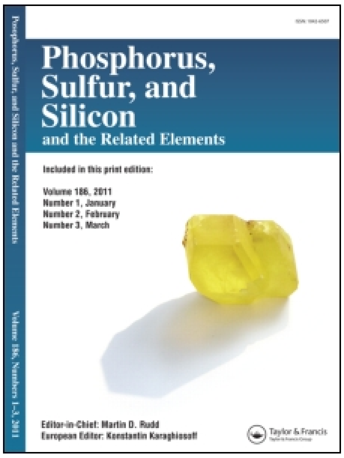

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Coordination Chemistry of Antimony and Bismuth: Lewis Acidity, σ^*-Orbitals and Coordination Geometry

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COORDINATION CHEMISTRY OF ANTIMONY AND BISMUTH: LEWIS ACIDITY, σ^*-ORBITALS AND COORDINATION GEOMETRY.

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Aspects of the coordination chemistry of antimony and bismuth trihalides and phenyl bismuth dihalides with phosphine and ether ligands are discussed together with a description of the bonding in these complexes. The bonding model described provides a rationalisation of the coordination geometries and the observed trends in some of the bond lengths and angles.

Key words: Antimony, bismuth, coordination complexes, structure, bonding.

INTRODUCTION

We and others have observed that antimony and bismuth trihalides, SbX_3 and BiX_3, and phenyl bismuth dihalides, $BiPhX_2$, are sufficiently Lewis acidic to exhibit quite an extensive coordination chemistry with ligands such as phosphines, PR_3, phosphine oxides, OPR_3, ethers, OR_2, and halide ions, X^-. The origin of this Lewis acidity together with many of the structural features of these complexes, such as bond lengths and coordination geometry, can be rationalised on the basis of a bonding model in which Sb–X or Bi–X σ^*-orbitals are the primary acceptor orbitals through which the ligands bond (as opposed to a more conventional description which employs vacant d orbitals). In this paper, we shall develope some of these ideas using a number of coordination complexes of antimony and bismuth as examples.

RESULTS AND DISCUSSION

The compounds $BiPhX_2$ (X = Cl, Br, I) can be crystallised from thf (tetrahydrofuran)-hexane mixtures to give the thf solvates [$BiPhX_2$(thf)] (**1**, X = Cl; **2**, X = Br; **3**, X = I).[1,2] The structures of these complexes are very similar (see Figure 1) and comprise monomeric units, $BiPhX_2$(thf), linked by halide bridges to form a one-dimensional polymer such that the overall coordination number of the bismuth centre is five with a regular, square-based pyramidal coordination geometry. Specifically, the phenyl group occupies the apical site whilst the basal plane contains three halides (one from an adjacent monomeric unit) and the oxygen atom of a coordinated thf ligand.

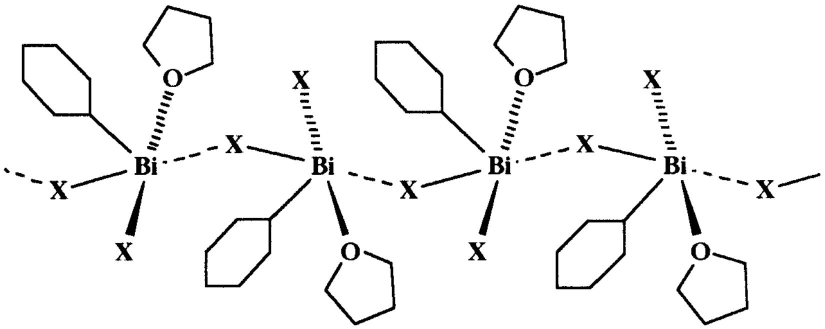

Figure 1. **1**, X = Cl; **2**, X = Br; **3**, X = I

For each bismuth centre, we may consider this arrangement as a coordination complex of a trigonal pyramidal $BiPhX_2$ unit to which a thf ligand and a halide from a neighbouring unit are attached such that they lie opposite the original Bi–X bonds thereby resulting in the observed square-based pyramidal geometry. Furthermore, for the two *trans* related halides, there is a shorter and a longer bond which we can define as primary and secondary bonds respectively after Alcock;[3] the remaining halide (*trans* to the thf) we will refer to as terminal. Relevant bond distances for the structures of **1** - **3** are listed in Table 1 from which a number of trends are apparent.

