min^{-1}.

X-Ray powder diffractometry

The X-ray powder patterns were recorded on a STOE Stadi-P diffractometer (Co-K$_\alpha$ radiation, $\lambda = 1.788965$ Å) in transmission geometry.

EDAX experiments

Scanning electron microscopic investigations and energy dispersive analysis of X-rays were conducted with a Philips Environmental Scanning Electron Microscope ESEM XL 30.

Preparation of $[Co(tren)]_2Sb_4S_8$

Dark green needles of $[Co(tren)]_2Sb_4S_8$ were prepared by reacting a mixture of elemental Co (0.058 g, 1 mmol), Sb (0.121 g, 1 mmol) and S (0.096 g, 3 mmol) in a 95% solution of tren (3 mL) (Fluka Chemicals) under mild solvothermal conditions. The syntheses were performed in Teflon-lined steel autoclaves (inner volume: 30 mL). The autoclaves were heated to 140 °C, held at this temperature for 4 days and cooled to room temperature within 3 h. The products were filtered off, washed with water and dried under vacuum. The yield was 90% based on Co. Stirring the solution during the syntheses a phase pure product was obtained within 1 day applying Co : Sb : S in a 1 : 1 : 3 ratio (identical mmol amounts) in an aqueous solution of 10 mL tren (50%) at 140 °C. C, H, N analysis: found: C: 12.63%, H: 3.27%, N: 9.60%; calc.: C: 12.49%, H: 3.15%, N: 9.71%.

Preparation of $[Co(tren)]_2Sb_2S_5$

$[Co(tren)]_2Sb_2S_5$ was synthesised by reacting elemental Co (0.058 g, 1 mmol), Sb (0.121 g, 1 mmol) and S (0.096 g, 3 mmol) in 3 mL 95% tren solution. The mixture was heated for 12 days at 140 °C in the autoclave. The crystalline dark green product was filtered off, washed with water and acetone and stored under vacuum. We note that under dynamic conditions $[Co(tren)]_2Sb_4S_8$ is always formed independent from the amine concentration and reaction time. The yield was 80% based on Co. C, H, N analysis: found: C: 17.8%, H: 4.41%, N: 12.80%; calc.: C: 17.7%, H: 4.4%, N: 13.8%.

Results and discussion

The syntheses

Solvothermal syntheses are heterogeneous multicomponent reactions and the product formation depends on different reaction parameters. Changing one of these parameters influences several others in a poorly understood manner. Using elements as starting materials very basic solutions are required to dissolve and mobilise the educts. Solutions of amines yield such high pH values. The main goal of our syntheses is the preparation of new thioantimonate(III) compounds with transition metal cations (TM^{n+}) being incorporated into the anionic Sb_x-S_y^{z-} network. The suppression of full complexation of TM^{n+} ions is achieved by using a multidentate amine such as tris-(2-aminoethyl)amine (tren), and in the case of Co geometrically

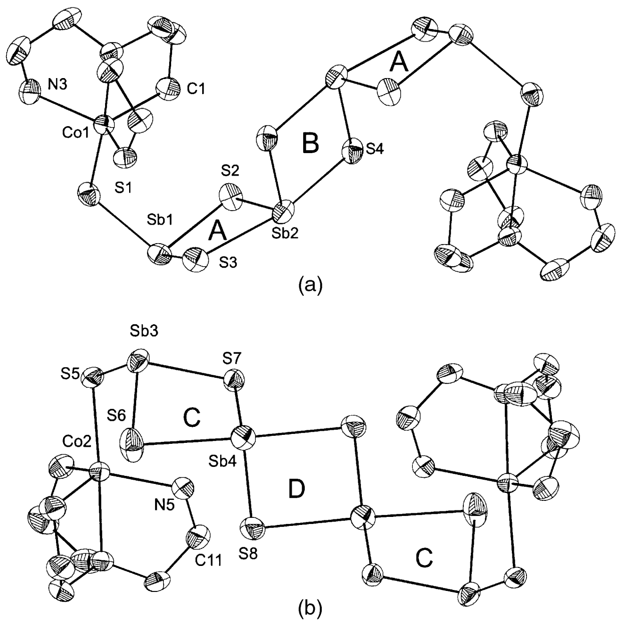

Fig. 1 The $[Co(tren)]_2Sb_4S_8$ molecules (a) and (b) with numbering scheme. The displacement ellipsoids are drawn at the 50% level (H-atoms are omitted for clarity).

