ORTHO-THIOBORATES AND ORTHO-SELENOBORATES: SYNTHESIS, STRUCTURE AND PROPERTIES OF Tl₃BS₃ AND Tl₃BSe₃*

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Summary

Tl₃BS₃ (1) and Tl₃BSe₃ (2) were prepared as black crystalline phases by reaction of stoichiometric amounts of the elements at 800 - 950 °C and subsequent annealing at 400 - 200 °C. They are the first orthothio- and orthoselenoborates which have been characterized. According to singlecrystal structure analyses, they contain trigonal planar BS₃³⁻ (B–S bond length 1.83 Å) and BSe₃³⁻ groups (B–Se bond length 1.95 Å). There are two structurally different thallium atoms in the structure with irregular 6 + 1- or 6 + 2-coordination by sulphur (selenium), the inert electron pair at Tl⁺ showing strong stereochemical activity. The crystal structures of 1 and 2 are isotypic to each other but not isotypic to any other M₃AB₃ structure. They are monoclinic, space group $P2_1/m$, with a = 5.444, b = 9.699, c =6.690 Å, $\beta = 98.13^{\circ}$ for 1; and a = 5.547, b = 10.099, c = 6.852 Å, $\beta =$ 97.59° for 2, Z = 2. Vibrational spectra, mass spectra and thermoanalytic results for 1 and 2 are reported.

1. Introduction

The development of appropriate methods for the synthesis and crystallization, together with systematic structural work, brought about considerable progress in the chemistry and structural chemistry of binary and ternary boron sulphides and selenides. Besides the layer-structured B_2S_3 [1-3], novel boron sulphides and selenides with a boron:chalcogen ratio of 1:2 were prepared which were identified structurally as porphin-like molecular B_8S_{16} [3-6] and as chain polymers $(BS_2)_n$ and $(BSe_2)_n$ [3, 5, 6]. In the glassy state their bonding and coordination remains largely unchanged [7]. Amongst ternary phases, tetrahedral BS_4 coordination has been shown to be present in the heavy atom thioborates $Ag_6B_{10}S_{18}$ [2, 3, 8] (which is an Ag^+ ionic

^{*}Dedicated to Professor Harald Schäfer on the occasion of his 75th birthday.

conductor), $Pb_4B_4S_{10}$ [3, 9, 10] and $TlBS_2$, as well as in $TlBS_3$, the first perthioborate with a known structure [3, 11, 12]. Analogous novel boron-selenium compounds are $TlBSe_2$ and $TlBSe_3$ [3, 12]. Compared with the binary phases which have trigonal planar BS₃ coordination these tetrahedral compounds are considerably stable towards nucleophilic attack by water or oxygen. Planar six-membered B_3S_3 rings with trigonal planar coordination around boron are present in the $B_3S_6^{3-}$ ions of $Na_3B_3S_6$ and $K_3B_3S_6$ [3, 9, 13] which are derivatives of metathioboric acid $H_3B_3S_6$ [14].

For the solid phases proposed to exist in the pseudobinary systems $Tl_2S-B_2S_3$ and $Tl_2S-B_2Se_3$, contradictory results are reported in the literature [15, 16]. We have now investigated the reaction conditions and have prepared and characterized a number of phases in both systems. As part of our results we report in the following the synthesis and properties of the two isotypic orthochalcogenoborates Tl_3BS_3 and Tl_3BSe_3 [11, 12]. They are the first thio- and selenoborates with mononuclear anions.

2. Preparation and properties

The synthesis of well-defined and highly pure binary and ternary boron-sulphur and boron-selenium compounds is difficult because of the high reactivity of the boron chalcogenides towards a variety of container materials at elevated temperatures. The fused silica tubes usually employed are attacked by boron sulfide and boron selenide at temperatures above 300-400 °C, with B-Si exchange and formation of silicon-sulphur(selenium) compounds resulting. For the synthesis of pure samples two methods were used: (i) the inner walls of the quartz glass ampoules were coated with glassy carbon by anaerobic pyrolysis of acetone vapour (see also ref. 15), or (ii) crucibles made of glassy carbon or boron nitride (100 mm length; cap/ outer/inner diameter, 18/12/5 mm) were furnished with a tight screw cap and used as sample containers. These were inserted into the outer fused silica tube. The inner walls of this outer tube were again coated with glassy carbon.

