



The effect of temperature onto the crystal structure of thioantimonates: solvothermal syntheses and crystal structures of $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4] \cdot 2.0.5 \text{ H}_2\text{O}$ and $\{[\text{Co}(\text{tren})]_2[\text{CoSb}_2\text{S}_6]\} \cdot \text{H}_2\text{O}$

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The effect of temperature onto the crystal structure of thioantimonates: solvothermal syntheses and crystal structures of $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 0.5 \text{H}_2\text{O}$ and $\{[\text{Co}(\text{tren})]_2[\text{CoSb}_2\text{S}_6]\} \cdot \text{H}_2\text{O}$

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Dedicated to Prof. Dr. Martin Jansen on the occasion of his 65th birthday

Keywords: Solvothermal Synthesis, Thioantimonates, Crystal Structure

The two new compounds $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 0.5 \text{H}_2\text{O}$ (**1**) and $\{[\text{Co}(\text{tren})]_2[\text{CoSb}_2\text{S}_6]\} \cdot \text{H}_2\text{O}$ (**2**) were synthesized applying mixtures of amines as structure directing molecules (dien = diethylenediamine; tren = tren = tris(2-aminoethyl)amine). Compound **1** crystallizes in the monoclinic space group C2/c with $a = 29.378(3)$, $b = 7.6643(4)$, $c = 22.507(2)$ Å, $\beta = 115.39(1)^\circ$ and represents a pseudo-polymorph to the compound $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 4\text{H}_2\text{O}$. The structure consists of the two complexes $[\text{Co}(2)(\text{dien})_2]^{2+}$ and $[\text{Co}(1)(\text{tren})\text{SbS}_4]^-$ with the latter

containing a $[\text{Sb}(\text{V})\text{S}_4]^{3-}$ anion bonded to the Co^{2+} cation. Compound **2** crystallizes in space group P2₁/c, $a = 13.870(2)$, $b = 14.708(1)$, $c = 14.700(2)$ Å, $\beta = 94.62(2)^\circ$. The central and new feature of the structure is a heterometallic $[\text{CoSb}_2\text{S}_6]$ core composed of two $[\text{Sb}(\text{III})\text{S}_3]$ pyramids and a $[\text{CoS}_4]$ tetrahedron. The $[\text{CoS}_4]$ tetrahedron shares two edges with two $[\text{Sb}(\text{III})\text{S}_3]$ units. The remaining S atom of the $[\text{Sb}(\text{III})\text{S}_3]$ groups are bonded to two independent $[\text{Co}(\text{tren})]$ complexes.

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Introduction

In the past few years we and other groups demonstrated that a large variety of amines are suitable structure directing molecules for the preparation of thioantimonates under solvothermal conditions [1-24]. A challenge in the field of thioantimonate chemistry is the integration of transition metal ions into the thioantimonate networks. Using mono-, bi- or tridentate amine molecules like methylamine, ethylenediamine or diethylenetriamine (dien) mainly transition metal complexes are formed which are separated from the anionic network [25-38]. Exceptions are the chalcophilic cations Cu^+ and Ag^+ which easily form bonds to the S atoms of thioantimonate anions [39-45]. An interesting behavior is also observed for Mn^{2+} which seems to have a comparable affinity to N and S. Hence, many Mn^{2+} thioantimonates were synthesized even applying typical complex forming amines [46-53]. The integration of transition metal cations can be forced using special multidentate amines like tris(2-aminoethyl)amine (tren). This tetradentate amine saturates only four coordination sites of transition metal cations (TM^{n+}) like Cr^{3+} , Mn^{2+} , Co^{2+} ,

