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# PAPER

# Formation of $M_4Se_4$ cuboids (M = As, Sb, Bi) *via* secondary pnictogen–chalcogen interactions in the co-crystals $MX_3 \cdot Se = P(p-FC_6H_4)_3$ (M = As, X = Br; M = Sb, X = Cl; M = Bi, X = Cl, Br)†

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The reactions of the group 15 trihalides, MX<sub>3</sub> (M = As, Sb, Bi; X = Cl, Br), with the phosphine selenide SeP(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> result in the formation of co-crystals of formula MX<sub>3</sub>·SeP(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>. No reaction was observed with MI<sub>3</sub> (M = As, Sb, Bi). The structures of MX<sub>3</sub>·SeP(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> (M = As, X = Br **2**; M = Sb, X = Cl **3**; M = Bi, X = Cl **5**; M = Bi, X = Br **6**) have been established, and are isomorphous, crystallising in the cubic *I*23 space group. All the structures feature a primary MX<sub>3</sub> unit, which has three weak secondary M…Se interactions to SeP(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> molecules. However, each of these SeP(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> molecules bridges three MX<sub>3</sub> molecules, resulting in the generation of an M<sub>4</sub>Se<sub>4</sub> (M = As, Sb, Bi) distorted cuboid linked by the pnictogen–chalcogen interactions. Four opposing corners of the cuboid are occupied by the M atom (M = As, Sb, Bi) of an MX<sub>3</sub> pyramid, and the other four by the selenium atom of the phosphine selenide.

#### Introduction

The coordination chemistry of the main group elements is much less well established than that of the transition metals, and complexes of the group 15 trihalides (arsenic, antimony and bismuth) have received relatively little attention.<sup>1–4</sup> Studies of their complexes are often complicated, due to the labile nature of the ligands in solution, and the prevalence of significant secondary bonding interactions in the solid-state. These secondary interactions occur as the M–X (M = As, Sb, Bi)  $\sigma^*$  anti-bonding orbital has the potential to act as an acceptor orbital towards another donor atom.<sup>5</sup> The presence of primary and secondary "coordination spheres" often results in unpredictable structural variations, which may be further complicated by the presence of stereochemically active (or non-active) lone pairs.

Much of the coordination chemistry of group 15 halides with chalcogen donors has focused on thioether and selenoether complexes.<sup>3,4</sup> The structures of these complexes are usually polymeric, and frequently feature primary  $MX_3$  units, with weaker, secondary interactions to the chalcogen donor atoms. This usually results in the retention of a pyramidal  $MX_3$  unit. By contrast, far fewer reports have appeared with phosphine chalcogenide ligands. A number of phosphine oxide complexes of arsenic (III), antimony(III) and bismuth(III) halides (X = Cl, Br, I) have been reported,<sup>6,7</sup> of which [SbCl<sub>3</sub>(OPPh<sub>3</sub>)<sub>2</sub>],<sup>8</sup> [SbCl<sub>3</sub>(dppmO<sub>2</sub>)],<sup>9</sup>

and [Bi<sub>2</sub>I<sub>6</sub>(OPPh<sub>3</sub>)<sub>4</sub>],<sup>10</sup> have been crystallographically characterised. Recent reports have shown that AsF<sub>3</sub> and SbF<sub>3</sub> form hydrolytically unstable complexes with phosphine oxides, but BiF<sub>3</sub> does not.11 No reaction is observed between the trifluorides and sulfur donors, whilst in contrast, SbCl<sub>5</sub> forms complexes with phosphine oxide and sulfide donors, but not with phosphine selenides.<sup>12</sup> The only reported group 15 complexes with the softer phosphine chalcogenides (S and Se donors) are the tetrameric  $[Sb_4Br_{12}(SPMe_2Ph)_4]$ , and the dimeric  $[Sb_2Br_6(SPPh_3)_2]$ and  $[Sb_2I_6(SePPh_3)_2]$ .<sup>13,14</sup> The former contains antimony in a distorted octahedral environment, with bridging SPMe<sub>2</sub>Ph ligands, whilst the two dimeric structures consist of two [SbX<sub>3</sub>(EPR<sub>3</sub>)] units of see-saw geometry, which are linked into a dimer via two halide bridges. The overall geometry at antimony is square pyramidal with the aryl ring orientated over the vacant sixth coordination site. The only reported reaction between bismuth(III) trihalides and phosphine selenides is that of BiCl<sub>3</sub> with (Me<sub>2</sub>N)<sub>3</sub>PSe, which does not result in a bismuth phosphine selenide complex. Instead, an unusual Se-Se bridged ionic complex, [(Me<sub>2</sub>N)<sub>3</sub>PSe-SeP(NMe<sub>2</sub>)<sub>3</sub>][BiCl<sub>4</sub>]<sub>2</sub>, is formed which contains polymeric [BiCl<sub>4</sub>]<sup>-</sup> anions.

In view of the paucity of reports concerning group 15 halide complexes with tertiary phosphine chalcogenide ligands, and phosphine selenides in particular, we now report the results of the reactions between the group 15 trihalides,  $MX_3$  (M = As, Sb, Bi; X = Cl, Br, I) with SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>.

### **Results and discussion**

The reactions of  $SeP(p-FC_6H_4)_3$  with the series of group 15 trihalides MX<sub>3</sub> (M = As, Sb, Bi; X = Cl, Br, I) have been

School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK. E-mail: nick\_barnes28@hotmail.com †Electronic supplementary information (ESI) available: Table S1: Short F…F and F…H contacts in the structures of **2**, **3**, **5** and **6**. CCDC 881801–881804. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31010d



**Scheme 1** Formation of co-crystals from the reaction of  $MX_3$  (M = As, Sb, Bi; X = Cl, Br) with SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>.

undertaken, as outlined in Scheme 1. The reactions were performed in diethyl ether at room temperature, and solids were generally isolated *via* concentration of the solvent and precipitation upon the addition of anhydrous pentane. The exception was compound **4**, which precipitated from diethyl ether and was directly filtered from solution. The reactions of the group 15 iodides MI<sub>3</sub> (M = As, Sb, Bi) with SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> resulted in the isolation of highly insoluble powders (orange for As and Sb, and dark grey for Bi). Microanalysis of these solids revealed them to be the starting tri-iodides in all three cases. Evaporation of the filtrate from these reactions produced a white solid, which was shown by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy to be unreacted SeP-(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>.