Generally, the reaction of Tl_2S or Tl_2Se with boron and sulphur(selenium) is to be preferred to the reaction of the elements or of the binary components. The following procedure was employed for the synthesis of pure, crystalline samples.

 Tl_3BS_3 (1): in a sealed and evacuated (10^{-4} bar) fused silica tube (volume 10 - 15 ml) according to (i), or in a carbon or boron nitride insert within such a tube according to (ii), stoichiometric amounts of well-dried Tl_2S , boron (5% excess, crystalline, 5 - 250 μ m) and sulphur (5% excess) were heated to 800 °C within 5 h and kept at this temperature for 6 h for complete reaction. The sample is than annealed for crystallization in a horizontal one-zone furnace with linear cooling from 400 to 200 °C within 240 h. 1 is also formed by annealing of glassy samples (see also ref. 7) of composition $Tl_4B_2S_5$ and $Tl_8B_2S_7$ which correspond to compositions of phases predicted from phase diagram investigations [16]. TlBS₂ was identified as a by-product in the first case, Tl_4S_3 was found in the second case.

 Tl_3BSe_3 (2): the selenoborate is prepared in a similar way with heating at 950 °C for 20 h and a longer annealing period of 800 h with linear cooling from 500 to 200 °C. Tl_3BSe_3 is also obtained as a crystalline annealing product from glassy samples of composition $TlBSe_2$ and $Tl_4B_2Se_5$ [16] with $TlBSe_3$ as a by-product in both cases.

Differential thermal analysis (DTA) investigations indicate that the reactions proceed in two steps: the formation of B_2S_3 and B_2Se_3 at temperatures of 450 - 650 °C and subsequent reaction at 700 - 900 °C of Tl₂S and Tl₂Se respectively with the binary boron chalcogenides.

 Tl_3BS_3 forms black polyhedral crystals. Tl_3BSe_3 is also black, with a more elongated shape. In contrast to the tetrahedrally coordinated phases $TlBS_2$, $TlBS_3$ and $TlBSe_3$ [3, 11, 12] which react only slowly with water and acids, Tl_3BS_3 and Tl_3BSe_3 are very sensitive to nucleophilic attack by traces of moisture at the trigonal boron and consequently have to be handled under dry inert gas.

The formation of Tl_3BS_3 is in accordance with the results of Chopin *et al.* [15]. However, it is at variance with the phase investigations of Kirilenko *et al.* [16] who did not observe this phase nor did they observe Tl_3BSe_3 in the quasi-binary system $Tl_2Se-B_2Se_3$. From chemical analysis there is no sign of any significant deviations from the stoichiometric compositions of 1 and 2.

Both 1 and 2 were investigated by DTA (1 bar argon, platinum crucible, 2 deg min⁻¹). For 1, an endothermic effect is observed between 240 and 315 °C caused by reversible incongruent melting. Under vacuum, sublimation (decomposition to Tl_2S and $TlBS_2$) starts at about 530 °C. For 2, the reversible endothermic incongruent melting effect at an argon pressure of 1 bar is observed between 270 and 360 °C. Decomposition and sublimation at 10^{-4} bar starts at 440 °C.

3. Crystal structure determination

The complete crystal structures of Tl_3BS_3 and Tl_3BSe_3 were determined from single-crystal X-ray diffraction data. The unit cells were found to be monoclinic with the cell constants given in Table 1; they were determined by least-squares refinement from the diffractometer coordinates of 24 highangle reflections. The space group $P2_1/m-C_{2h}^2$ (No. 11) was obtained from systematic extinctions (0k0 observed only with k = 2n) and from intensity statistics. The diffraction data were corrected empirically for absorption by intensity scans around the diffraction vectors of certain reflections, the minimum transmission factors being as low as 0.28 for Tl_3BS_3 .

