



Synthesis and properties of $[\text{NR}_4]_3[\text{SbS}_4]$ ($\text{R} = \text{Me}, \text{Et}, n\text{-Pr}, n\text{-Bu}$) and the crystal structures of $[\text{N}(n\text{-Bu})_4]_3[\text{SbS}_4] \cdot 6\text{H}_2\text{O}$ and $[\text{N}(n\text{-Bu})_4]_3[\text{Sb}(\text{S}_2\text{O}_3)_3] \cdot 2\text{THF}$

Rhys P. King, William Levason, Gillian Reid*

School of Chemistry, University of Southampton Highfield, Southampton SO17 1BJ, U.K.



ARTICLE INFO

Article history:

Received 26 November 2022

Revised 3 January 2023

Accepted 4 January 2023

Available online 6 January 2023

ABSTRACT

The tetra-alkylammonium tetrathioantimonate(V) salts, $[\text{NR}_4]_3[\text{SbS}_4]$ ($\text{R} = \text{Me}, \text{Et}, n\text{-Pr}, n\text{-Bu}$), have been prepared in basic solution from aqueous $[\text{NR}_4]\text{OH}$, sulfur and Sb_2S_3 , and characterised by microanalysis, IR, Raman, ^1H and ^{121}Sb NMR spectroscopy. The crystal structure of $[\text{N}(n\text{-Bu})_4]_3[\text{SbS}_4] \cdot 6\text{H}_2\text{O}$ shows the presence of the tetrahedral $[\text{SbS}_4]^{3-}$ anion (disordered over two sites), and also connected through an H-bonding network with the lattice water molecules. The alkylammonium salts are soluble in water and, with the exception of $[\text{NMe}_4]_3[\text{SbS}_4]$, are also soluble in weakly polar organic solvents, including halocarbons and MeCN. Solubility increases with the R group $\text{Me} < \text{Et} < n\text{-Pr} < n\text{-Bu}$, making the $[\text{N}(n\text{-Bu})_4]_3[\text{SbS}_4]$ a convenient reagent to explore coordination chemistry or materials applications for which water as the solvent is not suitable. $[\text{N}(n\text{-Bu})_4]_3[\text{Sb}(\text{S}_2\text{O}_3)_3] \cdot 2\text{THF}$, the first thiosulfate complex of a p-block element, was produced by slow decomposition of $[\text{N}(n\text{-Bu})_4]_3[\text{SbS}_4]$ in THF solution in the presence of the $[\text{NH}(n\text{-Bu})_3]\text{Cl}$ (as a source of H^+), confirming the instability of the $[\text{SbS}_4]^{3-}$ anion in acidic media, and the crystal structure of $[\text{N}(n\text{-Bu})_4]_3[\text{Sb}(\text{S}_2\text{O}_3)_3] \cdot 2\text{THF}$ shows a trigonal antiprismatic coordination geometry with a S_3O_3 donor set at the antimony(III) centre in the anion.

© 2023 The Author(s). Published by Elsevier B.V.

This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>)

1. Introduction

The complex anions of the heavier p-block elements of groups 15 and 16 have attracted interest as ligands for transition metals and synthons for semi-conductor materials [1,2]. One of the best known is the tetrathioantimonate ion, $[\text{SbS}_4]^{3-}$, which is usually met as the sodium salt, $\text{Na}_3[\text{SbS}_4] \cdot 9\text{H}_2\text{O}$ (Schlippe's salt) [3,4]. The heavier alkali metal salts are also known, and all contain the tetrahedral $[\text{SbS}_4]^{3-}$, viz $\text{K}_3[\text{SbS}_4]$ [5], $\text{K}_3[\text{SbS}_4] \cdot 4.5\text{H}_2\text{O}$ [6], $\text{Rb}_3[\text{SbS}_4]$ [7] and $\text{Cs}_3[\text{SbS}_4]$ [8]. Examples of coordination complexes include, $[\{\text{Mn}(\text{bipy})_2\}_2(\mu\text{-SbS}_4)][\text{ClO}_4]$ [9], $[\text{Co}_3(\text{SbS}_4)_2(\{14\}\text{janeN}_4)_3] \cdot 2\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$ ($\{14\}\text{janeN}_4 = 1,4,8,11\text{-tetraazacyclotetradecane}$) [10], and $[\text{Zn}_3(\text{SbS}_4)(\{14\}\text{janeN}_4)_3] \cdot 2\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$ [11], made from the transition metal cation and $\text{Na}_3[\text{SbS}_4]$ in water or aqueous MeCN. Antimony sulfides, including Schlippe's salt and Sb_2S_3 , the latter an important V-VI semi-conductor material, have also attracted much recent attention for application in electronics, for example in Na-ion batteries

and solar cells, not least because they contain elements that are both earth-abundant and have relatively low toxicities [2,12,13]. We have recently demonstrated anodic electrodeposition of amorphous Sb_2S_3 from $\text{Na}_3[\text{SbS}_4] \cdot 9\text{H}_2\text{O}$ in an aqueous sodium citrate electrolyte [14]. These Sb_2S_3 films can be crystallised by annealing in a sulfur-rich atmosphere and were shown to display interesting solid-state RRAM (resistive random-access memory) characteristics [14].