Crystals of **2** were grown by layering of a concentrated dichloromethane solution of the product with pentane, whilst crystals of **3**, **5** and **6** were formed by layering of dichloromethane solutions with diethyl ether. The structures of the four compounds are isomorphous, all crystallising in the cubic space group *I*23. The asymmetric unit of each of the four structures consists of a trigonal pyramidal MX<sub>3</sub> molecule (with crystallographically imposed  $C_{3v}$  symmetry), which weakly interacts with a SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> molecule (which has crystallographically imposed  $C_3$  symmetry). An ORTEP representation of the molecular structure of **2** is shown in Fig. 1, and selected bond lengths and angles for **2**, **3**, **5** and **6** are shown in Table 1.

In all of the structures the interaction between the group 15 metal atom and the selenium donor atom of the SeP(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> molecule is too long to be considered a bond, and all the structures are better represented as 1 : 1 co-crystals of MX<sub>3</sub> and SeP(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, which are linked by weak pnictogen…chalcogen interactions. The As…Se interaction in **2** is 3.372(2) Å, the Sb…Se interaction in **3** is 3.3640(15) Å, and the Bi…Se interactions in **5** and **6** are 3.3464(12) and 3.3691(13) Å respectively. All of these are significantly longer than the sum of the relevant covalent radii, (As & Se: 2.37–2.39 Å, Sb & Se: 2.56–2.59 Å, Bi & Se: 2.67–2.68 Å), which have recently been re-determined by Alvarez and co-workers,<sup>16</sup> and Pyykkö and co-workers.<sup>17</sup> A comparison of the Sb…Se interaction in **3** can be made with the only other reported antimony(III) phosphine selenide complex [Sb<sub>2</sub>I<sub>6</sub>(SePPh<sub>3</sub>)<sub>2</sub>], where the Sb–Se bond is considerably shorter at 2.861(2) Å.<sup>13,14</sup>

No phosphine selenide complexes of arsenic(III) or bismuth(III) are known for comparison with the structures of **2**, **5** and **6**. However, a comparison can be made with related selenoether complexes. The As…Se interaction of 3.372(2) Å in **2** is significantly longer than has been generally observed for the As–Se bonds in macrocyclic selenoether complexes, which range between 2.7840(7) and 3.1633(19) Å.<sup>18–20</sup> However, the complex [(AsCl<sub>3</sub>)<sub>2</sub>{1,2,4,5-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>SeMe)<sub>4</sub>}] shows long



**Fig. 1** ORTEP representation of the monomeric unit of AsBr<sub>3</sub>·SeP-(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **2**. Thermal ellipsoids are shown at the 30% probability level. The structures of SbCl<sub>3</sub>·SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **3**, BiCl<sub>3</sub>·SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **5** and BiBr<sub>3</sub>·SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **6** are isomorphous with that of **2**. Symmetry operations used to generate equivalent atoms in **2**: (i): 1 + z, -1 + x, *y*, (ii): 1 - y, z, 1 - x, (iii): 1 + y, z, -1 + x, (iv): 1 - z, 1 - x, *y*.

secondary As...Se interactions of 3.289(2) and 3.423(2) Å,<sup>21</sup> which are of comparable distance to the As...Se interaction in 2. Similarly, the Bi...Se interactions in 5 and 6 [3.3464(12) and 3.3691(13) Å] are significantly longer than the Bi-Se bonds observed in selenoether complexes, which range between 2.952(2) and 3.156(4) Å.<sup>21–23</sup> Despite the M…Se interactions being significantly longer in all cases than the sum of the relevant covalent radii, they are still considerably shorter (by 0.4 to 0.6 Å) than the sum of the relevant van der Waals radii (3.75 Å for As and Se, 3.96 Å for Sb and Se, 3.97 Å for Bi and Se).<sup>24</sup> There appears to be no direct correlation between the magnitude of the M…Se interaction and the size of the group 15 atom, reinforcing the interpretation of these complexes as co-crystals. A comparison of the two bismuth structures 5 and 6 shows an increase in the length of the Bi...Se interaction with an increase in the size of the halide, from 3.3464(12) Å in the BiCl<sub>3</sub> structure 5. to 3.3691(13) Å in the BiBr<sub>3</sub> structure 6.

The P-Se bonds of 2.182(3) Å and 2.189(3) Å observed for the two bismuth compounds 5 and 6 are somewhat longer than those in the structures of 2 and 3, which are 2.155(5) and 2.152(3) Å respectively. However, these are all lengthened when compared with the P=Se bonds of 2.1100(13) Å and 2.1115(12) Å in the structure of SeP(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> (which contains two independent molecules).<sup>25</sup> The P-Se bonds in 2, 3, 5 and 6 still have considerable double bond character, (sum of the single bond covalent radii of P and Se is 2.27 Å, compared to the sum of the double bond covalent radii, which is 2.09 Å),<sup>17</sup> and are shorter than typical single P-Se bonds observed for phenyl-seleno phosphonium cations [2.2189(15) to 2.2686(18) Å],<sup>26-29</sup> or in phosphine adducts of selenium substituted N-heterocycles [2.284(1) to 2.327(1) Å].<sup>30</sup> However, it should be noted that the P-Se bonds in 2, 3, 5 and 6 are similar in magnitude to those of 2.1659(18) to 2.1673(18) Å observed for the two independent

Compound	M–X (Å)	P–Se (Å)	M…Se (Å)	X–M–X (°)	X–M···Se (°)	P–Se····M (°)
AsBr <sub>3</sub> ·SeP( $p$ -FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> , <b>2</b>	2.379(3)	2.155(5)	3.372(2)	96.54(9)	84.72(7)/106.13(8)/157.02(9)	113.90(15)
$SbCl_3 \cdot SeP(p-FC_6H_4)_3, 3$	2.388(3)	2.152(3)	3.3640(15)	94.19(11)	85.61(8)/105.47(8)/160.31(9)	115.54(10)
$BiCl_3 \cdot SeP(p-FC_6H_4)_3, 5$	2.495(3)	2.182(3)	3.3464(12)	94.38(11)	86.68(8)/106.73(8)/158.75(8)	113.75(9)
$BiBr_3 \cdot SeP(p-FC_6H_4)_3, 6$	2.6401(14)	2.189(3)	3.3691(13)	94.40(4)	85.92(4)/106.50(4)/159.03(4)	114.52(9)

Table 1 Selected bond lengths [Å] and angles [°] for the structures of 2, 3, 5 and 6

molecules in the structure of  $(p\text{-FC}_6\text{H}_4)_3\text{PSeI}_2$ .<sup>25</sup> A similar small elongation of the P=Se bond upon complexation was observed for  $[\text{Sb}_2\text{I}_6(\text{SePPh}_3)_2]$ , where the P=Se is 2.162(2) Å, <sup>13,14</sup> compared to the P=Se bond lengths reported for the polymorphs of Ph<sub>3</sub>PSe [2.105(1) to 2.114(4) Å].<sup>31,32</sup>