Ni^{2+} , Fe^{2+} or Zn^{2+} [54-62] opening the possibility of bond formation between the chelated TM^{n+} and the thioantimonate network. On the other hand the advantage of isolated $[\text{TM}(\text{amine})_x]^{n+}$ complexes is their large size and often thioantimonates are formed being characterized by large rings or cavities [27, 34, 35]. A new approach in the field of thioantimonate chemistry is to combine isolated $[\text{TM}(\text{amine})_x]^{n+}$ complexes as space fillers and charge compensating ions with coordinatively unsaturated complexes bonded to the network. The final goal is the synthesis of structural architectures containing large pores or tunnels due to the presence of the complexes and a thioantimonate network with integrated TM^{n+} cations. Very recently we reported the synthesis and structure of $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 4\text{H}_2\text{O}$ [63] which contains isolated $[\text{Co}(\text{dien})_2]^{2+}$ and $[\text{Co}(\text{tren})\text{SbS}_4]^-$ complexes. The compound represents one of the few samples of a thioantimonate(V) with the $[\text{SbS}_4]^{3-}$ anion being bonded to a TM^{n+} cation. We further explored the system Co-Sb-S-dien-tren by changing the dien:tren ratio and varying the temperature. In the paper we present the crystal structures of two new thioantimonates, namely $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 0.5 \text{H}_2\text{O}$ (**1**) which is a pseudo-polymorph to $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 4\text{H}_2\text{O}$ and $\{[\text{Co}(\text{tren})]_2[\text{CoSb}_2\text{S}_6]\} \cdot \text{H}_2\text{O}$ (**2**). A new structural feature of **2** is the heterometallic $[\text{CoSb}_2\text{S}_6]$ core which was not observed before.

Results and Discussion

The two new compounds were obtained in a mixture of dien and tren applying the ratio dien:tren = 2.4:0.6 mL in 1 mL water. Phase pure $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 0.5 \text{ H}_2\text{O}$ is formed exclusively at 110 °C whereas mixtures of both compounds were observed at 120 and 130 °C. A series of experiments was performed at 120 and 130 °C varying the reaction time between 3 and 6 d. But in all products a mixture of the two title compounds was obtained. Variation of the ratio of the amines ($T = 120$ and 130 °C, dien:tren = 2.7:0.3, 2.6:0.4 and 2.5:0.5 with 1 mL H_2O) and also the absolute amount of the amine in 1 mL water (dien:tren: 1.3:0.2 – 1.8:0.3) resulted in mixtures of the two compounds. After increasing the temperature above 130 °C only an unknown polycrystalline compound is obtained. We note that the pseudo-polymorphic compound $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 4\text{H}_2\text{O}$ [63] was synthesized at 140 °C in a mixture of 2 mL 50% tren and 1 mL 50% dien, i.e. the amine solution was more diluted than that used for the synthesis of compound **1**. At the lower reaction temperature compound **1** is formed containing the $[\text{Sb}(\text{V})\text{S}_4]^{3-}$ anion whereas $[\text{Sb}(\text{III})\text{S}_3]^{3-}$ units are observed in compound **2**. A more diluted amine mixture and a higher reaction temperature afforded the formation of $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 4\text{H}_2\text{O}$ which also contains the Sb(V) species. The analysis of the synthesis conditions where the $[\text{Sb}(\text{V})\text{S}_4]^{3-}$ species was obtained give no clear rules concerning the reaction temperature and amine concentration. For instance, $[\text{Mn}(\text{tren})\text{trenH}][\text{SbS}_4]$ was obtained at 140 °C applying a concentrated tren solution [60]. On the other hand $[\text{Mn}(\text{chxn})_3][\text{Mn}(\text{chxn})_2(\text{SbS}_4)_2] \cdot 6\text{H}_2\text{O}$ crystallized in 50% 1,2-diaminocyclohexane (chxn) solution [61]. In several cases we obtained $[\text{Sb}(\text{III})\text{S}_3]^{3-}$ containing compounds like $[\text{Ni}(\text{tren})]\text{Sb}_2\text{S}_4$, $[\text{Co}(\text{tren})]\text{Sb}_2\text{S}_4$ [55] in diluted tren or $[\text{Co}(\text{tren})]_2\text{Sb}_4\text{S}_8$ resp. $[\text{Co}(\text{tren})]_2\text{Sb}_2\text{S}_5$ in concentrated tren solution [54]. Summarizing shortly there are no rules at hand for the prediction whether the reaction product contains Sb(III) or Sb(V) species.