Most of the reported synthetic approaches to form metal complexes incorporating $[\text{SbS}_4]^{3-}$ as a ligand have, of necessity, used water or highly polar organic solvents, such as 1,2-diaminoethane, since the sodium tetrathioantimonate(V) salt is very poorly soluble in most organic media. However, many transition metal complexes are decomposed by water and hence there is interest in exploring the preparation and properties of other salts of $[\text{SbS}_4]^{3-}$ that can be used in organic media.

Here we report the synthesis and properties of several new tetra-alkylammonium tetrathioantimonate salts, which are soluble in low polarity solvents, such as halocarbons and nitriles. Crystal structures of $[\text{N}(n\text{-Bu})_4]_3[\text{SbS}_4] \cdot 6\text{H}_2\text{O}$ and a by-product, $[\text{N}(n\text{-Bu})_4]_3[\text{Sb}(\text{S}_2\text{O}_3)_3] \cdot 2\text{THF}$ are also described.

* Corresponding author.

E-mail address: G.Reid@soton.ac.uk (G. Reid).

2. Experimental

2.1. Reagents and methods

Tetralkylammonium hydroxides, sulfur and Sb_2S_3 were obtained from Sigma-Aldrich and used as received. CH_2Cl_2 and MeCN were dried by distillation from CaH_2 and THF from Na-benzophenone ketyl and were stored over activated molecular sieves. NMR solvents were also stored over 4 Å sieves.

IR spectra were recorded as Nujol mulls between CsI plates using a Perkin Elmer Spectrum 100 spectrometer over the range of 4000–200 cm^{-1} . Raman spectra on both solids and solutions were obtained using a Renishaw InVia confocal Raman microscope coupled with a 785 nm laser diode, with a rated power of 500 mW. NMR spectra were recorded using a Bruker AVII 400 spectrometer. ^1H NMR spectra were referenced to residual solvent resonances, and ^{121}Sb NMR spectra to $[\text{N}(\text{n-Bu})_4][\text{SbCl}_6]$. Microanalytical measurements were performed by London Metropolitan University.

2.2. X-Ray crystallography

Single crystals were grown as described in the Discussion section. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum ($\lambda = 0.71073$ Å) rotating anode generator with HF Vari-max optics (100 μm focus) with the crystal held at 100 K, or a Rigaku UG2 goniometer equipped with a Rigaku hybrid pixel array detector (Hypix 6000 HE detector) mounted at the window of an FR-E+ SuperBright molybdenum ($\lambda = 0.71073$ Å). Structure refinements were performed with either SHELX(S/L)97 or SHELX(S/L)2013 through Olex225 [15] and were mostly straightforward, with H atoms bonded to C atoms placed in calculated positions using default C–H distances and refined using a riding model. CCDC reference numbers for the crystallographic information files in cif format are: 2221883 ($[\text{N}(\text{n-Bu})_4]_3[\text{Sb}(\text{S}_2\text{O}_3)_3] \cdot 2\text{THF}$) and 2221884 ($[\text{N}(\text{n-Bu})_4]_3[\text{SbS}_4] \cdot 6\text{H}_2\text{O}$)

2.3. Synthesis of $[\text{NMe}_4]_3[\text{SbS}_4]$

A round bottom flask was charged with $[\text{NMe}_4]\text{OH}$ (4.83 g, 53.0 mmol), Sb_2S_3 (1.0 g, 3.00 mmol) and sulfur (0.56 g, 18.0 mmol). To this, 100 mL of distilled water was added and the mixture was refluxed for 2 h. The resulting solution was filtered and the solvent was removed *in vacuo* to afford a yellow solid, which was washed with water (1 \times 20 mL), *i*-PrOH (3 \times 20 mL) and diethyl ether (3 \times 20 mL), before the solid was dried *in vacuo*. Yield 2.51 g (90%). Required for $\text{C}_{12}\text{H}_{36}\text{N}_3\text{S}_4\text{Sb}$ (472.40): C, 30.2; H, 7.7; N, 8.9. Found: C, 30.1; H, 7.8; N, 8.7%. IR (Nujol/ cm^{-1}): $\nu = 385$ s (Sb-S). Raman (cm^{-1}): $\nu = 382$, 365 (Sb-S). ^1H NMR (D_2O , 298 K): $\delta = 3.16$ (s, Me). ^{121}Sb NMR (D_2O , 298 K): $\delta = 1033$.