The NMR spectroscopic data of **1** to **6** reflect the lack of significant change in the P—Se bond.  $\delta_{\rm P}$  are observed between 29.9 and 32.3 ppm for the six co-crystals, which are close to the shift of 33.6 ppm for SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>.<sup>25,33</sup> Due to the limited solubility of most of these compounds we were only able to obtain <sup>77</sup>Se{<sup>1</sup>H} NMR spectra and <sup>1</sup>*J*(SeP) coupling constants for **1** and **2**. The <sup>1</sup>*J*(SeP) coupling of 740 Hz, and the <sup>77</sup>Se{<sup>1</sup>H} NMR shifts ( $\delta_{\rm Se}$ : -248.3 ppm for **1** and -249.4 ppm for **2**), are very similar to those of the free phosphine selenide ( $\delta_{\rm Se}$ : -246.1 ppm with a <sup>1</sup>*J*(SeP) coupling of 741 Hz).<sup>25</sup> The Raman spectra of **1** to **6** all show peaks around 530 to 538 cm<sup>-1</sup>, which are similar to the *v*(P–Se) band of 532 cm<sup>-1</sup> observed for (*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PSeI<sub>2</sub>,<sup>25</sup> and reflect the partial double bond character of the P–Se bond in **1** to **6**, as the bands are shifted to lower frequency compared with the *v*(P–Se) band observed at 552 cm<sup>-1</sup> for SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>.<sup>25</sup>

The pyramidal MX<sub>3</sub> units in each of the four structures all have three primary M–X bonds of equal length, and each MX<sub>3</sub> unit further interacts with three SeP(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> groups resulting in an overall distorted [3 + 3] octahedral arrangement around M, as shown for **2** in Fig. 2. However, each of the SeP(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> groups also bridges three MX<sub>3</sub> units, resulting in the generation of a distorted M<sub>4</sub>Se<sub>4</sub> (M = As, Sb, Bi) cuboid, as shown for **2** in Fig. 3, where four opposing corners of the cuboid are occupied by the M atom of an MX<sub>3</sub> pyramid, and the other four by the selenium atom of the phosphine selenide.

This arrangement of primary and secondary bonds around M is similar to the structures of the parent trihalides, where pyramidal MX<sub>3</sub> molecules extend their coordination sphere *via* additional secondary interactions to halide atoms from neighbouring MX<sub>3</sub> molecules.<sup>34</sup> In the case of the structures of MCl<sub>3</sub> or MBr<sub>3</sub> (M = As, Sb, Bi) there are commonly either five or six secondary M···X interactions, resulting in overall coordination numbers of [5 + 3] (bicapped trigonal prismatic geometry) as seen for SbCl<sub>3</sub>,<sup>35</sup> β-SbBr<sub>3</sub>,<sup>36</sup> BiCl<sub>3</sub>,<sup>37</sup> and α-BiBr<sub>3</sub>,<sup>38</sup> or [5 + 4] (tricapped trigonal prismatic geometry) as seen for AsCl<sub>3</sub>,<sup>39</sup> AsBr<sub>3</sub>,<sup>40</sup> and α-SbBr<sub>3</sub>.<sup>41</sup> The exception is the polymeric β-BiBr<sub>3</sub> form (which has an AlCl<sub>3</sub>-type structure), with six long Bi–Br bonds of intermediate distance between primary and secondary bonds.<sup>38</sup>

The structures of **2**, **3**, **5** and **6** have three M···Se interactions (in place of five or six M···X interactions) to give a distorted octahedral geometry. This is similar to the arrangement observed in the structure of the antimony selone complex [SbCl<sub>3</sub>(mbts) ( $\mu$ -mbts)<sub>2</sub>SbCl<sub>3</sub>(mbts)] (mbts = *N*-methylbenzothiazole-2-



Fig. 2 Octahedral [3 + 3] coordination environment around the arsenic atom in the structure of AsBr<sub>3</sub>·SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **2**, showing the primary AsBr<sub>3</sub> fragment interacting with three SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> molecules. The same [3 + 3] arrangement is also observed in the structures of **3**, **5** and **6**.

selone), where there are three primary Sb–Cl bonds, and three secondary Sb…Se interactions.<sup>42</sup> Table 2 summarises the geometrical parameters of the MX<sub>3</sub> fragments in **2**, **3**, **5** and **6**, along with those of the parent trihalides, and the related [SbCl<sub>3</sub>(mbts)- $(\mu$ -mbts)<sub>2</sub>SbCl<sub>3</sub>(mbts)].

The MX<sub>3</sub> fragments in **2**, **3**, **5** and **6** have crystallographically imposed  $C_{3v}$  symmetry, which results in equal lengths for the primary M–X bonds. In contrast, most of the structures of the parent trihalides have three slightly unequal bonds lengths, except for SbCl<sub>3</sub> ( $C_s$  symmetry with two equal Sb–Cl bonds),<sup>35</sup> and the polymeric  $\beta$ -BiBr<sub>3</sub> (where there are six bonds of intermediate distance rather than primary and secondary bonds).<sup>38</sup> In the case of **2** and **3** the geometrical parameters are broadly similar to the parent trihalide, with only small differences in the M–X bonds and X–M–X angles. However, both structures exhibit considerably shorter secondary M···Se interactions than the secondary M···X interactions in the structures of the parent trihalides. In the case of **5** the Bi–Cl bonds are intermediate in length between the rather large spread of the three different Bi–Cl bonds in BiCl<sub>3</sub>, whilst in **6** the Bi–Br bonds are similar to



Fig. 3 Generation of the  $As_4Se_4$  cuboid motif in the structure of  $AsBr_3 \cdot SeP(p-FC_6H_4)_3$ , 2, *via*  $As \cdots Se$  interactions. The cuboid motif in 3, 5 and 6 is generated in the same way.

those observed for the  $\alpha$ -form of BiBr<sub>3</sub>, and significantly shorter than those in the polymeric  $\beta$ -BiBr<sub>3</sub>. In both bismuth structures **5** and **6** the secondary Bi…Se interactions are of comparable magnitude to the secondary Bi…X interactions in the structures of BiCl<sub>3</sub> and  $\alpha$ -BiBr<sub>3</sub>.