Compound **1** crystallizes in the monoclinic space group $C2/c$ (Table 1) with all atoms except Co(2) being located on general positions. The structure is composed of isolated $[\text{Co}(2)(\text{dien})_2]^{2+}$ and $[\text{Co}(1)(\text{tren})\text{SbS}_4]^-$ complexes and $\frac{1}{2} \text{ H}_2\text{O}$ (Fig. 1). The $\text{Co}(2)^{2+}$ cation is octahedrally surrounded by two tridentate dien ligands in the *s-fac*-configuration. The $\text{Co}(2)$ -N bond lengths between 2.153(4) and 2.192(5) Å are in the range found in other Co amine compound [54–56]. The angles around $\text{Co}(2)^{2+}$ (Table 2) indicate a moderate distortion of the CoN_6 octahedron. In the anionic complex $[\text{Co}(1)(\text{tren})\text{SbS}_4]^-$ the $\text{Co}(1)^{2+}$ cation is in a trigonal bipyramidal geometry of four N atoms of the tren ligand and one S atom of the $[\text{SbS}_4]^{3-}$ anion (Fig. 1). Like in the pseudo-polymorph the $\text{Co}(1)$ -N bond in trans position to the $\text{Co}(1)$ -S(1) bond is longer (2.247(3) Å) than the remaining $\text{Co}(1)$ -N bonds (2.072(3) – 2.083(2) Å; Table 1). Such an elongation of a bond can be explained with the so-called *trans*-effect. The $\text{Co}(1)$ -S(1) bond at 2.3701(8) Å is in the range of data published in literature [54, 55]. The angles around the $\text{Co}(1)^{2+}$ cation suggest an appreciable distortion (Table 2). The Sb-S bond lengths and S-Sb-S angles are typical for a moderately distorted $[\text{Sb}(\text{V})\text{S}_4]^{3-}$ tetrahedron. The arrangement of the cations and anions in the unit cell is

very similar to that observed for the pseudo-polymorphic compound.

Figure 1. The $[\text{Co}(1)(\text{tren})\text{SbS}_4]^-$ (left) and the $[\text{Co}(2)(\text{dien})_2]^{2+}$ (right) complexes in compound **1**. Not all atoms are labeled.

Table 1. Selected technical details of data collection and results of the structure refinement of the title compounds.

	1	2
formula	$\text{C}_{20}\text{H}_{64}\text{Co}_3\text{N}_{14}\text{OS}_8\text{Sb}_2$	$\text{C}_{12}\text{H}_{38}\text{Co}_3\text{N}_8\text{OS}_6\text{Sb}_2$
MW / g mol^{-1}	1193.62	923.15
crystal system	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$
a / Å	29.378(3)	13.870(2)
b / Å	7.6643(4)	14.708(1)
c / Å	22.507(2)	14.700(2)
β / deg	115.39(1)	94.62(2)
V / Å ³	4578.3(7)	2989.0(4)
T / K	293	170
Z	4	4
D_{calc} / g cm^{-3}	1.732	2.105
μ / mm^{-1}	2.630	3.856
min/max transm.	0.629 / 0.732	0.0340 / 0.633
θ_{max} / deg	28.06	27.97
No. refl.	25442	30651
R_{int}	0.0375	0.0583
unique refl.	5490	7162
Refl. $[F_0 > 4\sigma(F_0)]$	4678	6159
parameter	242	290
$R_1^{[a]}$ $[F_0 > 4\sigma(F_0)]$	0.0345	0.0289
$wR_2^{[b]}$ [all data]	0.0949	0.0724
GOF	1.019	1.0002
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ / $e \text{ Å}^{-3}$	0.808, -0.840	0.777, -1.284

[a] $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$. [b] $wR_2 = [\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]]^{1/2}$.

The anions are grouped in pairs and form rods along [010] and [001]. The cations are arranged in a similar way with the difference that $[\text{Co}(2)(\text{dien})_2]^{2+}$ complexes and water molecules alternate along [001]. The main difference to the pseudo-polymorphic compound $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 4\text{H}_2\text{O}$ [63] is the hydrogen bonding pattern between the different constituents. An extended H-bonding network was observed in $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 4\text{H}_2\text{O}$ involving N, S and O atoms. Due to the lower water content in **1** the H-bonding interactions are less complex.

Fig. 2: Packing of the $[\text{Co}(1)(\text{tren})\text{SbS}_4]^-$ and the $[\text{Co}(2)(\text{dien})_2]^{2+}$ complexes in compound **1** with view along [010].

Table 2. Selected bond lengths (Å) and angles (°) for compound **1**. Estimated standard deviations are given in parentheses.