2.4. Synthesis of $[\text{NEt}_4]_3[\text{SbS}_4]$

A round bottom flask was charged with Sb_2S_3 (1.00 g, 3.00 mmol) and sulfur (0.560 g, 18.0 mmol). To this 10 mL of water was added, followed by 12.4 g of $[\text{NEt}_4]\text{OH}$ in a 35% w/w solution in water. This mixture was stirred under reflux for 16 h, before the solution was filtered to remove particulates and the solvent was removed *in vacuo* to afford a yellow solid. This was dissolved in 1:1 H_2O :THF and filtered and the solvent was then removed *in vacuo*. The resultant solid was washed with hexane (3 \times 10 mL) and dried *in vacuo*. Yield 2.84 g (75%). Required for $\text{C}_{24}\text{H}_{60}\text{N}_3\text{S}_4\text{Sb}$ (640.70): C, 45.0; H, 9.4; N, 6.6. Found: C, 44.6; H, 8.8; N, 6.4. IR

(Nujol/ cm^{-1}): $\nu = 386$ s (Sb-S). Raman (cm^{-1}): $\nu = 384$, 357 (Sb-S). ^1H NMR (D_2O , 298 K): $\delta = 1.11$ (tt, $^3J_{\text{HH}} = 7.30$, $J_{\text{NH}} = 2.00$ Hz, [3H], Me), 3.10 (d, $^3J_{\text{HH}} = 7.30$, [2H], CH_2). ^{121}Sb NMR (D_2O , 298 K): $\delta = 1035$.

2.5. Synthesis of $[\text{N}(\text{n-Pr})_4]_3[\text{SbS}_4]$

A round bottom flask was charged with Sb_2S_3 (1.00 g, 3.00 mmol) and sulfur (0.560 g, 18.0 mmol). To this, 10 mL of water was added and then 29 mL of a 1 M solution of $[\text{N}(\text{n-Pr})_4]\text{OH}$ was added. The mixture was then refluxed for 8 h, before particulates were removed by filtration and the filtrate taken to dryness *in vacuo*. The oily solid was then stirred with CH_2Cl_2 (50 mL) under anhydrous conditions, the solvent was then removed *in vacuo* to yield an orange solid which was dried. Yield: 1.49 g (31%). Required for $\text{C}_{36}\text{H}_{84}\text{N}_3\text{S}_4\text{Sb}$ (809.01): C, 53.4; H, 10.5; N, 5.2. Found: C, 53.1; H, 10.2; N, 5.2. IR (Nujol/ cm^{-1}): $\nu = 382$. Raman (cm^{-1}): 382 (Sb-S). ^1H NMR (D_2O , 298 K): $\delta = 0.79$ (t, $^3J_{\text{HH}} = 7.30$ Hz, [12H], Me), 1.52 (m, [8H], CH_2), 3.00 (m, [8H], CH_2). ^{121}Sb NMR (D_2O , 298 K): $\delta = 1035$.

2.6. Synthesis of $[\text{N}(\text{n-Bu})_4]_3[\text{SbS}_4]$

A round bottom flask was charged with Sb_2S_3 (0.500 g, 1.47 mmol) and sulfur (0.283 g, 8.84 mmol). To this, 10 mL of distilled water was added, followed by $[\text{N}(\text{n-Bu})_4]\text{OH}$ (10.5 g) as a 40% w/w solution, causing the solution to turn red. The mixture was refluxed for 2 h, leading to clear dark yellow solution, which was filtered to remove unreacted starting material. The filtrate was concentrated to dryness and THF (100 mL) was added, resulting in an orange/yellow solution and a white precipitate. The precipitate was removed by filtration and the filtrate was concentrated to ca. 5 mL and stored at -18 °C for three days. This led to the growth of light yellow crystals, which were collected by filtration and washed with hexane (3 \times 10 mL), dried *in vacuo* and stored at -18 °C. Yield: 1.62 g (56%) Required for $\text{C}_{48}\text{H}_{108}\text{N}_3\text{S}_4\text{Sb}$ (977.31): C, 59.0; H, 11.1; N, 4.3. Found: C, 58.8; H, 11.0; N, 4.2. IR (Nujol/ cm^{-1}): $\nu = 385$ m (Sb-S). Raman (cm^{-1}): $\nu = 379$, 365 (Sb-S). ^1H NMR (D_2O , 298 K): $\delta = 1.00$ (t, $^3J_{\text{HH}} = 7.3$ Hz, [12H], Me), 1.40 (m, [8H], CH_2), 1.65 (m, [8H], CH_2), 3.20 (m, [8H], CH_2). ^{121}Sb NMR (D_2O , 298 K): $\delta = 1035$.