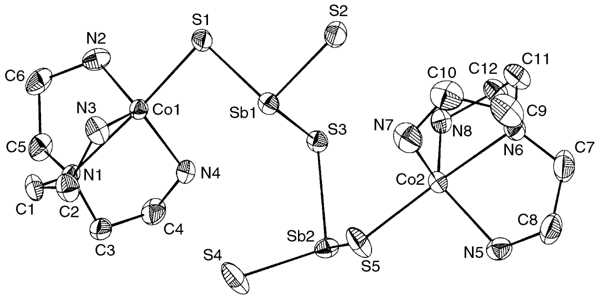

Fig. 2 $[Co(tren)]_2Sb_2S_5$ with numbering scheme and displacement ellipsoids drawn at the 50% level (hydrogen atoms are omitted for clarity).

Table 2 Selected distances (Å) for $[Co(tren)]_2Sb_4S_8$ and $[Co(tren)]_2Sb_2S_5$. Estimated standard deviations are given in parentheses

$[Co(tren)]_2Sb_4S_8$			
Sb(1)–S(1)	2.3860(9)	Sb(1)–S(2)	2.4595(9)
Sb(1)–S(3)	2.398(1)	Sb(2)–S(2)	2.446(1)
Sb(2)–S(3)	2.7340(9)	Sb(2)–S(4)[b]	2.3973(8)
Sb(2)–S(4)	2.7285(9)	Sb(3)–S(6)	2.392(1)
Sb(3)–S(5)	2.3775(9)	Sb(3)–S(7)	2.4680(8)
Sb(4)–S(6)	2.7599(9)	Sb(4)–S(7)	2.4885(8)
Sb(4)–S(8)	2.3934(9)	Sb(4)–S(8)[a]	2.7427(9)
Co(1)–S(1)	2.3521(9)	Co(2)–S(5)	2.3598(9)
Co(1)–N(1)	2.063(2)	Co(1)–N(2)	2.273(2)
Co(1)–N(3)	2.098(2)	Co(1)–N(4)	2.077(2)
Co(2)–N(5)	2.091(2)	Co(2)–N(6)	2.083(2)
Co(2)–N(7)	2.283(2)	Co(2)–N(8)	2.065(2)
$[Co(tren)]_2Sb_2S_5$			
Sb(1)–S(1)	2.4294(8)	Sb(1)–S(2)	2.3621(8)
Sb(1)–S(3)	2.4916(7)	Sb(2)–S(3)	2.4761(8)
Sb(2)–S(4)	2.332(1)	Sb(2)–S(5)	2.3935(8)
Co(1)–S(1)	2.3540(8)	Co(2)–S(5)	2.3337(8)
Co(1)–N(1)	2.318(2)	Co(1)–N(2)	2.073(2)
Co(1)–N(3)	2.107(2)	Co(1)–N(4)	2.065(2)
Co(2)–N(5)	2.094(2)	Co(2)–N(6)	2.268(2)
Co(2)–N(7)	2.067(2)	Co(2)–N(8)	2.076(2)

[a] $1 - x, 1 - y, 2 - z$. [b] $2 - x, -y, 2 - z$.

constrained $[Co(tren)]^{2+}$ cations can be incorporated into the thioantimonate(III) structure. Both compounds were obtained using an elemental ratio Co : Sb : S of 1 : 1 : 3, and different concentrations of the amine as well as different reaction times. In a few dozen experiments the concentration of the amine and reaction times were varied to optimise the syntheses. The results suggest that for short reaction times $[Co(tren)]_2Sb_4S_8$ is the more stable phase whereas prolonged heating yields the sulfur richer compound $[Co(tren)]_2Sb_2S_5$. At intermediate reaction times mixtures of both compounds were obtained. On stirring the mixture during the reaction only $[Co(tren)]_2Sb_4S_8$ is formed. A detailed explanation of these observations requires a knowledge of the building units within the solutions and their transformations as well as condensation into the final products.