1		
2	Sb(1)-S(3)	2.3078(10)
3	Sb(1)-S(2)	2.3189(9)
4	Sb(1)-S(4)	2.3196(11)
5	Sb(1)-S(1)	2.3701(8)
6	Co(1)-S(1)	2.3637(9)
7	Co(1)-N(1)	2.247(3)
8	Co(1)-N(2)	2.072(3)
9	Co(1)-N(3)	2.079(3)
10	Co(1)-N(4)	2.083(2)
11	S(3)-Sb(1)-S(1)	106.24(4)
12	S(2)-Sb(1)-S(1)	110.77(3)
13	S(4)-Sb(1)-S(1)	110.04(4)
14	S(3)-Sb(1)-S(2)	110.04(4)
15	S(3)-Sb(1)-S(4)	113.30(5)
16	S(2)-Sb(1)-S(4)	106.50(4)
17	Co(1)-S(1)-Sb(1)	104.50(3)
18	N(4)-Co(1)-N(1)	79.30(10)
19	N(2)-Co(1)-S(1)	101.67(8)
20	N(3)-Co(1)-S(1)	100.81(8)
21	N(4)-Co(1)-S(1)	98.92(7)
22	N(1)-Co(1)-S(1)	178.19(8)
23	N(2)-Co(1)-N(3)	113.18(13)
24	N(2)-Co(1)-N(4)	120.52(12)
25	N(3)-Co(1)-N(4)	116.63(11)
26	N(2)-Co(1)-N(1)	79.62(11)
27	N(3)-Co(1)-N(1)	79.76(11)
28	Co(2)-N(11)	2.192(5)
29	Co(2)-N(12)	2.153(4)
30	Co(2)-N(13)	2.180(4)
31	N(12)-Co(2)-N(13)	81.03(14)
32	N(12)-Co(2)-N(11)	98.97(15)
33	N(12)-Co(2)-N(11)	98.59(12)
34	N(12)-Co(2)-N(11)	81.41(12)
35	N(13)-Co(2)-N(11)	89.54(11)
36	N(13)-Co(2)-N(11)	90.46(11)

37
38 The shortest O...O, O...S and O...N separations are 3.054,
39 3.471 and 3.722 Å respectively which are all significantly
40 longer than in [Co(dien)₂][Co(tren)SbS₄]₂·4H₂O and too
41 long for significant H-bonding interactions. Nevertheless,
42 the S atoms join neighbored cations and anions to form
43 layers in the (001) plane (see Table 3).

44
45 Table 3: Geometric parameters [Å, °] of the hydrogen bonds in
46 compound **1**.

47	D-H	d(H...A)	<DHA	d(D...A)	A
48	N2-H1N	2.565	151.25	3.382	S2
49	N2-H2N	2.595	155.87	3.436	S1
50	N3-H3N	2.824	140.19	3.563	S2
51	N3-H4N	2.562	147.45	3.356	S1
52	N4-H5N	2.663	135.23	3.362	S2
53	N4-H6N	2.600	162.17	3.468	S4
54	N11-H7N	2.580	148.25	3.379	S4
55	N11-H8N	2.897	141.83	3.647	S3
56	N12-H9N	2.638	148.26	3.436	S2
57	N13-H10N	2.818	159.38	3.674	S3
58	N13-H11N	2.578	167.59	3.462	S4

59
60 The second new compound {[Co(tren)]₂[CoSb₂S₆]}·H₂O
(**2**) crystallizes in the monoclinic space group *P*2₁/*c* (Table

1) with all atoms being located on general positions. The structure may be viewed as consisting of a central [CoSb₂S₆]⁴⁻ core acting as a bidentate ligand to two independent [Co(tren)]²⁺ complexes (Fig. 3). Alternatively one may describe the structure as two independent [Co(tren)SbS₃] complexes which are connected by a Co²⁺ cation. The Co(1)²⁺ and Co(3)²⁺ cations are each coordinated by four N atoms of the tren ligand and by one S atom of a [SbS₃] trigonal pyramid. Like in compound **1** the Co-N bonds in *trans*-position to the Co-S bond are longer than the remaining Co-N bonds (Table 4).

Fig. 3: Interconnection of the different constituents in the structure of {[Co(tren)]₂[CoSb₂S₆]}(**2**). Note that not all atoms are labeled.