Although only small changes were generally observed in the geometrical parameters of the MX<sub>3</sub> fragments in 2, 3, 5 and 6 compared to the parent trihalide, an examination of the Raman spectra of 1 to 6 show that the v(M-X) bands often exhibit a marked shift from those of the parent trihalides. The most intense bands in the Raman spectra of MX<sub>3</sub> are the  $v_1$  symmetric M-X stretch and the  $v_3$  degenerate M-X stretch.<sup>43</sup> These bands also appear to be the most intense in the Raman spectra of 1 to 6, and can be compared with Raman data for the parent trihalides. The spectra of 1 and 2 show that the v(As-X) bands are shifted to lower wavenumbers than in AsX3, viz. v(As-Cl) of 364 and 337 cm<sup>-1</sup> in 1 compared with v(As-Cl) of 416 and 393 cm<sup>-1</sup> in AsCl<sub>3</sub>.<sup>44</sup> The Raman spectrum of 2 showed only one intense feature at 253 cm<sup>-1</sup>, which was assigned as v(As-Br), although the Raman spectrum of AsBr<sub>3</sub> does display both  $v_1$  and  $v_3$  bands close to each other at 281 and 277–254 cm<sup>-1,43</sup> so it may be that the peak in 2 is due to overlapping  $v_1$  and  $v_3$ bands. The antimony co-crystals show a similar trend, with v(Sb-Cl) of 327 and 307 cm<sup>-1</sup> in **3** compared with v(Sb-Cl) of 340 and 318–312 cm<sup>-1</sup> in SbCl<sub>3</sub><sup>45</sup> and v(Sb–Br) of 222 and 214 cm<sup>-1</sup> in 3 compared with v(Sb-Br) of 243 and  $238-230 \text{ cm}^{-1}$  in SbBr<sub>3</sub>.<sup>46</sup> It should be noted that weak "complexes" of SbCl<sub>3</sub> with aromatic hydrocarbons (such as benzene or phenanthrene) also show a shift of the  $v_1$ (Sb–Cl) band to lower wavenumbers (360 to 337 cm<sup>-1</sup>), and splitting of the  $v_3$ band to give two bands between 340 and 302  $\text{cm}^{-1}$ .<sup>47</sup>

In contrast, the v(Bi-X) bands of the bismuth complexes **5** and **6** are shifted slightly to higher wavenumbers, *viz.* v(Bi-Cl)of 298 and 274 cm<sup>-1</sup> in **5** compared with v(Bi-Cl) of 282 and 263–252 cm<sup>-1</sup> in BiCl<sub>3</sub>.<sup>43</sup> The Raman spectrum of **6** shows two intense bands at 199 and 187 cm<sup>-1</sup> which are assigned as v(Bi-Br), which are again slightly shifted to higher wavenumbers than the  $v_1$  and  $v_3$  bands of 189 and 180 cm<sup>-1</sup> observed for BiBr<sub>3</sub>.<sup>48</sup> Whilst the spectra of the bromide co-crystals **2**, **4** and **6** are dominated by intense v(M-Br) bands, other bands are observed at low wavenumbers for the chloride analogues **1**, **3** and **5** which may be features due to v(M-Se). The observed changes in the Raman spectra on formation of the co-crystals are likely to be due to the MX<sub>3</sub> fragments in **1** to **6** having crystallographically imposed  $C_{3v}$  symmetry, whilst in the solid state the majority of the parent trihalides usually have all three bond lengths different ( $C_1$  symmetry) or two equal bonds ( $C_s$  symmetry).

Whilst the presence of secondary bonding interactions to group 15 MX<sub>3</sub> fragments is not at all unusual, the generation of  $M_4E_4$  (M = As, Sb or Bi; E = Se) cuboid motifs *via* this type of interaction is, to the best of our knowledge, unprecedented. A cuboid-like motif has been observed for the bismuth thioether complex [Bi<sub>4</sub>Cl<sub>12</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SMe)<sub>4</sub>]<sub>*n*'nH<sub>2</sub>O,<sup>49</sup> but here a Bi<sub>4</sub>Cl<sub>4</sub> pseudo-cuboid was formed, with an open-cradle arrangement and very unequal Bi–Cl bonds. The formation of a Bi<sub>4</sub>Cl<sub>4</sub> cuboid is similar to the aggregation of [M<sub>*n*</sub>X<sub>*n*</sub>]<sup>-</sup> (M = As, Sb, Bi; X = Cl, Br, I) anions into larger networks, which is well documented for these systems,<sup>50</sup> and a few examples involving Sb<sub>4</sub>Cl<sub>4</sub> cuboids are known, in [CpFe(CO)<sub>2</sub>Cl]<sub>4</sub>[SbCl<sub>3</sub>]<sub>4</sub>,<sup>51</sup> and in the anion of [Et<sub>4</sub>N]<sub>4</sub>[Sb<sub>4</sub>Cl<sub>16</sub>].<sup>52</sup> However, the formation of an M<sub>4</sub>E<sub>4</sub> cuboid *via* weak pnictogen···chalcogen interactions has not previously been observed.</sub>

These cuboids can be thought of as being generated from a square made up of M atoms (M = As, Sb or Bi) with a smaller square made up of Se atoms sat inside it, which results in a significant distortion of both the M–Se–M and Se–M–Se from the 90° expected for a regular cube. This results in a lowering of the overall symmetry from  $T_d$  to T. Two different views of the framework of the cuboid are shown for AsBr<sub>3</sub>·SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **2** in Fig. 4. The M…Se distances and inter-cuboidal angles vary only slightly between the four structures, and are shown in Table 3. The M–Se–M angles range between 102.78(4)° for **3** to 104.87(3)° for **5**, whilst the Se–M–Se vary between 72.75(3)° for **5** to 75.53(4)° for **3**.

An examination of the crystal packing shows that the formation of the cuboid also results in F...F and F...H contacts being set up between the para-fluorophenyl rings, as shown for 2 in Fig. 5. In all cases the F…F and F…H contacts are very weak, and are around (or in some cases longer than) the sum of the van der Waals radii, see Table S1 in the ESI.<sup>†</sup> The F…F interactions vary between 2.897(14) Å for 3 and 2.972(11) Å for 6 (compared to 2.94 Å for twice the van der Waals radii of fluorine)<sup>24</sup> whilst the F…H interactions vary between 2.53 Å for 5 and 2.60 Å for 3 (compared to 2.57 Å for the sum of van der Waals radii of hydrogen and fluorine).<sup>24</sup> These F…F and F…H contacts result in aggregation of the fluorous portions of the molecules, and are present in conjunction with the M...Se interactions in all four structures, and although weak in terms of magnitude appear to assist in the formation of the M<sub>4</sub>Se<sub>4</sub> cuboid arrangement, as shown in Fig. 5.

