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Six new tin–sulfur containing compounds obtained under solvothermal conditions

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During explorative solvothermal syntheses six new compounds containing either the $[Sn_2S_6]^{4-}$ or the $[SnS_4]^{4-}$ anion were obtained and structurally characterized: $[Ni(1,2\text{-dach})_3]_2Sn_2S_6\cdot 4H_2O$ (**1**) (1,2-dach = trans-1,2-diaminocyclohexane), o-$\{[Ni(tepa)]_2Sn_2S_6\}$ (**2**) (tepa = tetraethylenepentamine), $[Ni(peha)]_2Sn_2S_6\cdot H_2O$ (**3**) (peha = pentaethylenehexamine), $[Ni(aepa)]_2Sn_2S_6$ (**4**) (aepa = N-2-aminoethyl-1,3-propandiamine), $[Co(dien)]_2Sn_2S_6$ (**5**) (dien = diethylenetriamine), and $\{[Mn(trien)]_2SnS_4\}$ (trien = triethylenetetramine). In all compounds in-situ formed transition metal amine complexes act as charge compensating ligands or are bound to the thiostannate anions. Compound **2** is an orthorhombic polymorph of a recently published monoclinic compound. In compound **6** the very rare $[Mn_2N_8S_2]$ bi-octahedron is observed as main structural motif. This compound contains a one-dimensional chain which was also observed in a pseudo-polymorphic compound. The structures of all compounds are characterized by an extended hydrogen bonding network between S atoms of the anions and the H atoms of the amine ligands and/or water molecules.

1. Introduction

During the past years a large variety of thiometalates were synthesized under solvothermal conditions. The structural chemistry of the thiometalates of main group elements exhibits remarkable differences. While the thioantimonate and thioarsenate chemistry is dominated by the trigonal $[SbS_3]^{3-}$ resp. $[AsS_3]^{3-}$ pyramid and condensation products of this building unit [1], thioindates and thiogermanates as well as thiostannate structures mainly contain $[MS_4]^{4-}$ tetrahedra (M = In, Ge, Sn), and higher hierarchical building units generated by interconnection of the tetrahedra [2]. An often observed structural building unit in thiostannates is the $[Sn_2S_6]^{4-}$ bi-tetrahedron being either present as isolated anion or directly connected to transition metal complexes [3]. But compared to the large number of $[Sn_2S_6]^{4-}$ or $[SnS_4]^{4-}$ containing compounds, compounds with higher hierarchical building blocks are relatively rare and examples are $[Sn_2S_5]^{2-}$ [4], $[Sn_3S_7]^{2-}$ [5], $[Sn_4S_9]^{2-}$ [6], $[Sn_4S_{10}]^{4-}$ [7], $[Sn_5S_{12}]^{4-}$ [8], $[Sn_3S_8]^{4-}$ [9], and $[SnS_3]^{2-}$ [[3a], [10]]. Comprehensive overviews about the structural diversity of main group thiometalates were published in several review articles [1,2a,2b,11].

A challenge in thiometalate chemistry is the integration of transition metal cations into the anionic frameworks. While Mn^{2+} easily form bonds to both N and S atoms [2k,5c,12] cations like Ni^{2+} or Co^{2+} must be forced to form bonds to the thiometalate anion. A strategy is to apply an amine like tetraethylenepentamine or tris(2-aminoethyl)amine which does not saturate the coordination requirements of the cations leaving sites free for bond formation to S atoms [3c,3j,13]. Recently we observed that such a synthetic trick is not necessary and the usage of Fe^{2+} with the bidentate amine trans-1,2-diaminocyclohexane afforded formation of a three-dimensional thioantimonate [14]. We also observed in the field of polyoxovanadate chemistry which are also prepared under solvothermal conditions that the hexadentate amine N-2-aminoethyl-1,3-propandiamine may act only as a pentadentate ligand for Co^{2+} and Ni^{2+} leaving a coordination site free for bond formation at the metal centers [15], or can generate three-dimensional thiometalate networks [16]. The in-situ formed $[Ni(dien)_2]^{2+}$ complex is a versatile structure directing molecule being able to force crystallization of thioantimonates exhibiting different dimensionalities of the inorganic framework [17]. Finally the tetradentate ligand triethylenetetramine is able to connect neighboured transition metal ions yielding a layered thioantimonate [12c]. Based on all these