3. Results and discussion

Initially, the alkali-metal tetrathioantimonate(V) salts $\text{M}_3[\text{SbS}_4]$ ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) [4–8] were prepared by literature routes from Sb_2S_3 , S and MOH in aqueous solution. For convenience, details are given in the *Supplementary Information* along with the key spectroscopic data (Table 2). In order to test whether these salts could be used for the synthesis of coordination complexes in organic media or for non-aqueous electrodeposition of Sb_2S_3 , their solubilities were tested. While they were all found to be easily soluble in H_2O , they were very poorly soluble in common organic solvents such as CH_2Cl_2 and MeCN and were decomposed by alcoholic solvents. To overcome this problem, salts with different counter cations were synthesised. $[\text{NR}_4]^+$ cations are usually good candidates for solubilising inorganic anions in solvents such as CH_2Cl_2 [16]. Tetraalkylammonium salts of $[\text{SbS}_4]^{3-}$ have not been reported in the literature, and therefore synthetic routes were explored. Cation metathesis is commonly used to synthesise alkylammonium salts of thiometallates (e.g. $[\text{MoS}_4]^{2-}$ or $[\text{WS}_4]^{2-}$) [17], but in the thioantimonate systems, attempts at metathesis led to decomposition of the anion. However, it was found that replacing the alkali metal hydroxides in the original synthesis with alkylammonium hydroxides, allowed the direct formation of pure $[\text{NR}_4]_3[\text{SbS}_4]$ ($\text{R} = \text{Me}, \text{Et}, \text{n-Pr}, \text{n-Bu}$) salts in good yield (Scheme 1). They are anhydrous as prepared after drying in *high vacuo*, but readily take up water

Table 1
Crystallographic parameters^a.

Compound	[N(<i>n</i> -Bu) ₄] ₃ [SbS ₄]·6H ₂ O	[N(<i>n</i> -Bu) ₄] ₃ [Sb(S ₂ O ₃) ₃]·2THF
Formula	Sb ₅ O ₆ N ₃ H ₁₂₀ C ₄₈	Sb ₆ O ₁₁ N ₃ H ₁₃₆ C ₅₆
M. Wt.	1085.53	1329.68
Crystal System	cubic	monoclinic
Space Group (No)	Pa-3 (205)	P2 ₁ (4)
a/ Å	23.4660(10)	13.09156(12)
b/ Å	23.4660(10)	16.35499(17)
c/ Å	23.4660(10)	16.72949(6)
α/°	90	90
β/°	90	94.5028(9)
γ/°	90	90
U/ Å ³	12,922.95(17)	3567.93(6)
Z	8	2
μ(Mo-Kα)/ mm ⁻¹	0.596	0.613
F(000)	4736	1432
Total No Reflins	253,282	114,347
R _{int}	0.058	0.035
Unique Reflins	7617	24,509
No of parameters	223	674
Restraints	1	67
GOF	1.155	1.050
R ₁ , wR ₂ [I > 2σ(I)] ^b	0.065, 0.157	0.048, 0.123
R ₁ , wR ₂ (all data)	0.095, 0.182	0.053, 0.127

^a common items: T = 100 K; wavelength (Mo-Kα) = 0.71073 Å; θ(max) = 27.5°.

^b R₁ = Σ||F_o - |F_c||/Σ|F_o|; wR₂ = [Σw(F_o² - F_c²)²/ΣwF_o⁴]^{1/2}.

Table 2
Comparative spectroscopic data.

Compound	IR ν(Sb-S) / cm ⁻¹	Raman ν(Sb-S) / cm ⁻¹	δ(¹²¹ Sb) in D ₂ O / ppm
Na ₃ [SbS ₄]·9H ₂ O	390	378, 363	1033
K ₃ [SbS ₄]	382	382, 370	1034
Rb ₃ [SbS ₄]	385	387, 370	1033
Cs ₃ [SbS ₄]	392	395, 383, 368	1033
[NMe ₄] ₃ [SbS ₄]	385	382, 365	1033
[NEt ₄] ₃ [SbS ₄]	386	384, 357	1035
[N(<i>n</i> -Pr) ₄] ₃ [SbS ₄]	382	382	1035
[N(<i>n</i> -Bu) ₄] ₃ [SbS ₄]	385	379, 365	1035