Firstly, it is clear that as we progress from chloride to iodide, i.e. **1** to **3**, the difference between the primary and secondary Bi–X bond lengths (Δ) decreases (were the distances to become equal, i.e. $\Delta = 0$, the distinction between primary and secondary would be lost). A complementary description, in this case, is that the Bi–X–Bi bridges become more symmetric. Moreover, the comparison is particularly appropriate for **1** and **2** since the crystals are isomorphous; compound **3** has a slightly different crystal structure but the configuration and conformation of the one-dimensional polymer is very similar to that found in **1** and **2**. This feature of the primary and secondary E–X bonds becoming more equal in length on progressing to the heavier halides is, in fact, quite general;[3] as another example we can consider the structures of $SbCl_3$ and the isomorphous α-$SbBr_3$ in which the difference between the three primary Sb–X bonds and a set of three *trans* secondary Sb–X bonds is about 1.25 and 1.10 Å respectively.[4]

Table 1 [a]

Bond	**1**, X = Cl[b]	**2**, X = Br[b]	**3**, X = I[c]	
Bi-X[d]	2.543(3)	2.684(1)	2.882(2)	2.892(2)
Bi-X[e]	2.654(3)	2.825(1)	3.056(2)	3.079(2)
Bi-X[f]	2.934(3)	3.038(1)	3.227(2)	3.211(2)
Δ [g]	0.280	0.213	0.171	0.132
δ [h]	0.111	0.141	0.174	0.187
Bi-O	2.608(7)	2.671(8)	2.808(17)	2.813(18)

[a] Bond lengths in Å, [b] isomorphous structures, [c] two crystallographically independent monomeric units, [d] terminal Bi-X bond, [e] primary Bi-X bond, [f] secondary Bi-X bond, [g] Δ = difference between Bi-X primary and Bi-X secondary, [h] δ = difference between Bi-X primary and Bi-X terminal.

In both the above examples, this trend towards smaller values of Δ can be taken as an indication of the increasing importance of secondary bonding (involving halides) where the heavier halides are concerned. We should also note, however, that in the structures **1** - **3**, the Bi–O(thf) bond lengths *increase* as we progress from chloride to iodide which implies that secondary bonding (or Lewis acidity) is *more* pronounced in the former case, i.e. in **1**. As a further point, it is observed when comparing a range of structures (for given E and X) that primary and secondary E–X bond distances are correlated such that as the secondary distance gets shorter, the primary distance gets longer.[1,3-5] We shall return to an explanation of these matters later, but a measure of the increasing length of the primary Bi–X bond in **1** - **3** (resulting from a decrease in Δ) can be had by comparing the difference (δ) between the so-called primary and terminal Bi–X bonds, this difference increasing from **1** to **3**, although we must exercise care in this comparison since the primary Bi–X distance will be influenced by the extent of the Bi–O interaction.

Having considered the effect on primary and secondary bond distances of changing the halide for a given group 15 element E, we now consider the effect of changing E whilst keeping the halide the same. An example of this situation is found in the centrosymmetric diphosphine antimony and bismuth bromide complexes [$E_2Br_6(dmpe)_2$] (dmpe = $Me_2PCH_2CH_2PMe_2$; **4**, E = Sb; **5**, E = Bi), the crystal structures of which are isomorphous and are represented in Figure 2.[6] The important feature here is the asymmetry of the E–Br–E bridge: for **4** the relevant Sb–Br distances are 2.828 and 3.595 Å (Δ = 0.767 Å) whereas for **5** the corresponding Bi–Br distances are 2.887 and 3.345 Å (Δ = 0.458 Å). Clearly, the bridge asymmetry is considerably smaller for bismuth than for antimony consistent with secondary bonding interactions being more pronounced for bismuth.

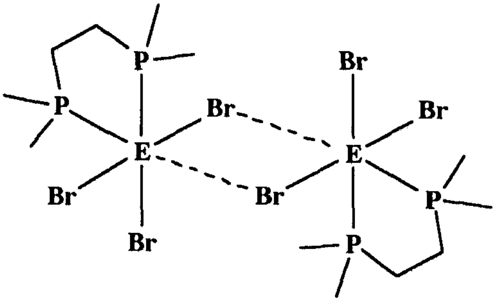

Figure 2. **4**, E = Sb; **5**, E = Bi

This second observation is also quite general and another example is found in the isomorphous element triiodides EI_3 (E = As, Sb, Bi).[4] These structures are based on a hexagonal close-packed array of iodines in which 2/3 of the octahedral holes in adjacent layers (1/3 of the total number of octahedral holes) are occupied by the E atoms. In AsI_3, the arsenic atom is displaced towards three mutually *cis* iodines giving three shorter As–I bonds and three *trans* bonds which are longer, whereas in BiI_3, the bismuth is in a regular octahedral environment with all six Bi–I distances equal. In SbI_3 the situation is intermediate and the relevant bond lengths and bond length differences for the three compounds are shown in Table 2.

Table 2

Compound	primary E–I	secondary E–I	Δ (E–I)
AsI_3	2.591	3.467	0.876
SbI_3	2.868	3.32	0.45
BiI_3	3.1	3.1	0

Thus overall, there are two important trends, at least as far as the element-halide interactions are concerned. Firstly, there is a tendency for secondary bonding to be more pronounced for the heavier halides, and secondly, secondary bonding is also seen to be more significant for the heavier group 15 elements.