The Sb-S bond lengths are between 2.3927(8) and 2.4332(8) Å as well as the angles S-Sb-S are typical for the [SbS₃]³⁻ anion [1-20]. The central Co(2)²⁺ cation is in a strongly distorted tetrahedral environment of four S atoms of the two independent [SbS₃] moieties with Co(2)-S bond lengths ranging from 3.452(8) to 2.3550(9) Å (Table 4). The angles S-Co(2)-S scatter from 95.26(3) to 120.63(3)° evidencing the severe distortion of the polyhedron. It can be assumed that the distortion is caused by the bulky [Co(tren)]²⁺ complexes not allowing a more relaxed [CoS₄] tetrahedron. The bidentate binding mode of the [SbS₃] pyramids to the Co(2)²⁺ cation leads to relative acute angles around S(2), S(3), S(5) and S(6) of about 86°. The compact arrangement of the different building units also affects the two [Co(tren)] environments. The *trans*-angles N(1)-Co(1)-S(1) and N(11)-Co(3)-S(6) deviate more from the ideal 180° than in compound **1** (see Table 4).

Table 4. Selected bond lengths [Å] and angles [deg] for compound **2**. Estimated standard deviations are given in parentheses.

Sb(1)-S(1)	2.4079(7)
Sb(1)-S(2)	2.4161(8)
Sb(1)-S(3)	2.4114(8)
Sb(2)-S(4)	2.4298(8)
Sb(2)-S(5)	2.4332(8)
Sb(2)-S(6)	2.3927(8)
S(1)-Sb(1)-S(3)	103.02(3)
S(1)-Sb(1)-S(2)	105.98(3)
S(3)-Sb(1)-S(2)	91.83(3)
S(6)-Sb(2)-S(4)	105.98(3)
S(6)-Sb(2)-S(5)	104.69(3)
S(4)-Sb(2)-S(5)	91.48(3)
Co(1)-N(1)	2.240(2)
Co(1)-N(2)	2.086(3)
Co(1)-N(3)	2.095(2)
Co(1)-N(4)	2.070(3)
Co(1)-S(1)	2.3500(9)
Co(2)-S(2)	2.3452(8)
Co(2)-S(4)	2.3398(8)
Co(2)-S(3)	2.3484(9)
Co(2)-S(5)	2.3594(9)
Co(3)-N(13)	2.080(3)
Co(3)-N(12)	2.096(2)
Co(3)-N(14)	2.099(2)

Co(3)-N(11)	2.254(3)
Co(3)-S(6)	2.3550(9)
N(4)-Co(1)-N(2)	119.12(11)
N(4)-Co(1)-N(3)	116.22(10)
N(2)-Co(1)-N(3)	115.12(11)
N(4)-Co(1)-N(1)	79.44(10)
N(2)-Co(1)-N(1)	79.82(10)
N(3)-Co(1)-N(1)	79.58(9)
N(4)-Co(1)-S(1)	104.96(8)
N(2)-Co(1)-S(1)	99.96(8)
N(3)-Co(1)-S(1)	95.98(7)
N(1)-Co(1)-S(1)	174.88(7)
S(4)-Co(2)-S(2)	116.84(3)
S(4)-Co(2)-S(3)	120.63(3)
S(2)-Co(2)-S(3)	95.26(3)
S(4)-Co(2)-S(5)	95.66(3)
S(2)-Co(2)-S(5)	119.50(3)
S(3)-Co(2)-S(5)	110.61(3)
N(13)-Co(3)-N(12)	118.26(11)
N(13)-Co(3)-N(14)	113.77(11)
N(12)-Co(3)-N(14)	117.86(10)
N(13)-Co(3)-N(11)	79.49(10)
N(12)-Co(3)-N(11)	79.38(9)
N(14)-Co(3)-N(11)	79.04(10)
N(13)-Co(3)-S(6)	103.41(8)
N(12)-Co(3)-S(6)	102.21(7)
N(14)-Co(3)-S(6)	96.34(8)
N(11)-Co(3)-S(6)	175.29(7)

The $\{[\text{Co}(\text{tren})]_2[\text{CoSb}_2\text{S}_6]\}$ units are stacked along [1-10] to form rods with several intermolecular N-H...S interactions. We note that there are also some intramolecular S...H distances which indicate hydrogen bonding interactions. In addition the S(5) and N(3) atoms have such H-bonding contacts to the O atom of the water molecule (Table 5).

Figure 4. Arrangement of $\{[\text{Co}(\text{tren})]_2[\text{CoSb}_2\text{S}_6]\}$ moieties and H_2O molecules in compound 2.

Table 5. Selected geometric parameters [\AA , $^\circ$] for the hydrogen bonds in compound 2.