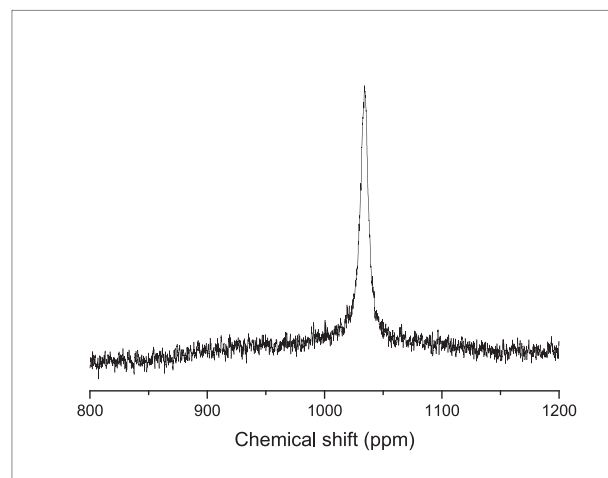
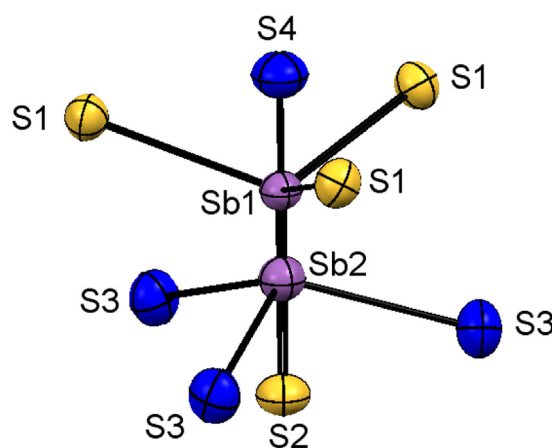
**Scheme 1.** Method for the preparation of the tetraalkylammonium tetrathioantimonate salts.

(evidence by their IR spectra), which can also be removed by further drying. The tetraalkylammonium salts are all soluble in water.

The tetraalkylammonium salts all have a peak characteristic of the [SbS₄]³⁻ anion in their IR spectra at 380–386 cm⁻¹, which can be assigned to the T₂ Sb-S stretching mode. The Raman spectra typically show two bands assigned as the T₂ and A₁ modes [18] (Table 2).

The salts were also studied by ¹²¹Sb NMR spectroscopy. ¹²¹Sb has a natural abundance of 57.3% with $\Xi = 23.93$ MHz, and a receptivity of 520 relative to ¹³C. It has a nuclear spin of 5/2 and a significant quadrupole moment (-0.53×10^{-28} m²), which means that resonances will only be observable in high symmetry environments. In lower symmetry environments, the non-zero electric field gradients present result in very fast relaxation and loss of the resonance [19,20]. The cubic (T_d) symmetry of the [SbS₄]³⁻ anion present in aqueous solutions of the alkali metal and tetraalkylammonium salts produces a broad resonance at $\delta \sim 1034$ in each case (Fig. 1).

Curiously, the [NR₄]₃[SbS₄] (R = Et, *n*-Pr, *n*-Bu) failed to exhibit ¹²¹Sb NMR spectra from solutions in CD₂Cl₂ although their solubilities are high. The probable explanation of this anomaly is that in weakly polar media some cation-anion association (ion-pairing) is present, and this causes a sufficient electric field gradient at the

**Fig. 1.** ¹²¹Sb NMR spectrum of [N(*n*-Bu)₄]₃[SbS₄] in D₂O at 298 K.**Fig. 2.** View of the structure of the [SbS₄]³⁻ anion disordered over two sites with the sulfur atoms associated with Sb1 in yellow (66% occupancy) and those associated with Sb2 in blue (33% occupancy). Selected bond lengths (Å) and angles (°) are: Sb1-S1 = 2.3251(9), Sb1-S2 = 2.3619(17), Sb2-S3 = 2.327(2), Sb2-S4 = 2.366(4), S1-Sb1-S1 = 110.91(2), S1-Sb1-S2 = 107.99(3), S3-Sb1-S3 = 111.03(6), S3-Sb1-S4 = 107.87(6). Symmetry operations: (½+z, ½-x, 1-y), (½-y, 1-z, ½+x).

antimony nucleus to cause fast relaxation and loss of the resonance.