The expression minimized in the full-matrix least-squares refinement was $\Sigma w(|F_0| - |F_c|)^2$; the refinement converged to conventional R values of 0.052 for Tl₃BS₃ and 0.058 for Tl₃BSe₃. Additional crystal data and details of the structure determination are given in Table 1. Scattering factors

TABLE 1

Tl₃BS₃ and Tl₃BSe₃: crystal data, details of the measurement and structure solution

	Tl_3BS_3		Tl_3BSe_3	
a (Å)	5.444(2)		5.547(2)	
b (Å)	9.699(3)		10.099(3)	
c(A)	6.690(2)		6.852(2)	
β (deg)	98.13(3)		97.59(3)	
V (Å ³)	349.7		380.5	
Space group		$P2_1/m$		
Z		2		
$d_{\mathbf{x}} (\text{g cm}^{-3})$	6.84		7.51	
$d_{\exp} (\text{g cm}^{-3})$	6.82(1)(6.75	[15])	7.47(2)	
Absorption coefficient (Mo K) (cm ⁻¹)	702		791	
Absorption correction		Empirical, ψ -scans		
Temperature (K)		295		
Crystal dimensions (mm)	$0.28 \times 0.24 \times$	0.15	0.46 imes 0.12 imes 0.14	
Diffractometer		SYNTEX P21		
Radiation		Mo Kα (λ = 0.71069 Å)		
Monochromator		graphite (parallel)		
Scan speed (deg min ^{-1})		4 - 30 (intensity- dependent)		
Scan mode/scan range		$\theta - 2\theta$ scan; $4^{\circ} < 2\theta < 54^{\circ}$		
Number of independent reflections	811		885	
Number of reflections with $I > 1.96\sigma(I)$	673		625	
Number of variables	26		33	
$R_1 = \Sigma(F_0 - F_c) / \Sigma F_0 $	0.052		0.058	
$R_{2} = \left[\sum w(F_{0} - F_{c})^{2} / \sum w F_{0} ^{2} \right]^{1/2}$	0.048		0.056	
Structure solution		Thallium atoms from <i>MULTAN</i> and from Patterson synthesis, sulphur and boron atoms from difference Fourier-maps		
Refinement Weighting scheme		Full-matrix least-squ selenium refined an (EXTL system) $w = [\sigma(F_0)^2 + (0.007) \sigma(F_0) = \sigma(I)/(2 F_0 L)$	pares, thallium and nisotropically $7 F_0 ^2]^{-1}$ (p)	

for neutral atoms including anomalous dispersion corrections were taken from ref. 17. The final atomic coordinates in the unit cell and the temperature parameters are shown in Table 2. The lists of final observed and calculated structure factors are available from the authors (B.K.).

4. Description of the structures and discussion

The crystal structures of Tl_3BS_3 and Tl_3BSe_3 are isotypic and consist of an arrangement of monomeric trigonal planar BS_3^{3-} (BSe_3^{3-}) anions

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TABLE 2

Atom	tom Position .			y/b	z/c	Biso
Tl_3BS_3						
Tl(1)	2(e)	0.8232(3)		0.2500	-0.0254(2)	1.89(5)
Tl(2)	4(f)	0.7298	(2)	0.5553(2)	0.3290(2)	2.05(4)
S(1)	2(e)	0.6772(21)		0.2500	0.4384(14)	1.72(12)
S(2)	4(f)	0.2461(15)		0.0858(7)	0.1722(14)	1.64(12)
В	2(e)	0.396(8)	0.2500	0.254(7)	2.0(8)
Tl_3BSe_3						
TI(1)	1) $2(e)$ 0.8088(4)		3(4)	0.2500	-0.0190(3)	2.80(5)
Tl(2)	4(f)	0.7322	2(3)	0.5582(2)	0.3327(2)	3.22(4)
Se(1)	2(e)	0.6911	.(8)	0.2500	0.4512(7)	2.59(9)
Se(2)	4(f)	0.2496	8(6)	0.0821(3)	0.1689(6)	2.47(6)
В	2(e)	0.399(8)		0.2500	0.254(7)	1.7(9)
	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
TI BS						
$T_{1}(1)$	2.45(7)	2.03(6)	0.77(6)	0.00	-0.03(6)	0.00
Tl(2)	3.06(6)	1.90(5)	1.06(5)	-0.63(4)	0.52(4)	-0.35(4)
Tl_3BSe_3						
Tl(1)	3.05(7)	2.94(7)	2.69(8)	0.00	0.59(7)	0.00
Tl(2)	3.49(5)	2.95(5)	3.52(6)	-0.07(7)	1.03(5)	-0.34(6)
Se(1)	2.54(16)	2.59(15)	2.39(18)	0.00	0.16(16)	0.00
Se(2)	2.46(11)	2.13(10)	2.75(14)	0.03(12)	0.18(11)	0.42(10)