D-H	d(H...A)	<DHA	d(D...A)	A
N2-H2N	2.829	137.25	3.559	S3
N3-H3N	2.70	145.84	3.500	S2
N3-H4N	2.133	146.69	2.945	O1
N4-H5N	2.494	160.80	3.376	S2
N4-H6N	2.425	173.46	3.341	S1
N12-H7N	2.724	145.24	3.519	S1
N12-H8N	2.868	135.54	3.583	S3
N12-H8N	2.877	136.97	3.605	S5
N13-H9N	2.429	162.29	3.318	S4
N13-H10N	2.725	144.28	3.513	S6
N14-H11N	2.719	153.84	3.568	S4
N14-H12N	2.594	169.28	3.502	S3
O1-H1O1	2.533	165.56	3.353	S5
O1-H2O1	2.544	170.02	3.374	S5

Conclusions

Changing the synthesis conditions we were able to synthesize a pseudo-polymorph of the recently published compound $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 4\text{H}_2\text{O}$ [63]. Compound 1 and the latter compound crystallize in different space groups which can be explained by the very different hydrogen bonding networks in the two structures. The geometric parameters in the two polymorphs are very similar and also the arrangement of the two different complexes is nearly identical. The second compound presents a new and hitherto never observed heterometallic $[\text{CoSb}_2\text{S}_6]$ core as main structural feature. Until now such heterometallic building units were only observed for Mn^{2+} like in $[\text{Mn}(\text{tren})]_2[\text{Mn}_2\text{Sb}_4\text{S}_{10}]$ where the $[\text{Mn}_2\text{Sb}_4\text{S}_{10}]$ core contains two edge-sharing $[\text{MnS}_4]$ tetrahedra [58], or in $[\text{Mn}(\text{tren})]_4\text{Mn}_2\text{Sb}_4\text{S}_{12}$ where two $[\text{MnS}_4]$ tetrahedra are joined by two $[\text{SbS}_3]$ pyramids [61]. A further surprise is the fact that one Co^{2+} cation prefers a S^{2-} environment whereas the other two Co^{2+} ions are surrounded by N and S atoms. In the syntheses of compound 2 the amines supplied are in a large excess compared to sulfur. Hence we can exclude that a deficiency of ligand atoms is responsible for the formation of the $[\text{CoS}_4]$ tetrahedral unit. The results of the present synthetic work encourage us to further explore the chemistry of thiometallates using amine mixtures.

Experimental Section

Sample synthesis

Both compounds were prepared applying Co, Sb and S in the 1:1:3 mmol ratio. A mixture of 0.4 mL tren, 2.6 mL dien and 1 mL water was used solvent and structure directing molecules. The slurries were heated either in Teflon lined steel autoclaves or in thin glass tubes placed in the steel autoclaves between 110 and 140 $^\circ\text{C}$ for varying reaction times. After the reaction the autoclaves were cooled to room temperature and the reaction products were filtered off and washed with water and ethanol. Both compounds are stable on air for a long time. $[\text{Co}(\text{dien})_2][\text{Co}(\text{tren})\text{SbS}_4]_2 \cdot 0.5 \text{H}_2\text{O}$ was obtained at 110 $^\circ\text{C}$ as orange needles (yield approx. 50 % based on Co, Sb, and S) grown on not reacted starting material. $\{[\text{Co}(\text{tren})]_2[\text{CoSb}_2\text{S}_6]\} \cdot \text{H}_2\text{O}$ crystallized as green needles (yield: 44 % based on Co, Sb, and S) at temperatures above 110 $^\circ\text{C}$.

For chemical analysis and X-ray powder diffractometry the crystals were manually separated.

CHNS analysis: compound 1: C 19.95, H 5.57, N 15.79, S 20.81 %. calc.: C 20.31, H 5.30, N 16.38, S 21.29 %; compound 2: C 15.25, H 4.25, N 11.26, S 19.25 %. calc.: C 15.61, H 4.15, N 12.14, S 20.38 %.

Crystal structure determination

The data were measured using an imaging plate diffraction system (IPDS-1) with Mo- K_α -radiation from STOE & CIE. The structure solution was performed with direct methods using SHELXS-97 and structure refinement was performed against F^2 using SHELXL-97 [64, 65]. A numerical absorption correction was applied using X-Red and X-Shape. All non-hydrogen atoms were refined with anisotropic displacement parameters. All C-H and most of the N-H hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters using a riding model. The O-H H atoms of the water

molecule in both compounds and the N-H H atom in compound 1 were located in difference maps, their bond lengths set to ideal values and finally they were refined using a riding model. In 1 three carbon atoms of the tren molecule are disordered and were refined using a split model. Details of the structure determination are given in Table 1.