Compound	M–X primary bonds (Å)	X–M–X angles of pyramidal MX <sub>3</sub> (°)	Secondary M…X or M…Se interactions (Å)	Ref.
AsBr <sub>3</sub> CN: 9 [3 + 6] (tricapped trigonal prism)	2.354(15), 2.354(15), 2.384(15)	97.3(5), 97.5(5), 98.2(5)	3.783, 3.863, 3.869, 3.947, 4.170, 4.210	40
AsBr <sub>3</sub> ·SeP( $p$ -FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> , <b>2</b> CN: 6 [3 + 3] (distorted octahedral)	2.379(3) × 3	96.54(9) × 3	3.372(2) × 3	This work
SbCl <sub>3</sub> CN: 8 [3 + 5] (bicapped trigonal prism)	2.368(1) × 2, 2.340(2)	95.70(5) × 2, 90.98(5)	$3.457(1) \times 2, 3.609(2),$ $3.736(1) \times 2$	35
SbCl <sub>3</sub> ·SeP( $p$ -FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> , <b>3</b> CN: 6 [3 + 3] (distorted octahedral)	2.388(3) × 3	94.19(11) × 3	3.3640(15) × 3	This work
[SbCl <sub>3</sub> (mbts) (μ-mbts) <sub>2</sub> SbCl <sub>3</sub> (mbts)] CN: 6 [3 + 3] (distorted octahedral)	Mol 1: 2.4593(16), 2.447(2), 2.4068(18) Mol 2: 2.4557(15), 2.4322(18), 2.4279(17)	Mol 1: 91.39(6), 92.64(6), 91.84(6) Mol 2: 89.25(6), 89.45(5), 93.02(6)	Mol 1: 3.1812(8), 3.2208(8), 3.1395(8) Mol 2: 3.1366(8), 3.2226(8), 3.3145(8)	42
BiCl <sub>3</sub> CN: 8 [3 + 5] (bicapped trigonal prism)	2.468(4), 2.513(7), 2.518(7)	84.45(14), 94.9(3), 93.2(3)	3.216(9), 3.224(3), 3.256(9), 3.398(8), 3.450(9)	37
BiCl <sub>3</sub> ·SeP( $p$ -FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> , <b>5</b> CN: 6 [3 + 3] (distorted octahedral)	2.495(3) × 3	94.38(11) × 3	3.3464(12)	This work
α-BiBr <sub>3</sub> CN: 8 [3 + 5] (bicapped trigonal prism)	2.636(4), 2.660(3), 2.692(3)	88.19(10), 90.08(11), 96.29(11)	3.246(4), 3.306(4), 3.397(3), 3.699(4), 4.106(3)	38
β-BiBr <sub>3</sub> CN: 6 long bonds (distorted octahedral)	$2.79(8) \times 2, 2.80(8) \times 2, 2.84(8) \times 2$ (AlCl <sub>3</sub> type structure)	N/A as not pyramidal	N/A as all six bonds are intermediate in length	38
BiBr <sub>3</sub> ·SeP( $p$ -FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> , <b>6</b> CN: 6 [3 + 3] (distorted octahedral)	2.6401(14) × 3	94.40(4) × 3	3.3691(13) × 3	This work
M = As, Sb or Bi, $X = Cl$ or Br,	mbts = N-methylbenzothiazole-2-selone.			

**Table 2** Geometric parameters of the  $MX_3$  fragment in the structures of **2**, **3**, **5** and **6**, and a comparison with the  $MX_3$  parent trihalide, and related complexes with selenium donors

# Conclusions

The reactions of  $MCl_3$  or  $MBr_3$  (M = As, Sb, Bi) with Se=  $P(p-FC_6H_4)_3$  result in the formation of 1:1 co-crystals, of which four examples have been structurally characterised. All four structures are isomorphous, and crystallise in the cubic space group I23. Unusually, these co-crystals aggregate as tetramers via secondary pnictogen-chalcogen interactions between the group 15 atom and the selenium donor atom of the phosphine selenide. Each of the structures consists of a pyramidal MX<sub>3</sub> unit of  $C_{3v}$  symmetry, which participates in three secondary interactions to the selenium atoms of three  $\mu_3$ -bridging Se=P(p-FC\_6H\_4)\_3 ligands. In this way a highly unusual distorted cuboid motif of T symmetry is formed for all of the four structures reported. The crystal packing of these four structures show that weak F...F and F...H contacts are also present which may also assist in directing the formation of the cuboid motif.

# **Experimental**

#### **Reagents and physical measurements**

Many of the reagents and compounds synthesised herein are somewhat moisture sensitive, therefore anhydrous and anaerobic conditions were used throughout their synthesis. Diethyl ether and pentane were purchased commercially (Fisher) and freshly distilled from sodium/benzophenone ketyl before their use. AsCl<sub>3</sub> (Aldrich), AsBr<sub>3</sub> (Acros), SbCl<sub>3</sub>, SbBr<sub>3</sub>, BiCl<sub>3</sub> and BiBr<sub>3</sub> (all Alfa Aesar) were purchased commercially, and used without further purification. (*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PSe was synthesised according to the literature method.<sup>25</sup> Elemental analyses were performed by the departmental microanalytical service. FT-Raman spectra were recorded as solid samples on a Nicolet-Nexus combined FT-IR/FT-Raman spectrometer using the OMNIC E.S.P. 5.1 software package. Spectra were recorded to the low frequency cut off point of 100 cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} and <sup>77</sup>Se{<sup>1</sup>H} NMR spectra



**Fig. 4** Two different views of the  $As_4Se_4$  cuboid in  $AsBr_3 \cdot SeP(p-FC_6H_4)_3$ , **2**.

Table 3 Geometric parameters of the  $M_4Se_4$  cuboid (M = As, Sb or Bi) in the structures of 2, 3, 5 and 6

AsBr <sub>3</sub> ·SeP( $p$ -FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> , <b>2</b> 3.372(2)         104.71(           SbCl <sub>3</sub> ·SeP( $p$ -FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> , <b>3</b> 3.3640(15)         102.78(           BiCl <sub>3</sub> ·SeP( $p$ -FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> , <b>5</b> 3.3464(12)         104.87(           BiBr <sub>4</sub> ·SeP( $p$ -FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> , <b>6</b> 3.3691(13)         103.99(	6)       72.98(5)         4)       75.53(4)         3)       72.75(3)         3)       73.95(3)



**Fig. 5** MERCURY representation of the crystal packing of  $AsBr_3$ ·SeP-(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **2**, showing the As···Se, F···F and F···H interactions present in the extended structure of the co-crystal. Hydrogen atoms are omitted for clarity.

were recorded on a Bruker AVANCE III 400 spectrometer operating at 162.0 (<sup>31</sup>P) and 76.3 (<sup>77</sup>Se) MHz, respectively. Peak positions are quoted relative to 85%  $H_3PO_4$  (<sup>31</sup>P) or Me<sub>2</sub>Se (<sup>77</sup>Se), using the high frequency positive convention throughout.