Atomic coordinates and temperature parameters for Tl_3BS_3 and Tl_3BSe_3 with standard deviations

The anisotropic temperature factors are defined as $T = \exp\{-0.25(B_{11}h^2a^{*2} + ... + 2B_{23}klb^*c^*)\}$.

connected by Tl^+ cations. In Figs. 1 and 2, two projections of the unit cell for Tl_3BS_3 are shown; Fig. 3 shows a stereo pair of the packing diagram of the structure.

In the present structures, ortho-thioborate and ortho-selenoborate ions which are not linked to other boron polyhedra are observed for the first time. They are isoelectronic to the trithiocarbonate CS_3^{2-} and triselenocarbonate CSe_3^{2-} ions and they are centred by an sp²-hybridized boron atom. $(n-p)\pi$ bonding, similarly weak to that in boron trichloride and boron tribromide, is assumed for these ions. Within the limits of error (which are rather large for physical reasons) they have D_{3h} symmetry. In Tables 3 and 4 interatomic distances and bond angles are given for the TIBS₃ and Tl₃BSe₃ structures. The mean B-S bond distance of 1.83 Å in BS₃³⁻ and the B-Se value of 1.95 Å in BSe₃³⁻ are slightly longer than the average of those in other trigonal planar compounds. Known B-S bond lengths are 1.808 Å for B₂S₃ [1], 1.805 Å in (BS₂)_n [3, 6], 1.807 Å for B₈S₁₆ [4], 1.805 and



Fig. 1. Tl_3BS_3 : projection of the unit cell along the *c* axis. Fig. 2. Tl_3BS_3 : projection of the unit cell along the *b* axis.



Fig. 3. Stereo pair of the crystal structure of Tl_3BX_3 (X = S or Se).

1.798 Å for Na₃B₃S₆ and K₃B₃S₆ [3, 9]. Only two values of B-Se distances in BSe₃ groups are available for comparison. They are 1.934 Å for $(BSe_2)_n$ [3, 5, 6] and 1.932 Å for B(SeCH₃)₃ [18]. The slight elongation of the bond lengths in BS₃³⁻ and BSe₃³⁻ may be caused by the relatively high charge on these anions. The values of B(sp²)-S and B(sp²)-Se single bond distances can be estimated to be 1.88 Å [3] and 2.01 Å respectively, indicating still appreciable π bonding in BS₃³⁻ and BSe₃³⁻ (see also ref. 2).

All BS_3^{3-} and BSe_3^{3-} ions of the two structures are arranged parallel to each other with the normals of their planes very close to the [101] direction of the unit cell. In Fig. 4 (see also Tables 3 and 4) the coordination by