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observations we systematically studied whether these amines generate new thiostannates in the presence of the cations Ni^{2+}, Co^{2+} and Mn^{2+}. During these investigations we obtained six new compounds of which five feature the $[Sn_2S_6]^{4-}$ anion and one the $[SnS_4]^{4-}$ tetrahedron which acts as bidentate ligand.

2. Experimental section

2.1. Syntheses

2.1.1. General

All chemicals were purchased and used without further purifications. All compounds were prepared under solvothermal conditions in Teflon-lined steel autoclaves (inner volume 30 mL) or glass tubes (inner volume 11 mL). The crystalline products were filtered off, washed with water and ethanol or acetone and dried in vacuum. The reaction products were separated manually and the homogeneity of the crystalline part was checked by X-ray powder diffraction (see Supporting Information) and elemental analysis.

2.1.2. Synthesis of $[Ni(1,2\text{-dach})_3]_2Sn_2S_6 \cdot 4H_2O$ (**1**)

88.10 mg (1.5 mmol) Ni, 118.70 mg (1 mmol) Sn and 128.90 mg (4 mmol) S with 5 mL of trans-1,2-diaminocyclohexane ($C_6H_{14}N_2$; 99%) were reacted in a Teflon-lined steel autoclave. The mixture was heated at 110 °C for 5 d. The yield of violet needles was about 30% based on Sn. Elemental analysis, results in %: found: C 31.9, H 7.1, N 12.0; calculated: C 31.4, H 7.3, N 12.2.

2.1.3. Synthesis of o-$[Ni(tepa)]_2Sn_2S_6$ (**2**)

47.50 mg (0.20 mmol) $NiCl_2 \cdot 6H_2O$, 45.10 mg (0.20 mmol) $SnCl_2 \cdot 2H_2O$ and 16.03 mg (0.50 mmol) S with 2 mL of tetraethylenepentamine (tepa, $C_8H_{23}N_5$; 98%) and 0.5 mL H_2O were reacted in a Teflon-lined steel autoclave. The mixture was heated at 160 °C for 24 h. The yield of the violet crystals was about 40% based on Sn. Elemental analysis, results in %: found: C 21.4, H 5.1, N 15.9; calculated: C 20.8, H 5.0, N 15.1.

2.1.4. Synthesis of $[Ni(peha)]_2Sn_2S_6 \cdot H_2O$ (**3**)

To 40.60 mg (0.18 mmol) $SnCl_2 \cdot 2H_2O$, 38.03 mg (0.16 mmol) $NiCl_2 \cdot 6H_2O$ and 19.88 mg (0.62 mmol) S in a glass tube were added 2.44 mL pentaethylenehexamine (peha, $C_{10}H_{28}N_6$, 98%) and 0.5 mL H_2O. The mixture was heated at 160 °C for 25 h. The yield of violet crystals of **3** was about 40% based on Sn. Elemental analysis, results in %: found: C 23.9, H 5.8, N 16.3; calculated: C 23.3, H 5.9, N 16.3.

2.1.5. Synthesis of $[Ni(aepa)]_2Sn_2S_6$ (**4**)

61.9 mg (1.05 mmol) Ni, 121.7 mg (1.03 mmol) Sn and 131.9 mg (4.11 mmol) S in 2 mL N-2-aminoethyl-1,3-propandiamine (aepa, $C_5N_3H_{15}$, 97%) were reacted for 17 d at 130 °C in a Teflon-lined steel autoclave. The yield of the violet crystals was very low and only about a few percent based on Sn.