CCDC- 733932 (1) and CCDC-733933 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

Acknowledgments

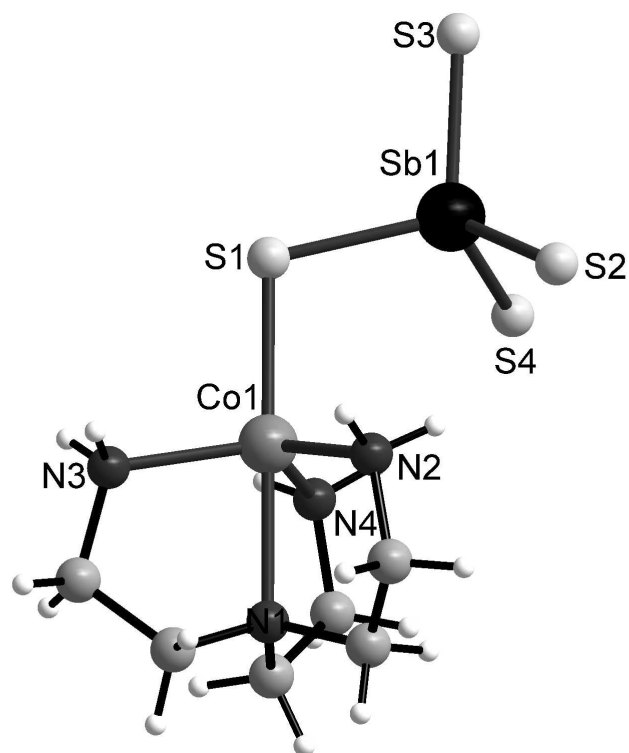
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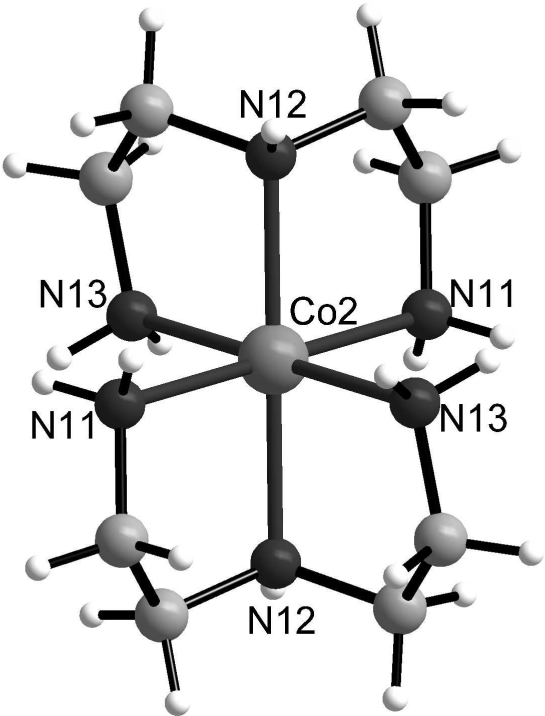
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