TABLE 3

Tl₃BS₃: interatomic distances (Å) and bond angles (deg) with standard deviations

$BS_{3}^{3-} anion B-S(1) B-S(2) B-S(2^{c}) S(1) S(2) S(1) S(2^{c}) S(2) S(2) S(2^{c}) S$	1.82 1.84 3.16 3.18	(4) (2) 8(11) 5(8)	S(1)-B-S(2) S(1)-B-S(2 ^c) S(2)-B-S(2 ^c)			120(2) 120(2)	
$\begin{array}{l} S(2) \dots S(2^{c}) \\ Thallium-sulphur \\ Tl(1) \dots S(1) \\ Tl(1) \dots S(1^{d}) \\ Tl(1) \dots S(2^{e}) \\ Tl(1) \dots S(2^{f}) \\ Tl(1) \dots S(2^{f}) \\ Tl(1) \dots S(2^{h}) \\ Tl(1) \dots S(2) \\ Tl(1) \dots S(2^{c}) \end{array}$	3.18 coordination 3.310(11) 3.563(11) 2.954(7) 3.407(6) 3.915(7)	$ \begin{array}{c} (Tl \dots S \ c \\ Tl(1)^* \\ S(1) \\ S(1^d) \\ S(2^e) \\ S(2^f) \\ S(2^g) \end{array} $	distances S(1 ^d) 153.5	< 4.8 Å) S(2 ^e) 81.7 120.0	S(2 ^f) 81.7 120.0 65.3	S(2 ^g) 103.8 73.1 70.2 133.8	S(2 ^h) 103.8 73.1 133.8 70.2 145.8
$\begin{array}{c} Tl(2) \dots S(1) \\ Tl(2) \dots S(1^{i}) \\ Tl(2) \dots S(1^{k}) \\ Tl(2) \dots S(2^{c}) \\ Tl(2) \dots S(2^{i}) \\ Tl(2) \dots S(2^{g}) \\ Tl(2) \dots S(2^{g}) \\ Tl(2) \dots S(2^{f}) \end{array}$	3.073(9) 3.446(8) 3.871(8) 3.021(6) 3.334(7) 3.387(7) 3.422(6)	Tl(2)*S(1)S(1i)S(2c)S(2i)S(2g)	S(1 ⁱ) 109.5	S(2°) 62.6 79.7	S(2 ⁱ) 80.7 55.7 107.3	S(2 ^g) 109.8 121.1 81.4 169.0	$S(2^{f})$ 78.2 165.1 115.2 115.1 65.4
$\begin{array}{l} Thallium-thallium\\ Tl(1) \dots Tl(2)\\ Tl(1) \dots Tl(2^c)\\ Tl(1) \dots Tl(2^l)\\ Tl(1) \dots Tl(2^l)\\ Tl(1) \dots Tl(2^m)\\ Tl(1) \dots Tl(2^n)\\ Tl(1) \dots Tl(2^p) \end{array}$	distances < 5 3.8 3.8 3.8	5.0 Å 72(2) 76(2) 74(2)		TI(2) TI TI(2) TI TI(2) TI	(2 ^q) (2 ^r) (2 ^s)	3. 3. 3.	624(2) 777(2) 777(2)
$\begin{array}{l} Intermolecular \ sulp \\ S(1) \ \dots \ S(2^e) \\ S(1) \ \dots \ S(2^f) \\ S(1) \ \dots \ S(2^i) \\ S(1) \ \dots \ S(2^b) \end{array}$	phur-sulphur 4.1 4.1	distance: 06(12) 55(9)	s < 5.0 Å	S(2) S(2 S(2) S(2	2 ^a) 2 ^h)	3. 4.	676(10) 186(10)
*Standard deviation Symmetry code: a: -x, -y, -z;	ons of the S b: -	. TI S -x + 1, -	bond ang $-y, -z + 1$	les: 0.2°. Sy l; c: x,	$-y + \frac{1}{2}, z$	ode:	

a. -x, -y, -z;b: -x + 1, -y, -z + 1;c: $x, -y + \frac{1}{2}, z;$ d: x, y, z - 1;e: x + 1, y, z;f: $x + 1, -y + \frac{1}{2}, z;$ g: $-x + 1, y + \frac{1}{2}, -z;$ h: -x + 1, -y, -z;i: $-x + 1, y + \frac{1}{2}, -z + 1;$ k: $-x + 2, y + \frac{1}{2}, -z + 1;$ l: $-x + 1, y - \frac{1}{2}, -z;$ m: -x + 1, -y + 1, -z;n: $-x + 2, y - \frac{1}{2}, -z;$ p: -x + 2, -y + 1, -z;m: -x + 2, -y + 1, -z + 1;r: $x, -y + \frac{3}{2}, z;$ s: -x + 1, -y + 1, -z + 1.