2.1.6. Synthesis of $[Co(dien)]_2Sn_2S_6$ (**5**)

66.8 mg (0.25 mmol) of $[Co(NH_3)_6]Cl_3$, 29.8 mg (0.25 mmol) Sn and 23.9 mg (0.75 mmol) S in 2 mL diethylenetriamine (dien, $C_4H_{13}N_3$, 98%) were reacted for 7 d at 140 °C. The yield of the yellow crystals was about 30% based on Sn. Elemental analysis, results in %: found: C 20.7, H 5.6, N 17.1; calculated: C 20.0, H 5.5, N 17.5.

2.1.7. Synthesis of $\{[Mn(trien)]_2SnS_4\}$ (**6**)

126.7 mg (0.64 mmol) $MnCl_2 \cdot 4H_2O$, 38.7 mg (0.33 mmol) Sn and 41.1 mg (1.28 mmol) S, 57.7 mg (0.32 mmol) 1,10-phenanthroline (phen, $C_{12}H_8N_2$, 99%) in 2 mL of triethylenetetramine (trien, $C_6H_{18}N_4$; 98%) were reacted in a glass tube. The mixture was heated at 160 °C for 72 h. The yield of the green–yellow crystals was about 30% based on Sn. Elemental analysis, results in %: found: C 22.5, H 5.6, N 17.3; calculated: C 22.2, H 5.6, N 17.3. The role of phen for the formation of **6** is not clear but attempts to prepare **6** without phen were not successful.

2.2. Structure determination

The intensity data for the compounds were collected using an STOE Imaging Plate Diffraction System IPDS-1 for compound **1**, **4**, **5** and **6** and IPDS-2 for compound **2** and **3** with Mo-K_α radiation. For all compounds a numerical absorption correction was performed. The structures were solved with direct methods using the program Shelxs-97 [18] and the refinements were done against F^2 with Shelxl-97 [19]. For most non-hydrogen atoms anisotropic displacement parameters were used. The hydrogen atoms were positioned with idealized geometry and were refined using a riding model. The O–H H atoms were located in difference map, their bond lengths were set to ideal values and finally they were refined using a riding model. However, the difference map shows several possible peaks for O–H H atoms in **1** and therefore, it can be assumed that some of them are disordered. In compound **1** and **5** some C atoms of one amine ligand are disordered (s.o.f. = 0.9:0.10 in **1** and 0.65:0.35 in **6**) and were refined using a split model and isotropic displacement parameters for the atoms of lower occupancy in compound **1**. In compound **3** the position of the water molecule is only half occupied. Selected refinement results are summarized in Table 1.

Structural data have been deposited in the Cambridge Crystallographic Data Centre as publication no. CCDC 996371 (**1**), CCDC 996372 (**2**), CCDC 996373 (**3**), CCDC 996374 (**4**), CCDC 996375 (**5**) and CCDC 996376 (**6**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (mail: deposit@ccdc.ca.ac.uk).

2.3. Spectroscopic characterizations

All samples were characterized with different spectroscopic techniques and the results are presented in the Supporting Information.

Raman spectra were recorded with a Bruker IFS 66 Fourier transform Raman spectrometer (wavelength: 541.5 nm) in the region from 100 to 3500 cm^{-1}. UV/Vis spectroscopic investigations were carried out at room temperature using an UV–Vis–NIR two-channel spectrometer Cary 5 from Varian Techtron Pty., Darmstadt. The optical properties of the compounds were investigated by analysing the UV/Vis reflectance spectra of the powdered samples (with $BaSO_4$ powder used as reference material). MIR spectra (450–3000 cm^{-1}) were recorded with an ATI Mattson Genesis spectrometer.

3. Results and discussion

3.1. Synthetic aspects

The syntheses were originally started using always an identical ratio of 1:1:3 mmol for the educt sources transition metal:tin:sulfur. Because there are no strict rules at hand what reaction parameter must be altered to afford crystallization of a new compound, the different parameters were changed until a crystalline material was obtained suitable for single crystal analysis. In the next step the synthesis parameters are varied to increase the yield of the desired product. As can be seen from the synthesis protocols different reaction conditions were required for the different compounds. Interestingly, we were not able to prepare Ni^{2+} compounds