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Solvothermal Synthesis, Crystal Structure Determination, and Properties of the Thioantimonate $[Ph_4P]_2[Sb_6S_{10}]$

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Summary. The reaction of elemental antimony with elemental sulfur and $[Ph_4P]Br$ in an aqueous solution of neopentanediamine under solvothermal conditions yields yellow needles of the new thioantimonate(III) $[Ph_4P]_2[Sb_6S_{10}]$. The structure consists of $[Ph_4P]^+$ cations and infinite one-dimensional anionic $(Sb_6S_{10}{}^{2-})_n$ chains running along the crystallographic a axis. The chains are composed of 10-membered Sb_5S_5 rings with alternating Sb and S atoms and separated by the tetraphenylphosphonium cations. Upon heating the compound decomposes in two distinct steps, starting at about 100°C. The final product was identified by X-ray powder diffractometry as Sb_2S_3.

Keywords. Thioantimonates(III); Solvothermal synthesis; Single crystal structure, Physical properties.

Introduction

Compared to the classical high temperature route, the low reaction temperatures applied in solvothermal syntheses retain thiometallate or polychalcogenide building blocks which can act as precursor molecules for the construction of molecular or extended structures with new and attractive architectures. The fast growth of experimental work in this field during the last few years stems from the interest to prepare new materials with useful electrical, optical, or ion-exchange properties [1]. New materials with relatively open networks of interconnected thiometallates have been synthesized on the basis of thioantimonates [2], thiostannates [3], and thiogermanates [4], using the solvothermal technique.

It is well known that thioantimonates(III) show a variable coordination chemistry with a pronounced tendency to enhance the coordination number from 3 up to 6. Hence, SbS_x units are attractive building blocks for the construction of new compounds. Another interesting feature of the thioantimonates(III) is the pronounced tendency to condensate, and the linkage of SbS_x polyhedra *via* common corners and/or edges results in the formation 1-dimensional chains, 2-dimensional layers, or 3-dimensional framework structures. A large number of thioantimonates(III) has been prepared *via* the classical high temperature route

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[5, 6], solvo- or ammonothermal syntheses [7], or by reacting Sb with alkaline polychalcogenide melts [8]. Several new compounds have been prepared using large organic salts or amines as templates [9]. Very recently we started to explore the possibility of creating novel structures by combining transition metals with SbS_x units using large organic cations as templates. Applying solvothermal conditions we prepared the first layered manganese(II)thioantimonates(III) [10]. In addition, depending on the reaction conditions and the counterion involved, new thioantiomonates(III) with molecular [11] or extended structures [12] were obtained.

In the present contribution we report the synthesis, structural characterization, and physicochemical properties of the new thioantimonate(III) $[Ph_4P]_2[Sb_6S_{10}]$.

Results and Discussion

Yellow needles of $[Ph_4P]_2[Sb_6S_{10}]$ were obtained by reacting $[Ph_4P]Br$, Sb, and S in a molar ratio of 1:3:5 in an aqueous solution of neopentanediamine (40%) under solvothermal conditions at 403 K. The yield was about 60% based on antimony.

$[Ph_4P]_2[Sb_6S_{10}]$ crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell (Table 1). The structure is built up of isolated $[Ph_4P]^+$ cations and anionic one-dimensional $(Sb_6S_{10}^{2-})_n$ chains running along the the *a* axis. The fundamental units of the anionic chains are SbS_3 pyramids (see Fig. 1). Five SbS_3 pyramids (Sb(1) to Sb(5)) are joinded *via* common edges to form a 10-membered Sb_5S_5 heteroring. Two S atoms of the $Sb(6)S_3$ pyramid and a common corner between the $Sb(5)S_3$ and $Sb(3)S_3$ moieties fuse the Sb_5S_5 heteroring to the next ring. Alternatively, the anionic chain may be viewed as being composed of fused Sb_5S_5 rings because the corner-linkage of the first 10-membered ring produces a second Sb_5S_5 ring. Another description of the structure is based on corner-linked SbS_3 pyramids (Sb(1), Sb(2), Sb(6) and Sb(3), Sb(4), Sb(5)) forming two independent 1-dimensional Sb_3S_5 anionic chains running parallel to the *a* axis. The two chains are joined into the final Sb_6S_{10} unit by corner-sharing.