sulphur of the two crystallographically independent Tl^+ ions of the asymmetric unit is shown. In both cases the stereochemical activity of the lone

1 4 9 4 4

Tl₃BSe₃: interatomic distances (Å) and bond angles (deg) with standard deviations

$BSe_3^{3^-}$ anion B-Se(1) B-Se(2) B-Se(2 ^c) Se(1) Se(2) Se(1) Se(2 ^c) Se(2) Se(2 ^c)		1.97(4) 1.94(2) 3.371(5) 3.391(4)		Se(1)—B- Se(1)—B- Se(2)—B-	—Se(2) —Se(2 ^c) —Se(2 ^c)		119(2) 121(2)
Thallium-selenium $Tl(1) \dots Se(1)$ $Tl(1) \dots Se(1^d)$ $Tl(1) \dots Se(2^e)$ $Tl(1) \dots Se(2^f)$ $Tl(1) \dots Se(2^g)$ $Tl(1) \dots Se(2^h)$ $Tl(1) \dots Se(2)$ $Tl(1) \dots Se(2)$ $Tl(1) \dots Se(2^c)$	coordinati 3.371(5) 3.603(5) 3.111(4) 3.510(3) 3.900(4)	on (TlS Tl(1)* Se(1) Se(1 ^d) Se(2 ^e) Se(2 ^f) Se(2 ^g)	e distances Se(1 ^d) 158.6	< 5.0 Å) Se(2 ^e) 81.1 116.4	Se(2 ^f) 81.1 116.4 66.1	Se(2 ^g) 104.9 73.0 68.7 132.8	Se(2 ^h) 104.9 73.0 132.8 68.7 145.7
$\begin{array}{l} Tl(2) \dots Se(1) \\ Tl(2) \dots Se(1^{i}) \\ Tl(2) \dots Se(1^{k}) \\ Tl(2) \dots Se(2^{c}) \\ Tl(2) \dots Se(2^{c}) \\ Tl(2) \dots Se(2^{l}) \\ Tl(2) \dots Se(2^{g}) \\ Tl(2) \dots Se(2^{f}) \end{array}$	$\begin{array}{c} 3.232(4) \\ 3.518(3) \\ 3.863(4) \\ 3.105(4) \\ 3.412(4) \\ 3.460(4) \\ 3.515(3) \end{array}$	$Tl(2)^*$ Se(1) Se(1 ⁱ) Se(2 ^c) Se(2 ⁱ) Se(2 ^g)	Se(1 ⁱ) 110.6	Se(2 ^c) 64.2 79.2	Se(2 ⁱ) 79.1 58.2 107.7	Se(2 ^g) 109.2 119.2 79.0 171.3	$\begin{array}{c} {\rm Se(2^f)}\\ 77.3\\ 167.1\\ 113.7\\ 115.5\\ 65.1 \end{array}$
$\begin{array}{l} Thallium-thallium\\ Tl(1) \dots Tl(2)\\ Tl(1) \dots Tl(2^c)\\ Tl(1) \dots Tl(2^l)\\ Tl(1) \dots Tl(2^l)\\ Tl(1) \dots Tl(2^m)\\ Tl(1) \dots Tl(2^n)\\ Tl(1) \dots Tl(2^p) \end{array}$	distances	< 5.0 Å 3.993(2) 3.959(2) 4.037(2)		Tl(2) Tl(2) Tl(2)	Tl(2 ^q) Tl(2 ^r) Tl(2 ^s)		3.697(2) 3.874(2) 3.852(2)
$\begin{array}{l} Intermolecular \ sele \\ Se(1) \dots Se(2^e) \\ Se(1) \dots Se(2^f) \\ Se(1) \dots Se(2^l) \\ Se(1) \dots Se(2^b) \end{array}$	enium–sele	nium distar 4.219(5) 4.232(4)	nces < 5.0 Å	Se(2) Se(2)	Se(2 ^a) Se(2 ^h)		3.753(4) 4.187(4)

*Standard deviations of the Se ... Tl ... Se bond angles: 0.1° .