Crystals of [N*n*-Bu₄]₃[SbS₄] were grown from a saturated THF solution of the compound stored at -18 °C. The compound crystallised as the hexahydrate, [N(*n*-Bu)₄]₃[SbS₄]·6H₂O due to incorporation of adventitious water. The anions in the structure are disordered over two independent positions with both tetrahedra interpenetrating (Fig. 2). The sites are occupied in a 1:2 ratio. Each of the [SbS₄]³⁻ anions is surrounded by six H₂O molecules forming a hydrogen bonded network around the unit (Fig. 3), forming an 18-membered ring, including three sulfurs from the anion; three water molecules also interact with the remaining sulfur. It seems that (adventitious) water is needed to grow crystals suitable for X-ray diffraction, but the powder initially formed was confirmed to be anhydrous (evidenced by IR spectroscopy and elemental analysis) and this can be reformed by drying these crystals *in vacuo*. The antimony-sulfur bond lengths, d(Sb-S), are similar to those reported before for this anion (~ 2.33 Å) and the S-Sb-S angles are also similar to those reported (~ 109.23 °) [2,5,8].

Each of these [SbS₄]³⁻ units is encapsulated in an octahedron of [N(*n*-Bu)₄]⁺ cations (Fig. 4a), these octahedra are connected in a vertex-sharing fashion with a void at the centre of eight of these units remaining empty (Fig. 4b).

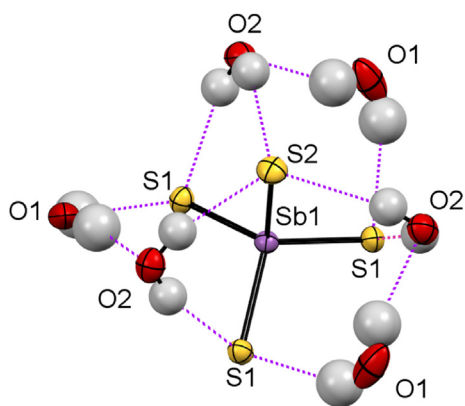


Fig. 3. View of the hydrogen bonding network involving the $[\text{SbS}_4]^{3-}$ anion (Sb1) in $[\text{N}(n\text{-Bu})_4]_3[\text{SbS}_4]\cdot 6\text{H}_2\text{O}$.

With several new tetraalkylammonium salts in hand, further solubility tests were undertaken. $[\text{NMe}_4]_3[\text{SbS}_4]$ has similar solubility to the alkali metal salts, in that it is not soluble in non-alcoholic organic solvents. However, the longer chain alkylammonium salts were found to be soluble in a variety of organic solvents, including CH_2Cl_2 and MeCN. Unsurprisingly, the tetrabutylammonium salt is soluble in the widest range of organic solvents, even including THF, in which none of the other salts had any appreciable solubility. Hence, this salt is expected to be the best candidate as a synthon for coordination chemistry.

Given the need for basic conditions during the syntheses, and the known instability of the alkali metal salts to acid, we were interested to establish if a solution of $[\text{N}(n\text{-Bu})_4]_3[\text{SbS}_4]$ and $[\text{NH}(n\text{-Bu})_3]\text{Cl}$ in THF (source of H^+) would be stable. A mixture of $[\text{N}(n\text{-Bu})_4]_3[\text{SbS}_4]$ and $[\text{NH}(n\text{-Bu})_3]\text{Cl}$ in THF was allowed to stand for ~ 3 days at -18°C , producing a few crystals of an Sb(III) reduction product, identified as the antimony(III) thiosulfate complex, $[\text{N}(n\text{-Bu})_4]_3[\text{Sb}(\text{S}_2\text{O}_3)_3]\cdot 2\text{THF}$ (Fig. 5) from its single crystal X-ray structure. The $(\text{S}_2\text{O}_3)^{2-}$ presumably results from a sequence of hydrolysis and oxidation reactions. This unexpected homoleptic thiosulfate complex is the first such complex with a p-block Lewis acid.