The anionic part of the structure is similar to that reported for $Sb_3S_5 \cdot N(C_3H_7)_4$ [13], as is evidenced by projecting the anionic parts onto each other. A weighted root mean square deviation of only 0.0651 Å was found, indicating that the shape and size of the counterion has no significant influence onto the anionic part of the structure.

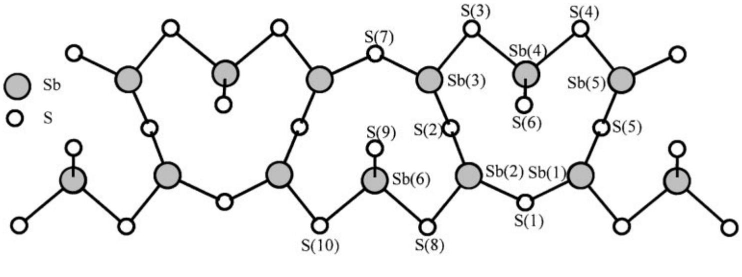

Fig. 1. View of the $[Sb_6S_{10}]^{2-}$ anionic chain together with the numbering scheme

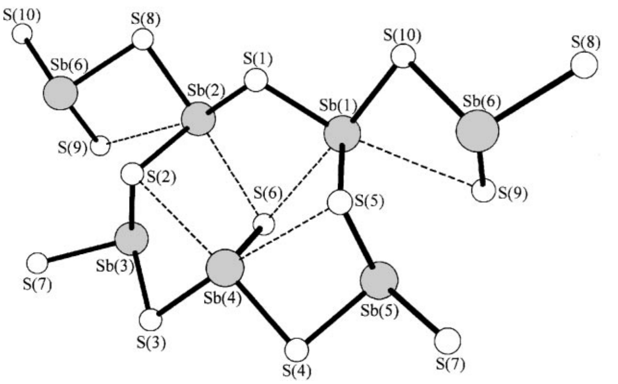

Fig. 2. Short (full lines) and long (dotted lines) Sb-S distances; only the secondary Sb-S distances of Sb(1), Sb(2), and Sb(4) are shown

The Sb atoms are in approximately pyramidal coordination of 3 sulfur atoms with Sb-S distances ranging from 2.391(2) to 2.481(2) Å. These distances are typical for Sb-S single bonds and agree well with data reported in the literature [2]. The Sb atoms are about 1.3 Å above the triangle of S atoms. It is very common that the environment of Sb(III) is completed by additional sulfur atoms at clearly longer distances (Table 2). If all Sb-S distances up to 3.5 Å are considered, the antimony atoms are surrounded by 5 S atoms. Including the lone-pair of the Sb atoms, the resulting polyhedra can be described as ψ-SbS_5-octahedra (Fig. 2). The stereochemical activity of the Sb $5s^2$ lone pair (LEP) is related with the loss of sphericity of the $5s^2$ electron distribution. The activity of the LEP is seen in the Sb-S discrepancies and the coordination number. For the title compound it can be concluded that the LEP is not very active.

The $[Ph_4P]^+$ cations separate the chains, and interchain interaction is not possible. The closest interchain distance is 6.8 Å.

The tetraphenylphosphonium cations in $[Ph_4P]_2[Sb_6S_{10}]$ form pairs with a sixtuple embracement which is the most frequently occurring supramolecular motif for $[Ph_4P]^+$ cations. The interpenetration of the cations leads to interactions between the three phenyl rings of each cation. The phenyl groups are located around a centre with a *pseudo*-S_6 symmetry. The shortest intermolecular distance between the phosphorous centres in these pairs of 6.569(4) Å is in the normal range of 5.7 to 6.9 Å reported in the literature [14]. The $[Ph_4P]^+$ cations are arranged in a way that channels are formed accommodating the anionic chains.