pair on thallium is evident: both Tl(1) and Tl(2) are coordinated on one side by six chalcogen ligands with respectively two and one much more distant additional neighbours on the other side. Their distances to the thallium atoms are of the same order of magnitude as the Tl...Tl distances in the structures (Tables 3 and 4). It is interesting to note that the coordination by the softer selenium leads to a more symmetrical coordination of thallium. Comparison of Tables 3 and 4 shows that the difference between the shortest and longest Tl-S(Se) distances becomes smaller on going from

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Fig. 4. Thallium-sulphur coordination in the crystal structure of Tl_3BS_3 (sulphur: open circles). The two polyhedra are projected approximately along the *c* axis (compare with Fig. 1). The corresponding $Tl \dots$ Se distances in the isotypic Tl_3BSe_3 structure are given in Table 4.

sulphur to selenium. In addition to the directly bonded sulphur(selenium) neighbours each Tl(1) and Tl(2) has six other thallium atoms as secondnearest neighbours at distances given in Tables 3 and 4. However, each sulphur atom, S(1) and S(2), has respectively, besides the boron atom to which it is bonded, eight and seven direct thallium neighbours to which it is in bonding contact at the distances listed in Tables 3 and 4.

It appears that there is no close structural relationship of the Tl_3BS_3 structure type to other known $M_3(XY_3)$ structure types with trigonal planar anions. In Tl_3BO_3 , which is hexagonal [19], thallium exhibits asymmetric three-coordination by oxygen; in other metal-rich orthoborates such as Na_3BO_3 [20] and Li_3BO_3 [21] the more symmetrically surrounded cations also have lower coordination numbers.

5. X-ray powder diagrams, vibrational and mass spectra

Powder diffraction patterns of Tl_3BS_3 and Tl_3BSe_3 were recorded with a Simon-Guinier camera using Cu K α_1 radiation. The evaluation of the patterns is shown in Table 5 and compared with the calculated diffraction data from the single-crystal structures (programs SQT and INT by K.-F. Tebbe). The pattern for Tl_3BS_3 is, in its essential features, similar to the diagram reported by Chopin *et al.* [15], however, it could not be indexed by the authors. No similarities are observed between our Tl_3BS_3 and Tl_3BSe_3 diagrams and our powder pattern of $TlBS_2$ [22] on one hand and those reported by Kirilenko *et al.* [16] for phases with proposed compositions $TlBS_2$, $Tl_4B_2S_5$, $Tl_8B_2S_7$, $TlBSe_2$, $Tl_4B_2Se_5$ and $Tl_8B_2Se_7$ on the other hand. All six patterns given in ref. 16 seem to represent mixtures of different unidentified phases.

IR spectra were measured on samples of Tl_3BS_3 and Tl_3BSe_3 in CsI pellets in the region between 1200 and 200 cm⁻¹. The samples were prepared under inert gas in a glove box; the cell was purged with dry nitrogen during measurement. The strongest absorptions by far are doublet bands at 837 (vs)

TABLE	5
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X-ray powder diffraction data for Tl₃BS₃ and Tl₃BSe₃