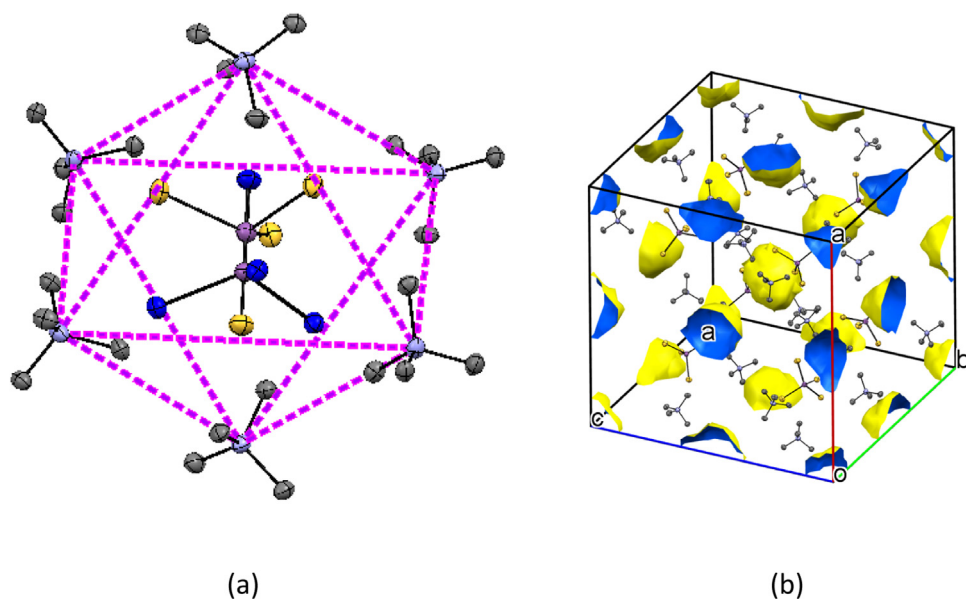


Fig. 4. (a) The $[\text{SbS}_4]^{3-}$ anions inside an octahedron of $[\text{N}(n\text{-Bu})_4]^+$ cations (carbon chain truncated at the first carbon and H atoms and H_2O omitted for clarity; purple dashed lines show the edges of the octahedron, not an interaction) (b) The unit cell of crystal showing the void space in the unit cell; the SbS_4 trianions are centred around $(0.25, 0.25, 0.25)$ and the 7 other related points. With the central void at $(0.5, 0.5, 0.5)$.

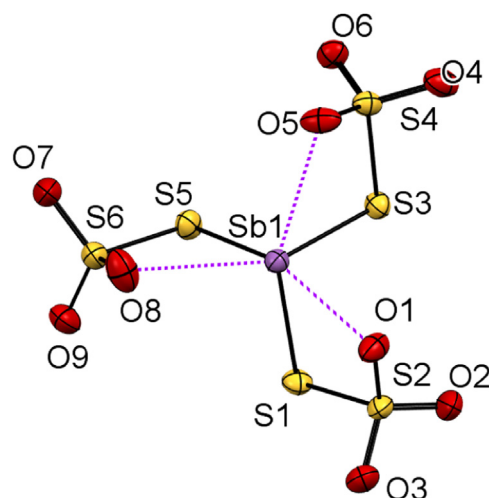


Fig. 5. The structure of the anion in $[\text{N}(n\text{-Bu})_4]_3[\text{Sb}(\text{S}_2\text{O}_3)_3]\cdot 2\text{THF}$ showing the atom labelling scheme. The ellipsoids are drawn at the 50% probability level and H atoms, THF molecules, and cations are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$) are: Sb1–S1 = 2.4654(10), Sb1–S3 = 2.4535(10), Sb1–S5 = 2.4521(10), Sb1 \cdots O1 = 2.709(3), Sb1 \cdots O5 = 2.818(3), Sb1 \cdots O8 = 2.913(4), S1–Sb1–S3 = 92.08(4), S3–Sb1–S5 = 90.89(4), S5–Sb1–S1 = 92.35(4).

In the $[\text{Sb}(\text{S}_2\text{O}_3)_3]^{3-}$ trianion, the thiosulfate ligands are primarily bound through the terminal sulfur atoms; the Sb–S bond distances are longer than those in $[\text{SbS}_4]^{3-}$. There are also three long Sb \cdots O interactions, the oxygens involved in these interactions are on the opposite face to the sulfurs completing a trigonal antiprismatic geometry.

4. Conclusions

A convenient synthesis for a new series of $[\text{NR}_4]_3[\text{SbS}_4]$ ($R = \text{Me}, \text{Et}, n\text{-Pr}, n\text{-Bu}$) salts, and their characterisation by NMR and vibrational spectroscopy and, for $R = n\text{-Bu}$, by a single crystal X-ray structure analysis, are described. Aside from the $[\text{Me}_4\text{N}]^+$ salt, they are soluble in a range of weakly coordinat-

ing, low polarity organic solvents, which may enable the synthesis of tetrathioantimonate(V) complexes with a wider range of transition metal and organometallic species beyond the small number of examples that is known at present, and especially where the metal species are intolerant of water. Like their alkali metal counterparts, the alkylammonium salts are somewhat reactive in acidic media. The unusual antimony(III) thiosulfate reduction product, $[N(n\text{-Bu})_4]_3[\text{Sb}(\text{S}_2\text{O}_3)_3]\cdot 2\text{THF}$, has been identified by its X-ray crystal structure.

Declaration of Competing Interest

The authors have no conflicts to declare.

CRediT authorship contribution statement

Rhys P. King: Conceptualization, Methodology, Writing – review & editing. **William Levason:** Conceptualization, Writing – review & editing. **Gillian Reid:** Conceptualization, Writing – review & editing.