Thermal Properties

The thermal stability of the compound was investigated by TG measurements in an argon atmosphere. As can be seen from the TG curve, $[Ph_4P]_2[Sb_6S_{10}]$ decomposes in two steps starting at about 100°C (Fig. 3). The total experimental weight loss amounts to 34.96%. After the DTA/TG experiment the product was identified as Sb_2S_3 using X-ray powder diffraction. However, the calculated weight loss of 39.9% for the removal of the two tetraphenylphosphonium species is significantly

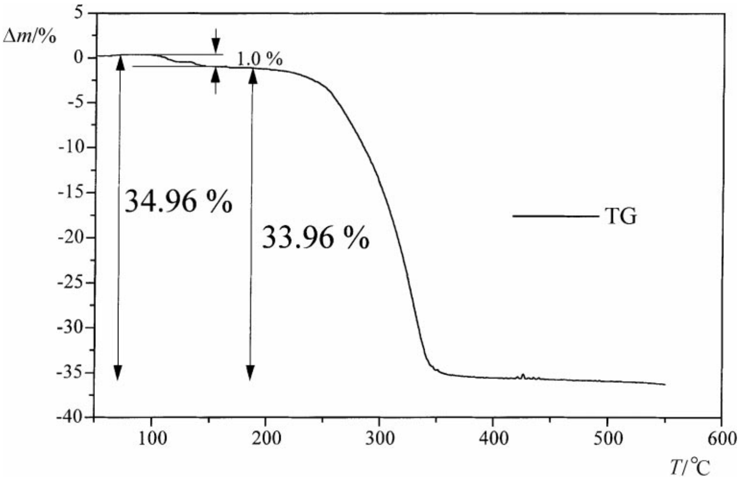

Fig. 3. TG curve of $[Ph_4P]_2[Sb_6S_{10}]$

higher than the experimental value. Spectroscopic investigations clearly demonstrate that the product contains no residues of Ph_4P^+. May be the product of the heat treatment contains no single phase, and the second product cannot be detected by X-ray powder diffraction.

Table 1. Technical details of X-ray data acquisition and selected refinement results for $[Ph_4P]_2[Sb_6S_{10}]$

a/Å	10.390(2)
b/Å	16.002(3)
c/Å	18.246(3)
$\alpha/^\circ$	93.65(2)
$\beta/^\circ$	105.06(1)
$\gamma/^\circ$	103.67(2)
V/Å^3	2821.5(9)
Z	2
Molecular weight (g/mol)	1729.84
μ/mm^{-1}	3.292
Space group	P$\bar{1}$ (IT-No.: 2)
Density (calc) [g/cm^3]	1.917
$\lambda(\mathrm{Mo} - K_\alpha)$/Å	0.7107
2Θ-range	$3^\circ \leq 2\Theta \leq 52^\circ$
Data collected	11246
Unique data	10824
Data used ($I > 2.0\sigma(I)$)	8101
R_{int}/%	1.95
Min./max.transmission	0.338/0.394
$\Delta\rho$/e/Å^3	0.54/−0.55
R for 8101 ($I > 2.0\sigma(I)$)	0.0253
wR_2 for all	0.0616
Goodness of fit	1.450

Experimental

Synthesis

Sb, S, and $[Ph_4P]Br$ (molar ratio 3:5:1) were reacted in $4\,cm^3$ of an aqueous solution of neopentanediamine (40% (v/v)) in teflon lined steel autoclaves at 403 K for 5 days, yielding yellow needles of $[Ph_4P]_2[Sb_6S_{10}]$, a yellow powder, and a grey powder which was identified as Sb_2S_3. The yield of $[Ph_4P]_2[Sb_6S_{10}]$ is about 60% based on antimony.