#### Crystallographic details

Details of the structural analysis for **2**, **3**, **5** and **6** are summarised in Table 4. Diffraction data were recorded on a Nonius  $\kappa$ -CCD four-circle diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). All data were collected at 100(2) K. Structural data were solved by direct methods, with fullmatrix least squares refinement on  $F^2$  using the SHELX-97 program.<sup>53</sup> Absorption corrections were applied by the multiscan method, using the SORTAV program.<sup>54</sup> Non-hydrogen atoms were refined with anisotropic thermal parameters, whilst all hydrogen atoms were modelled in ideal positions. Flack parameters are 0.03(7), 0.40(6), 0.002(19) and 0.057(19) for **2**, **3**, **5** and **6** respectively. All thermal ellipsoid plots were generated using ORTEP-3 for Windows,<sup>55</sup> whilst all other pictures were generated using the MERCURY program.<sup>56</sup>

#### Synthetic details

Synthesis of MX<sub>3</sub>·SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> co-crystals (M = As, Sb. Bi; X = Cl, Br). The co-crystals formed in the reaction of (*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PSe with MX<sub>3</sub> (M = As, Sb, Bi; X = Cl, Br) were synthesised by mixing the two reagents together in diethyl ether at room temperature, the synthesis of AsCl<sub>3</sub>·SeP(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, 1 being typical: 0.500 g (1.26 mmoles) of (*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PSe was added to a pre-dried rotaflo tube containing 50 mL of anhydrous diethyl ether, against a stream of dry nitrogen. 0.216 g (0.10 mL, 1.26 mmoles) of arsenic(III) chloride was added to the solution which was stirred for approx. 48 hours. After this time the solution of 15 mL of anhydrous pentane which resulted in the precipitation of a white solid. This solid was isolated using standard Schlenk techniques, and dried *in vacuo* for two hours.

**AsCl<sub>3</sub>·SeP**(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **1.** Yield = 37%. White solid. Calculated for C<sub>18</sub>H<sub>12</sub>F<sub>3</sub>Cl<sub>3</sub>PSeAs: C, 37.5; H, 2.1; Cl, 18.5; Found: C, 38.0; H, 1.9; Cl, 18.1. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 32.3 [s, <sup>1</sup>*J* (SeP) = 740 Hz]. <sup>77</sup>Se{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): -248.3 [d, <sup>1</sup>*J*(SeP) = 740 Hz]. Raman (cm<sup>-1</sup>): 3076, 1591, 1302, 1228, 1167, 1093, 827, 638, 538 *v*(P–Se), 499, 364 *v*(As–Cl), 337 *v*(As–Cl), 241, 218, 187, 156.

**AsBr<sub>3</sub>·SeP**(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **2.** Was synthesised *via* the method used for **1** above, except using 0.400 g (1.26 mmoles) of arsenic(III) bromide and 0.500 g (1.26 mmoles) of (p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PSe. Yield = 39%. White solid. Calculated for C<sub>18</sub>H<sub>12</sub>F<sub>3</sub>Br<sub>3</sub>PSeAs: C,

	AsBr <sub>3</sub> ·SeP( $p$ -FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> , <b>2</b>	$SbCl_3 \cdot SeP(p-FC_6H_4)_3, 3$	$BiCl_3 \cdot SeP(p-FC_6H_4)_3, 5$	$BiBr_3 \cdot SeP(p-FC_6H_4)_3, 6$
Empirical formula	C <sub>18</sub> H <sub>12</sub> Br <sub>3</sub> F <sub>3</sub> PSeAs	C <sub>18</sub> H <sub>12</sub> Cl <sub>3</sub> F <sub>3</sub> PSeSb	C <sub>18</sub> H <sub>12</sub> Cl <sub>3</sub> F <sub>3</sub> PSeBi	C <sub>18</sub> H <sub>12</sub> Br <sub>3</sub> F <sub>3</sub> PSeBi
Fw	709.83	623.31	/10.54	843.89
Colour, habit	Colourless, block	Colourless, block	Colourless, block	Yellow, block
Crystal system	Cubic	Cubic	Cubic	Cubic
Space group	<i>I</i> 23 (no. 197)	<i>I</i> 23 (no. 197)	<i>I</i> 23 (no. 197)	<i>I</i> 23 (no. 197)
Crystal size	$0.07 \times 0.07 \times 0.05 \text{ mm}^3$	$0.08 \times 0.08 \times 0.08 \text{ mm}^3$	$0.07 \times 0.07 \times 0.07 \text{ mm}^3$	$0.12 \times 0.12 \times 0.10 \text{ mm}^3$
Unit cell dimensions	$a = 16.2032(18)$ Å, $\alpha = 90^{\circ}$	$a = 16.1817(5)$ Å, $\alpha = 90^{\circ}$	$a = 16.1403(9)$ Å, $\alpha = 90^{\circ}$	$a = 16.3328(8)$ Å, $\alpha = 90^{\circ}$
	$b = 16.2032(18)$ Å, $\beta = 90^{\circ}$	$b = 16.1817(5)$ Å, $\beta = 90^{\circ}$	$b = 16.1403(9)$ Å, $\beta = 90^{\circ}$	$b = 16.3328(8)$ Å, $\beta = 90^{\circ}$
	$c = 16.2032(18)$ Å, $\gamma = 90^{\circ}$	$c = 16.1817(5)$ Å, $\gamma = 90^{\circ}$	$c = 16.1403(9)$ Å, $\gamma = 90^{\circ}$	$c = 16.3328(8)$ Å, $\gamma = 90^{\circ}$
Volume	4254.0(8) Å <sup>3</sup>	4237.1(2) Å <sup>3</sup>	4204.7(4) Å <sup>3</sup>	4356.9(4) Å <sup>3</sup>
Т	100(2) K	100(2) K	100(2) K	100(2) K
Ζ	8	8	8	8
$D_{\text{calcd}}$	$2.217 \text{ mg m}^{-3}$	$1.954 \text{ mg m}^{-3}$	$2.245 \text{ mg m}^{-3}$	$2.573 \text{ mg m}^{-3}$
λ	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
$\mu$ (Mo-K $\alpha$ )	$9.047 \text{ mm}^{-1}$	$3.501 \text{ mm}^{-1}$	$10.602 \text{ mm}^{-1}$	$15.367 \text{ mm}^{-1}$
F(000)	2672	2384	2640	3072
$\theta$ range	3.56 to 26.36°	3.56 to 25.98°	3.09 to 25.99°	3.06 to 27.49°
No. of reflections	1670 (1011 unique)	1401 (777 unique)	2214 (1379 unique)	2034 (1491 unique)
R <sub>int</sub>	0.105	0.055	0.078	0.082
$R_1/WR_2$	0.0631/0.1376	0.0587/0.1551	0.0469/0.1005	0.0454/0.0978
$R_1/wR_2$ (all data)	0.0907/0.1600	0.0711/0.1669	0.0632/0.1092	0.0571/0.1062
Largest diff. peak and hole	0.744 and $-0.673 \text{ e} \text{ Å}^{-3}$	2.555 and $-1.222$ e Å <sup>-3</sup>	$1.378 \text{ and } -1.391 \text{ e } \text{\AA}^{-3}$	$1.697 \text{ and } -1.158 \text{ e } \text{\AA}^{-3}$
GOF	1.077	1.107	1.116	1.061
Flack parameter	0.03(7)	0.40(6)	0.002(19)	0.057(19)