The structures

The new compound $[Co(tren)]_2Sb_4S_8$ **1** (tren = tris(2-aminoethyl)amine) crystallises in the monoclinic space group $P2_1/c$ with four formula units in the unit cell and $[Co(tren)]_2Sb_2S_5$ **2** crystallises in the monoclinic space group $C2/c$ with eight formula units in the unit cell (Table 1). In both compounds two crystallographically independent Co atoms are found in a distorted trigonal bipyramidal environment of four N atoms from the tren ligand and one S atom from the thioantimonate(III) anion (CoN_4S_1) (Fig. 1a,b and Fig. 2). The Co–N distances in **1** vary between 2.063(2) and 2.283(2) Å and in **2** between 2.065(2) and 2.318(2) Å (Table 2) with N–Co–N angles ranging from 78.67(8) to 120.3(1)° (**1**) and 77.68(8) to 120.87(9)° (**2**). In **1** the Co–S distances are between 2.3521(9) and 2.3598(9) Å and in **2** between 2.3337(8) and 2.3540(8) Å (see Table 2). As expected the long Co–N distances are in *trans* position to the Co–S bonds.[35] The angles S–Co–N slightly deviate from the ideal value of 180° and spread from 173.51(6) to 173.66(6)° in **1** and are between 172.91(6) and 174.59(5)° in **2**. We note that penta coordinated tren ligand complexes of transition metal elements have been known for a long time,[36–38] and they were intensively studied.[39–42]

Formal valence considerations suggest that all Sb atoms in compounds **1** and **2** are trivalent. The crystallographically independent parts of the two anions in **1** are composed of two SbS_3 pyramids sharing a common edge leading to *cis*-Sb_2S_4 moieties (Fig. 1a,b). The $[Sb_4S_8]^{4-}$ anions are then formed by two such units that are related by a centre of symmetry. The terminal S atoms are bound to the Co^{2+} cations. The Sb1 and Sb3 atoms of the anions are coordinated by three S atoms with distances ranging from 2.3775(9) to 2.4680(8) Å being typical for Sb–S single bonds. Interestingly, the $Sb2S_3$ and $Sb4S_3$ pyramids have two short bonds to S atoms (2.392(1)–2.4885(8) Å) and one relatively long separation of 2.7340(9) Å and 2.7599(9) Å respectively. The connection of the *cis*-Sb_2S_4 units enhances the coordination number of Sb2 and Sb4 from three to four and the Sb–S distances to the symmetry related S4a and S8a atoms are 2.7285(9) and 2.7427(9) Å. We note that the two long Sb–S distances are nearly *trans* to each other (see Table 2) as is evidenced by the S–Sb–S angles. Taking the electron lone pair into account the SbS_4 units may be viewed as distorted ψ-trigonal bipyramids. Another way to describe the geometry base on the connection of three Sb_2S_2 heterorings with two terminal sulfur atoms at the periphery of the Sb_4S_6 unit (see Fig. 1a,b). The rings are not planar as evidenced by the mean root square deviations of 0.4413 Å (**A**), 0.5649 Å (**B**) (see Fig. 1a), 0.7570 Å (**C**), 0.6064 Å (**D**) (see Fig. 1b). Fitting the two crystallographically independent Sb_2S_4 rings onto each other the different conformations become obvious (root mean square deviation (rms) = 0.7522 Å). A pronounced difference between the two independent $[Sb_4S_8]^{4-}$ anions becomes obvious taking into account Sb–S distances up to 4 Å. The Sb4 atom has a contact of about 3.7 Å to a terminal S atom of a neighbouring molecule (see Fig. 3) whereas no S atoms below 4.3 Å are found around all other Sb atoms.