Crystal structure determination

$[Ph_4PBr]_2[Sb_6S_{10}]$; molecular weight: 1729.84; orange needles; crystal size: $0.05\times0.05\times0.5\,mm^3$; STOE AED 4-circle diffractometer ($T = $ RT), MoK_α radiation, graphite monochromator, *psi* scan absorption correction; structure solution with SHELXS-86 [15], structure refinement against F^2 using SHELXL-93 [16]; 595 parameters, $w = l/(\sigma^2(F_o^2) + (0.0308 \cdot P)^2)$. All heavy atoms were refined using anisotropic displacement parameters. All hydrogen atoms were positioned with idealized geometry and refined isotropically using the riding model. Technical details of data acquisition and some selected refinement results are summarised in Table 1. Interatomic bond lengths and selected angles are given in Table 2.

Table 2. Selected interatomic distances (Å), long Sb···S contacts (Å), and angles ($\circ$) for $[Ph_4P]_2[Sb_6S_{10}]$

Sb(1)-S(1)	2.4473(11)	Sb(4)-S(6)	2.3850(12)
Sb(1)-S(10)	2.4591(12)	Sb(4)-S(4)	2.4864(11)
Sb(1)-S(5)	2.4674(11)	Sb(4)-S(3)	2.4920(11)
Sb(2)-S(1)	2.4610(11)	Sb(5)-S(7)	2.4468(11)
Sb(2)-S(8)	2.4686(12)	Sb(5)-S(5)	2.4702(11)
Sb(2)-S(2)	2.4750(11)	Sb(5)-S(4)	2.4714(11)
Sb(3)-S(7)	2.4433(12)	Sb(6)-S(9)	2.3910(12)
Sb(3)-S(2)	2.4768(11)	Sb(6)-S(8)	2.4906(11)
Sb(3)-S(3)	2.4806(11)	Sb(6)-S(10)	2.4960(12)
Sb(1)-S(6)	3.213(2)	Sb(1)-S(9)	3.506(2)
Sb(2)-S(6)	3.210(2)	Sb(2)-S(9)	3.434(2)
Sb(3)-S(6)	3.112(2)	Sb(3)-S(9)	3.490(2)
Sb(4)-S(2)	3.228(2)	Sb(4)-S(5)	3.194(2)
Sb(5)-S(6)	3.509(2)	Sb(5)-S(9)	3.161(2)
Sb(6)-S(2)	3.196(2)	Sb(6)-S(5)	3.223(2)
S(1)-Sb(1)-S(8)	88.54(4)	S(7)-Sb(5)-S(4)	89.33(4)
S(1)-Sb(1)-S(5)	97.59(4)	S(5)-Sb(5)-S(4)	94.03(4)
S(8)-Sb(1)-S(5)	93.57(4)	S(9)-Sb(6)-S(8)	98.05(4)
S(1)-Sb(2)-S(10)	89.86(4)	S(9)-Sb(6)-S(10)	96.88(4)
S(1)-Sb(2)-S(2)	97.22(4)	S(8)-Sb(6)-S(10)	96.19(4)
S(10)-Sb(2)-S(2)	94.05(4)	Sb(1)-S(1)-Sb(2)	103.25(4)
S(7)-Sb(3)-S(2)	98.28(4)	Sb(2)-S(2)-Sb(3)	93.61(4)
S(7)-Sb(3)-S(3)	88.83(d)	Sb(3)-S(3)-Sb(4)	91.86(4)
S(2)-Sb(3)-S(3)	93.48(4)	Sb(5)-S(4)-Sb(4)	92.17(4)
S(6)-Sb(4)-S(4)	97.39(4)	Sb(1)-S(5)-Sb(5)	93.71(4)
S(6)-Sb(4)-S(3)	98.64(4)	Sb(3)-S(7)-Sb(5)	101.68(4)
S(4)-Sb(4)-S(3)	97.60(4)	Sb(1)-S(8)-Sb(6)	92.91(4)
S(7)-Sb(5)-S(5)	96.70(4)	Sb(2)-S(10)-Sb(6)	91.69(4)

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 139848. Copies of the data can be obtained free of change on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: +44-(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Thermal investigations

Thermal investigations were performed on a Netzsch 429 DTA-TG measurement device. The samples were heated in Al_2O_3 crucibles with a rate of $2\,K \cdot min^{-1}$ up to 450°C and purged in an argon stream of approximately $50\,cm^3 \cdot min^{-1}$.

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