Data availability

Data have been attached and CCDC numbers provided in manuscript.

Acknowledgments

We thank the EPSRC for funding through grants EP/P025137/1 and EP/N035437/1.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.molstruc.2023.134925](https://doi.org/10.1016/j.molstruc.2023.134925).

References

- [1] G.W. Drake, J.W. Kolis, The chemistry of mixed 15/16 main group clusters, *Coord. Chem. Rev.* 137 (1994) 131–178.
- [2] A. Bertrand, A. Paecklar, T. Barbier, F. Gascoin, Rapid synthesis process and characterization for high purity sodium thioantimonate nonahydrate, *Dalton Trans.* 51 (2022) 11340–11345.
- [3] F. von Schlippe, Schweiggers, *J. Chem. Phys.* 33 (1821) 320.
- [4] K. Mereiter, A. Preisinger, H. Guth, Hydrogen bonds in Schlippe's salt: refinement of the crystal structures of $\text{Na}_3\text{SbS}_4\cdot 9\text{H}_2\text{O}$ by X-ray diffraction and $\text{Na}_3\text{SbS}_4\cdot 9\text{D}_2\text{O}$ by neutron diffraction at room temperature, *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* 35 (1979) 19–25.
- [5] W. Bensch, P. Durichen, Crystal structure of a new modification of potassium tetrathioantimonate, $\beta\text{-K}_3\text{SbS}_4$, *Z. Kristallogr. - New Cryst. Struct.* 212 (1997) 95–96.
- [6] H. Meyer, K. Mereiter, Crystal structure of $\text{K}_3\text{SbS}_4\cdot 1/2\text{H}_2\text{O}$, *Monatsh. Chem.* 123 (1992) 515–520.
- [7] W. Bensch, P. Duerichen, Crystal structure of rubidium tetrathioantimonate(V), Rb_3SbS_4 , *Z. Kristallogr.* 211 (1996) 636.
- [8] W.W. So, B.R. Martin, P.K. Dorhout, Crystal structure of caesium tetrathioantimonate(V), Cs_3SbS_4 , *Z. Kristallogr. - New Cryst. Struct.* 217 (2002) 302.
- [9] C. Anderer, C. Näther, W. Bensch, Room temperature synthesis, crystal structure and selected properties of the new compound $[\text{Mn}_2(\text{bipy})_4\text{SbS}_4](\text{ClO}_4)$, *Z. Naturforsch. B.* 71 (2016) 395–401.
- [10] C. Näther, F. Danker, W. Bensch, Synthesis and crystal structure of poly[[di- μ_3 -tetrathioantimonato-tris(cyclam)cobalt(II)]] acetonitrile disolvate dihydrate] (cyclam = 1,4,8,11-tetraazacyclotetradecane), *Acta Cryst. E78* (2022) 270–274.
- [11] C. Näther, F. Danker, W. Bensch, Crystal structure of μ_3 -tetrathioantimonato-tris(cyclam)zinc(II)] tetrathioantimonate acetonitrile disolvate dihydrate showing Zn disorder over the cyclam ring planes (cyclam = 1,4,8,11-tetraazacyclotetradecane), *Acta Cryst. E78* (2022) 490–495.
- [12] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Research development on sodium-ion batteries, *Chem. Rev.* 114 (2014) 11636–11682.
- [13] M. Shimoda, M. Maegawa, S. Yoshida, H. Akamatsu, K. Hayashi, P. Gorai, S. Ohno, Controlling defects to achieve reproducibly high ionic conductivity in Na_3SbS_4 solid electrolytes, *Chem. Mater.* 34 (2022) 5634–5643.
- [14] A.G. Wallace, R.P. King, N. Zhelev, A.H. Jaafar, W. Levason, R. Huang, G. Reid, P.N. Bartlett, Anodic Sb_2S_3 electrodeposition from a single source precursor for resistive random-access memory devices, *Electrochim. Acta* 4321 (2022) 141162.
- [15] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.* 42 (2009) 339–341.
- [16] S. Thomas, D.E. Smith, V.K. Greenacre, Y.J. Noori, A.L. Hector, C.H. de Groot, G. Reid, P.N. Bartlett, Electrodeposition of MoS_2 from dichloromethane, *J. Electrochem. Soc.* 167 (2020) 106511.
- [17] M. Poisot, W. Bensch, S. Fuentes, G. Alonso, Decomposition of tetra-alkylammonium thiomolybdates characterised by thermoanalysis and mass spectrometry, *Thermochim. Acta* 444 (2006) 35–45.
- [18] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, 1986.
- [19] J. Mason, *Multinuclear NMR*, Plenum New York, 1987.
- [20] J. Emsley, *The Elements*, Oxford, 1989.