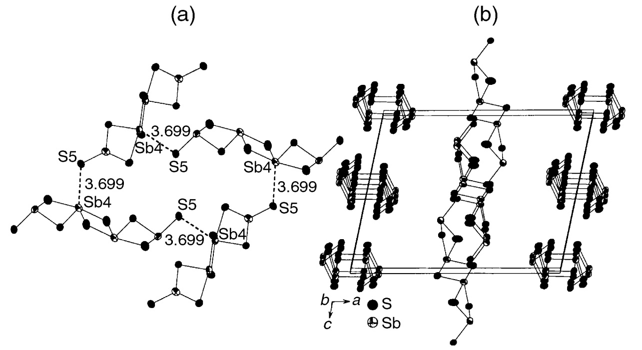

Fig. 3 Arrangement of the $[Co(tren)]_2Sb_4S_8$ molecules. Ellipsoids are drawn at the 50% probability level. (a) The $[Sb_4S_8]^{4-}$ anion with the intermolecular Sb···S contact of 3.699 Å. (b) Arrangement of the anions with view along the *b* axis (Co, H, N and C atoms are omitted for clarity).

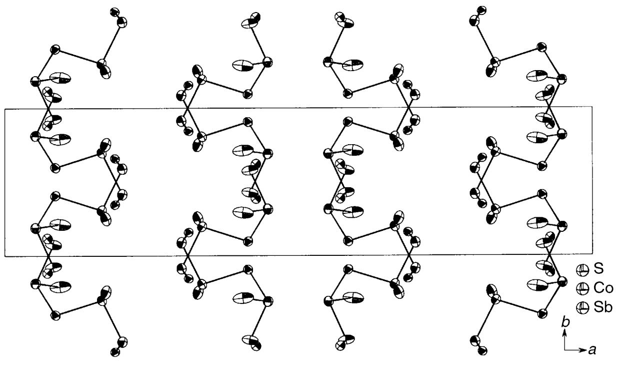

Fig. 4 Packing of $[Co(tren)]_2Sb_2S_5$ molecules with view parallel to the *c* axis. All ellipsoids are drawn at the 50% probability level (the tren ligand is omitted for clarity).

The angles about the Sb atoms within the *cis*-Sb_2S_4 moieties spread from 82.14(3)° to 107.60(3)° which is rather large compared to values reported for other thioantimonates(III).

The SbS_4 units were observed in $(CH_3NH_3)_2Sb_8S_{13}$,[24] $Cs_2Sb_8S_{13}$[43] and $Cs_5Sb_8S_{13}(HCO_3)$[44] with Sb–S distances between 2.4 and 2.85 Å. The A_2B_2 (A = As, Sb; B = S, Se) heterorings are common and were observed for example as *trans*-$[As_2Se_4]^{2-}$ in $Ba_2As_2Se_5$[45] and as *trans*-$[Sb_2S_4]^{2-}$ in $(CH_3NH_3)_2Sb_2S_4$.[46]

The arrangement of the $[Co(tren)]_2Sb_4S_8$ molecules within the crystal structure is shown in Fig. 3. One molecule (Co1, Sb1, Sb2) is stacked in columns parallel to the *b* axis with no Sb–S contacts below 4.3 Å. For the second molecule (Co2, Sb3, Sb4) with the Sb4–S5 separation of 3.7 Å a layer-like arrangement within the (100) plane is observed. Hydrogen bonding with N···S contacts between 2.492 and 2.763 Å (angles: 148.2–172.6°) (N–H···S) may contribute to the stability of the structure.

The $[Sb_2S_5]^{4-}$ anion (Fig. 2) in $[Co(tren)]_2Sb_2S_5$ **2** is built up from two SbS_3 trigonal pyramids sharing a common corner. Two terminal S atoms are bound to the Co^{2+} cations. The Sb–S distances vary between 2.332(1) and 2.4916(7) Å (Table 2) with S–Sb–S angles between 97.91(2) and 103.65(3)°. Together with the lone pair of Sb(III) the environment may be viewed as ψ-SbS_3 tetrahedra. As expected the terminal distances Sb1–S2 (2.3621(8) Å) and Sb2–S4 (2.332(1) Å) are shorter than the μ-Sb–S bonds (Table 2). We note that the Sb_2S_5 unit is similar to the $[As_2Se_5]^{4-}$ anion in $\{K_5[Ag_2(AsSe_4)(As_2Se_5)]\}$.[47]

Fig. 4 shows the arrangement of $[Co(tren)]_2Sb_2S_5$ within the unit cell. The molecules are stacked in columns parallel to the *b* axis leading to a layer-like arrangement within the (001) plane. N···S separations ranging from 2.454 to 2.824 Å with angles between 141.7 and 169.8° indicate weak hydrogen bonding.