Table 4Crystallographic parameters for compounds 2, 3, 5 and 6

30.4; H, 1.7; Br, 33.8; P, 4.8; Found: C, 29.7; H, 1.1; Br, 33.5; 4.8.  ${}^{31}P{}^{1}H$  NMR (CDCl<sub>3</sub>): 32.3 [s,  ${}^{1}J(SeP) = 740$  Hz].  ${}^{77}Se{}^{1}H$  NMR (CDCl<sub>3</sub>): -249.4 [d,  ${}^{1}J(SeP) = 740$  Hz]. Raman (cm<sup>-1</sup>): 3072, 1591, 1302, 1228, 1167, 1093, 827, 638, 619, 534  $\nu$ (P–Se), 496, 341, 253  $\nu$ (As–Br), 218.

**SbCl<sub>3</sub>·SeP**(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **3.** Was synthesised *via* the method used for **1** above, except using 0.250 g (1.13 mmoles) of antimony(III) chloride and 0.450 g (1.13 mmoles) of (*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PSe. Yield = 80%. White solid. Calculated for C<sub>18</sub>H<sub>12</sub>F<sub>3</sub>Cl<sub>3</sub>PSeSb: C, 34.7; H, 1.9; Cl, 17.1; Found: C, 35.2; H, 1.6; Cl, 17.3. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 30.8 [s]. Raman (cm<sup>-1</sup>): 3074, 1591, 1490, 1299, 1237, 1167, 1097, 828, 641, 536 *v*(P–Se), 497, 327 *v*(Sb–Cl), 307 *v*(Sb–Cl), 242, 217, 152, 127.

**SbBr<sub>3</sub>·SeP**(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **4.** Was synthesised *via* the method used for **1** above using 0.450 g (1.26 mmoles) of antimony(III) bromide and 0.500 g (1.26 mmoles) of (p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PSe. The product was filtered off after 48 hours stirring and dried *in vacuo* for two hours. Yield = 34%. Yellow solid. Calculated for C<sub>18</sub>H<sub>12</sub>F<sub>3</sub>Br<sub>3</sub>PSeSb: C, 28.6; H, 1.6; Br, 31.7; Found: C, 29.4; H, 1.4; Br, 31.5. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 32.3 [s]. Raman (cm<sup>-1</sup>): 3072, 1591, 1298, 1232, 1163, 1093, 827, 634, 615, 530 *v*(P-Se), 492, 411, 337, 222 *v*(Sb–Br), 214 *v*(Sb–Br), 168.

**BiCl<sub>3</sub>·SeP**(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **5**. Was synthesised *via* the method used for **1** above, except using 0.360 g (1.13 mmoles) of bismuth(III) chloride and 0.450 g (1.13 mmoles) of (p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PSe. Yield = 41%. Pale yellow solid. Calculated for C<sub>18</sub>H<sub>12</sub>F<sub>3</sub>Cl<sub>3</sub>PSeBi: C, 30.4; H, 1.7; Cl, 15.0; P, 4.4; Found: C, 30.4; H, 1.1; Cl, 15.0; P, 4.2. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 30.8 [s]. Raman (cm<sup>-1</sup>): 3078, 1595, 1502, 1394, 1300, 1234, 1167, 1092, 828, 636, 531 v(P–Se), 494, 413, 337, 298 v(Bi–Cl), 274 v(Bi–Cl), 238, 219. **BiBr<sub>3</sub>·SeP**(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, **6.** Was synthesised *via* the method used for **1** above, except using 0.560 g (1.26 mmoles) of bismuth(III) bromide and 0.500 g (1.26 mmoles) of (*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PSe. Yield = 32%. Yellow solid. Calculated for C<sub>18</sub>H<sub>12</sub>F<sub>3</sub>Br<sub>3</sub>PSeBi: C, 25.6; H, 1.4; Br, 28.4; P, 3.7; Found: C, 25.8; H, 1.0; Br, 28.7; P, 3.7.  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>): 29.9 [s]. Raman (cm<sup>-1</sup>): 3076, 1591, 1495, 1394, 1298, 1232, 1163, 1093, 827, 634, 615, 530 *v*(P–Se), 488, 415, 337, 237, 199 *v*(Bi–Br), 187 *v*(Bi–Br).

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#### References

- S. M. Godfrey, C. A. McAuliffe, A. G. Mackie and R. G. Pritchard, in *Chemistry of Arsenic, Antimony and Bismuth*, ed. N. C. Norman, Blackie, London, 1998, ch. 4.
- 2 W. Levason and G. Reid, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier, Oxford, 2004, vol. 3, p. 465.
- 3 W. Levason and G. Reid, J. Chem. Soc., Dalton Trans., 2001, 2953.
- 4 W. Levason, G. Reid and W. Zhang, Dalton Trans., 2011, 40, 8491.
- 5 C. J. Carmalt and N. C. Norman, in *Chemistry of Arsenic, Antimony and Bismuth*, ed. N. C. Norman, Blackie, London, 1998, ch. 1.
- M. Zackrisson and K. I. Alden, *Acta Chem. Scand.*, 1960, 14, 994;
   D. J. Phillips and S. Y. Tyree Jr., *J. Am. Chem. Soc.*, 1961, 83, 1806;
   M. J. Frazer, W. Gerrard and R. Twaits, *J. Inorg. Nucl. Chem.*, 1963, 25, 637.
- 7 S. Milićev and D. Hadži, *Inorg. Nucl. Chem. Lett.*, 1971, 7, 745;
   S. Milićev and D. Hadži, *Inorg. Chim. Acta*, 1977, 21, 201.
- 8 L. Golič and S. Milićev, Acta Crystallogr., Sect. B: Struct. Crystallogr: Cryst. Chem., 1978, 34, 3379.