Tl ₃ BS ₃					Tl ₃ BSe ₃					
hkl	d (Å)		Intensity (%)		hkl	d (Å)	d (Å)		Intensity (%)	
	observed	calculated	observed	calculated		observed	calculated	observed	calculated	
001	5.46	5.469	40	65	011	5.64	5.635	<10	26	
110	4.721	4.711	20	39	110	4.835	4.829	40	46	
101	4.510	4.504	< 10	15	111	4.175	4.171	30	43	
111	4.090	4.084	50	68	021	4.055	4.052	50	49	
101	2 010	3.918	40	93	$1 \ 0 \ 1$	4.020	4.022	40	48	
021	3.919	3.913	40	75	012	3.221	3.219	<10	23	
$1 2 \overline{1}$	3.306	3.300	20	33	$10\bar{2}$	3.078	3.077	100	100	
012	3.137	3.134	<10	14	$1 \ 1 \ 2$	2.945	2.943	10	20	
$1 \ 0 \ \bar{2}$	3.030	3.018	100	100	130	2.870	2.871	80	59	
031	2.909	2.906	10	23	022	2.822	2.818	60	35	
$1 \ 3 \ 0$	2.775	2.773	70	45	102	2.736	2.732	60	43	
022	2.737	2.735	20	25	$1 \ 1 \ 2$	2.642	2.638	40	38	
102	2.656	2.659	10	27	040	2.526	2.525	<10	15	
$2\ 1\ 0$	2.599	2.596	<10	16	003	2.258	2.264	20	15	
$1 \ 1 \ 2$	2.569	2.564	20	37	$23\bar{2}$	1.889	1.893	10	16	
040	2.428	2.425	<10	14	$30\bar{2}$	1.709	1.710	20	21	
003	2.210	2.208	10	29	$1 5 \bar{2}$	1 697	1.688	10	15	
151	1.739	1.738	<10	13	060	1.687	1.683	10	14	
$3 \ 0 \ \overline{2}$	1 690	1.682		17	152	1 690	1.624	20	13	
301	1.000	1.675	10	14	$2\ 5\ ar{1}$	1.020	1.612	30	15	
$25\overline{1}$	1.562	1.561	<10	17	260	1.435	1.436	<10	15	

and 805 (m) cm⁻¹ for Tl₃BS₃ and 730 (vs) and 696 (m) cm⁻¹ for Tl₃BSe₃. All other features in the spectra are very weak and ill-defined. The four fundamental vibrations of the BS_3^{3-} ion with idealized D_{3h} symmetry are the two symmetric and antisymmetric stretching modes $v_1 = v_s(A'_1)$ and $v_3 =$ $v_{as}(E')$ together with the bending modes $v_2 = \pi(A''_2)$ and $v_4 = \delta(E')$. According to intensity and frequency considerations in comparison with similar D_{3h} species, the strong bands have to be assigned to the ν_{as} vibrations for the pairs $^{10}\text{BS}_3^{3-11}\text{BS}_3^{3-}$ and $^{10}\text{BSe}_3^{3-}-^{11}\text{BSe}_3^{3-}$ respectively. The frequencies of ν_{as} are remarkably low in relation to (a) the values of BCl₃ (989-951 cm^{-1} [23]), B(SCH₃)₃ (930–905 cm⁻¹ [24]), to the coupled BS₃ groups in Na₃B₃S₆ $(915-878 \text{ cm}^{-1} [9, 13])$ and $K_3B_3S_6$ (895-870 cm⁻¹ [9, 13]), and (as expected) to CS_3^{2-} in Tl_2CS_3 (900 cm⁻¹ [25]) and (b) to BBr₃ (856-816 cm⁻¹) [23]), $B(SeR)_3$ (835-800 cm⁻¹ [26]), and (as expected) to CSe_3^{2-} (802 cm^{-1} [27]). The weaker bonds indicated from this lowering of the frequencies are caused mainly by the high negative charge on the BS_3^{3-} and BSe₃³⁻ anions and by the lower π bond orders compared with the carbon compounds. They are in accordance with the slightly elongated B-S and B-Se bonds in the crystal structures of Tl_3BS_3 and Tl_3BSe_3 .

The mass spectrum of the gas phase in contact with crystalline Tl_3BS_3 (70 eV, 390 °C) shows the following species (relative intensity in parentheses): S⁺ (57), BS⁺ (13), S₂⁺ (98), BS₂⁺ (7), Tl⁺ (1000), TlB⁺ (8), TlS⁺ (47), TlBS⁺ (8), TlBS₂⁺ (155). The intensity distribution is remarkably similar to that of the TlBS₂ and TlBS₃ mass spectra, and the high concentration of the TlBS₂⁺ species clearly shows the ease of the decomposition of Tl₃BS₃ to TlBS₂ and Tl₂S at temperatures above 300 °C under vacuum. Analogous observations are made for Tl₃BSe₃ where TlBSe₂⁺ occurs with especially high intensity; the mass spectrum resembles closely the spectrum of TlBSe₃, and it also shows Se₂⁺ in high concentration.

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