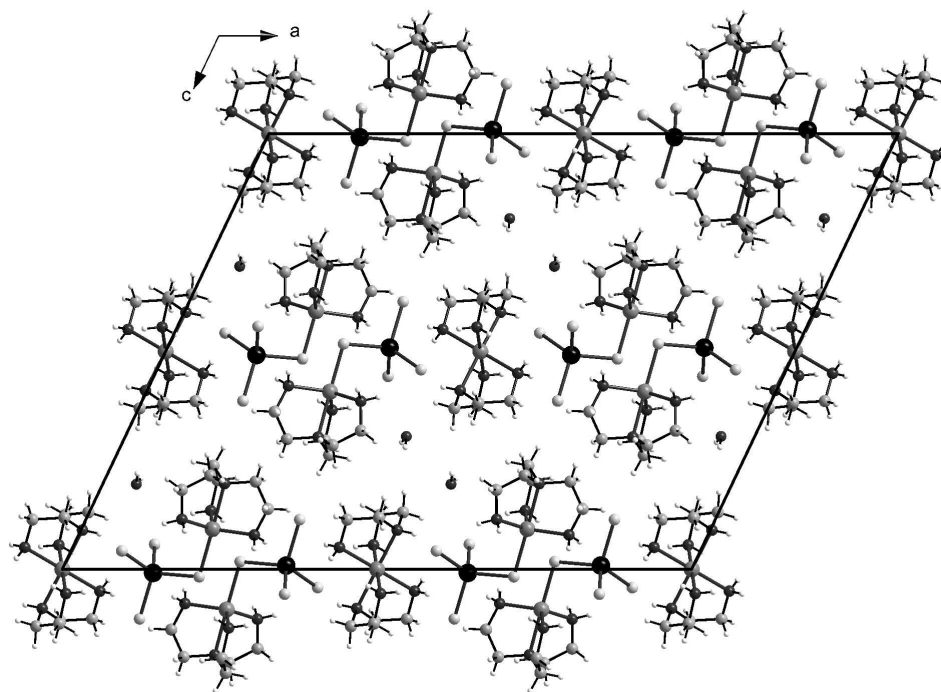
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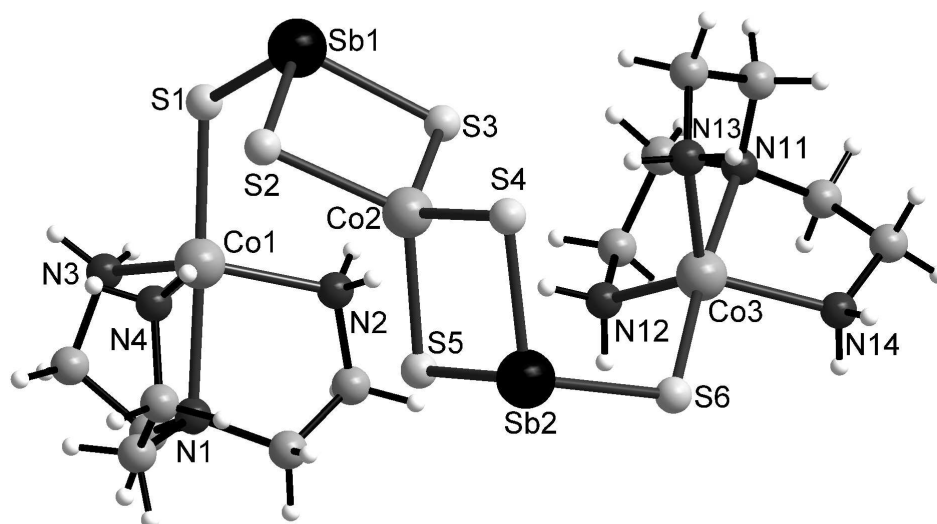
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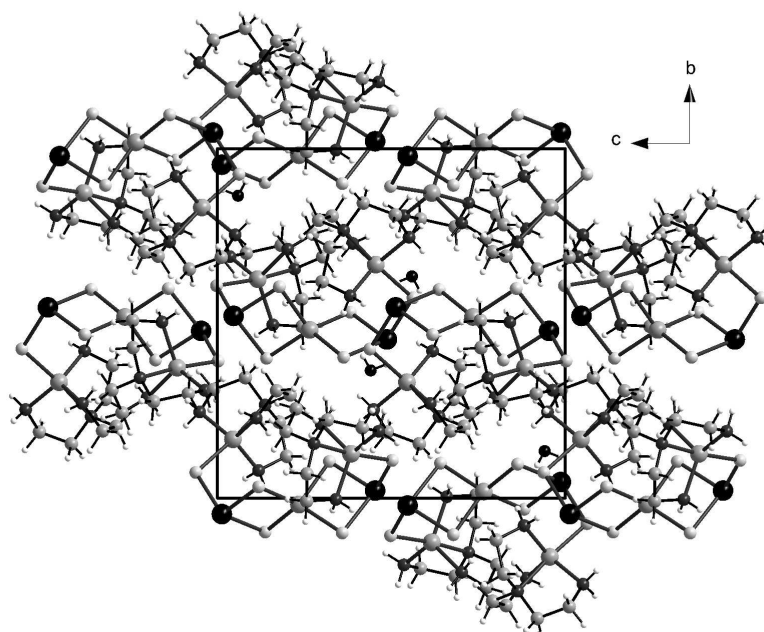
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