- 9 I. Abdul Razak, H.-K. Fun, B. M. Yamin, K. Chinnakali, H. Zakaria and N. Binti Ismail, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1999, 55, 172.
- 10 F. Lazarini and S. Milićev, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1976, **32**, 2873.
- 11 W. Levason, M. E. Light, S. Maheshwari, G. Reid and W. Zhang, *Dalton Trans.*, 2011, 40, 5291.
- 12 S. Corcoran, W. Levason, R. Patel and G. Reid, *Inorg. Chim. Acta*, 2005, **358**, 1263.
- 13 D. Haase, R. Lotz and S. Pohl, Z. Kryst., 1989, 186, 111.
- 14 S. Pohl, W. Saak, R. Lotz and D. Haase, Z. Naturforsch., Teil B, 1990, 45, 1355.
- 15 G. R. Willey, J. R. Barras, M. D. Rudd and M. G. B. Drew, J. Chem. Soc., Dalton Trans., 1994, 3025.
- 16 B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán and S. Alvarez, *Dalton Trans.*, 2008, 2832.
- 17 P. Pyykkö and M. Atsumi, *Chem.-Eur. J.*, 2009, **15**, 186; P. Pyykkö and M. Atsumi, *Chem.-Eur. J.*, 2009, **15**, 12770.
- 18 A. J. Barton, N. J. Hill, W. Levason and G. Reid, J. Am. Chem. Soc., 2001, 123, 11801.
- 19 N. J. Hill, W. Levason and G. Reid, Inorg. Chem., 2002, 41, 2070.
- 20 N. J. Hill, W. Levason, R. Patel, G. Reid and M. Webster, *Dalton Trans.*, 2004, 980.
- 21 W. Levason, S. Maheshwari, R. Ratnani, G. Reid, M. Webster and W. Zhang, *Inorg. Chem.*, 2010, **49**, 9036.
- 22 A. J. Barton, A. R. J. Genge, W. Levason and G. Reid, J. Chem. Soc., Dalton Trans., 2000, 859.
- 23 A. J. Barton, A. R. J. Genge, W. Levason and G. Reid, J. Chem. Soc., Dalton Trans., 2000, 2163.
- 24 M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer and D. G. Truhlar, J. Phys. Chem. A, 2009, 113, 5806.
- 25 N. A. Barnes, S. M. Godfrey, R. T. A. Halton, R. Z. Khan, S. L. Jackson and R. G. Pritchard, *Polyhedron*, 2007, 26, 4294.
- 26 S. M. Godfrey, R. T. A. Ollerenshaw, C. L. Richards and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 2001, 508.
- 27 N. A. Barnes, S. M. Godfrey, R. T. A. Halton, I. Mushtaq, R. G. Pritchard and S. Sarwar, *Dalton Trans.*, 2006, 1517.
- 28 N. A. Barnes, S. M. Godfrey, R. T. A. Halton, I. Mushtaq and R. G. Pritchard, *Dalton Trans.*, 2006, 4795.
- 29 N. A. Barnes, S. M. Godfrey, R. T. A. Halton, I. Mushtaq and R. G. Pritchard, *Dalton Trans.*, 2008, 1346.
- 30 J. L. Dutton and P. J. Ragogna, Inorg. Chem., 2009, 48, 1722.
- 31 P. W. Codding and K. A. Kerr, Acta Crystallogr., Sect. B: Struct. Crystallogr: Cryst. Chem., 1979, 35, 1261.

- 32 P. G. Jones, C. Kienitz and C. Thöne, Z. Kristallogr., 1994, 209, 80.
- R. F. de Ketelaere and G. P. van der Kelen, J. Mol. Struct., 1975, 27, 363;
  J. Malito and E. C. Alyea, Phosphorus, Sulfur Silicon Relat. Elem., 1990, 54, 95;
  J. A. S. Howell, N. Fey, J. D. Lovatt, P. C. Yates, P. McArdle, D. Cunningham, E. Sadeh, H. E. Gottlieb, Z. Goldschmidt, M. B. Hursthouse and M. E. Light, J. Chem. Soc., Dalton Trans., 1999, 3015.
- 34 J. Galy and R. Enjalbert, J. Solid State Chem., 1982, 44, 1.
- 35 A. Lipka, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1979, 35, 3020.
- 36 D. W. Cushen and R. Hulme, J. Chem. Soc., 1962, 2218.
- 37 S. C. Nyburg, G. A. Ozin and J. T. Szymański, *Acta Crystallogr., Sect. B:* Struct. Crystallogr. Cryst. Chem., 1971, **27**, 2298.
- 38 H. von Benda, Z. Kristallogr., 1980, 151, 271.
  39 J. Galy, R. Enjalbert, P. Lecante and A. Burian, *Inorg. Chem.*, 2002, 41, 693.
- 40 J. Trotter, Z. Kristallogr., 1965, 122, 230.
- 41 D. W. Cushen and R. Hulme, J. Chem. Soc., 1964, 4162.
- 42 N. A. Barnes, S. M. Godfrey, R. G. Pritchard and S. Ratcliffe, Poly-
- *hedron*, 2010, 29, 1822.
  43 A. Kondyurin, N. Byelousova, S. Byelousova and A. Kozulin, *J. Raman Spectrosc.*, 1993, 24, 825.
- 44 T. M. Klapötke, Main Group Met. Chem., 1997, 2, 81.
- 45 K. W. Fung, G. M. Begun and G. Mamantov, Inorg. Chem., 1973, 12, 53.
- 46 J. C. Evans, J. Mol. Spectrosc., 1960, 4, 435.
- 47 A. V. Kondyurin, S. N. Mikov and A. T. Kozulin, J. Raman Spectrosc., 1991, 22, 249.
- 48 K. Ichikawa and K. Fukushi, J. Raman Spectrosc., 1986, 17, 139.
- 49 A. R. J. Genge, W. Levason and G. Reid, Chem. Commun., 1998, 2159.
- 50 G. A. Fisher and N. C. Norman, Adv. Inorg. Chem., 1994, 41, 233.
- 51 Trinh-Toan and L. F. Dahl, *Inorg. Chem.*, 1976, **15**, 2953.
- 52 U. Ensinger, W. Schwarz and A. Schmidt, Z. Naturforsch. Teil B, 1982, 37, 1584; J. Zaleki, Ferroelectrics, 1997, 192, 71.
- 53 G. M. Sheldrick, *SHELX-97*, University of Göttingen, Göttingen, Germany, 1998.
- 54 R. H. Blessing, Acta Crystallogr., Sect. A: Found. Crystallogr., 1995, 51, 33.
- 55 ORTEP 3 for Windows: L. J. Farugia, J. Appl. Crystallogr., 1997, 30, 565.
- 56 MERCURY: C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453.