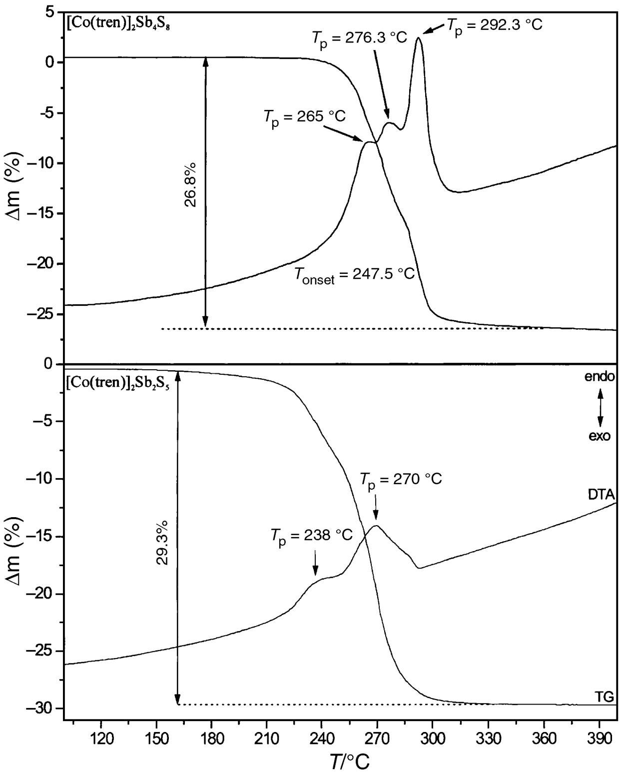

Fig. 5 DTA-TG curves of $[Co(tren)]_2Sb_4S_8$ (atmosphere: argon; weight: 70.9 mg) and $[Co(tren)]_2Sb_2S_5$ (atmosphere: argon; weight: 48.4 mg; powdered crystals). T_p = Peak temperature.

Thermal investigations

The experiments conducted with simultaneous difference thermal analysis and thermogravimetry should demonstrate whether stable intermediates are formed that could be isolated and characterised. Furthermore, the removal of the organic part occurs at relatively low temperatures so that the formation of a new Co thioantimonate may be achieved which cannot be prepared at higher temperatures. The compound $[Co(tren)]_2Sb_4S_8$ starts to decompose at T_{onset} = 247.5 °C with a total weight loss of 26.8% (Fig. 5). The process is accompanied by three well resolved endothermic events at T_p = 265, 276.3 and 292.3 °C. The experimental weight loss is in rough agreement with the loss of the tren ligands (Δm_{theo} = 25.35%). But in the dark grey residue appreciable amounts of C and N were found (C: 4.287%; N: 2.030%; H: 0%) indicative of a more complex decomposition reaction. In the IR spectra no vibrations of the tren ligand could be observed and the X-ray powder pattern could be explained on the basis of crystalline Sb_2S_3, CoSbS, CoS and a very small amount of an unknown phase (EDAX results in atom%: S: 43.33 ± 1.07; Sb: 26.98 ± 1.27; Co: 29.57 ± 1.68).

Heating $[Co(tren)]_2Sb_2S_5$ the decomposition starts at T_{onset} = 224 °C with a weight loss of Δm_{exp} = 29.3% (Fig. 5). The decomposition reaction is accompanied by two broad endothermic signals at T_p = 238 and 270 °C. Assuming that all tren ligands are emitted during the thermal reaction a weight change of 35.9% is calculated. The discrepancy between the experimental and expected weight loss is in part explained by the presence of C and N in the dark grey residue (C: 3.03%; N: 1.3%). Again, no C–C, C–N, C–H, or N–H vibrations could be detected with IR and Raman spectroscopy. In the X-ray powder pattern Sb_2S_3, CoSbS, and CoS could be identified.

Acknowledgements

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