In seeking to account for these observations we should comment first on a general model that is often employed to explain the Lewis acidity of the heavier main-group elements, or, more generally, the expansion of coordination number commonly seen in the second and subsequent rows. This model centres on the availability of vacant d orbitals which are then employed to form hybrid sets such as dsp^3 and d^2sp^3 for five and six-coordination respectively. This is not the place to comment on the validity of this model in detail, although the availability of the d orbitals, in terms of their energy, has been seriously questioned on the basis of recent calculations.[7]

An alternative model involves the use of E–X σ^*-orbitals, rather than d orbitals, and we can rationalise many of the trends commented on above, at least in a qualitative sense, according to a simple model of this type.

If we consider first, a two-orbital σ interaction between atoms E and X where X is the more electronegative, we arrive at a diagram as shown in Figure 3.

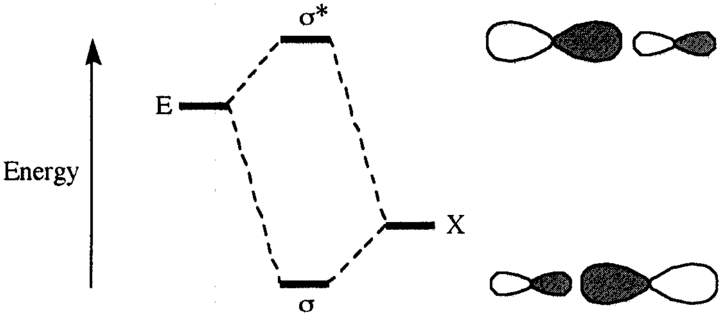

Figure 3. A σ-orbital interaction diagram for E–X

The first point to note is that the bonding σ-orbital will be polarised towards X since this is the lower energy atomic orbital (represented as a p orbital here) whereas the antibonding σ^*-orbital will be polarised more towards the less electronegative element E. If this σ^*-orbital is sufficiently low in energy, it can act as an acceptor orbital on E through which a Lewis base, L, can bond. Moreover, the polarisation of this orbital towards the E atom will tend to ensure that the Lewis base bonds to E (rather than X) and also that the geometry of the L–E–X interaction should be close to linear. Furthermore, as the L–E interaction becomes stronger (and the L–E bond shorter) the population of the σ^*-orbital is increased which will lead to a lengthening of the E–X bond, precisely the correlation which is observed.

If we now turn our attention to why heavier element E complexes should show more pronounced secondary bonding (or Lewis acidity), two factors become important. Firstly, on descending the group, the electronegativity of E will decrease which will be reflected in a raising of the energy of the valence E orbital(s). This will result in a greater difference between the energies of the atomic orbitals of E and X (providing X is more electronegative than E) leading to poorer overlap and a correspondingly lower energy σ^*-orbital (and higher energy σ-orbital). Secondly, the increasing size of the heavier element E means larger and more diffuse orbitals which will also result in poorer overlap with, importantly, the same consequences for the energies of the σ and σ^*-orbitals. The lower the energy of the σ^*-orbital, the more available for bonding this orbital becomes resulting in a corresponding increase in the likely extent of secondary bonding interactions, which in this case is the same as an increase in Lewis acidity.

In the case where we vary X for a given element E, we also observe that secondary bonding is apparently more significant where the heavier, and less electronegative, halides are concerned, but the situation here is a little more complicated as we must consider not only the acceptor properties of E but also the donor properties of X since the latter is acting as a bridging group. In this situation, a distinction is necessary between secondary bonding and Lewis acidity.

With regard to the E centre, increasing the size of X will lead to poorer orbital overlap, just as it did for E, resulting in a decrease in the energy of the σ^*-orbital. However, raising the energy of the X atomic orbitals (due to decreasing electronegativity) will reduce the energy separation between E and X which should tend to raise the energy of the σ^*-orbital and reduce the extent of polarization of this orbital on E. Clearly these two factors work in opposition rather than in concert and we must therefore be careful in our application of these qualitative ideas with regard to the acceptor properties, and hence acidity, of the E centre. It would seem when considering the halides, that the more important factor in understanding the observed trend towards increased secondary bonding, is that since the heavier halides are less electronegative, they will be better electron donors and should therefore tend to bridge more readily. Thus, it is probably the donor properties of X rather than the acceptor properties of E that are important here and we must therefore be careful of the distinction between secondary bonding and Lewis acidity; secondary bonding is apparently more pronounced even in the absence of factors which would tend to affect the acceptor properties (acidity) of E.

This latter point is reinforced if we consider the Bi–O bond distances in **1** - **3**, which increase on going from the chloride to the iodide. This implies that secondary bonding and Lewis acidity is more important in the chloride complex **1**. However, this is now purely a function of the acceptor ability of the E centre (since the donor, O, is the same in all compounds) and is consistent with the Bi–Cl σ^*-orbital being lower in energy than the Bi–I σ^*-orbital as a result of the electronegativity differences mentioned earlier (these presumably being more important than the size effects). With these ideas in mind, we can now look at coordination geometries in more detail.

If we consider a trigonal pyramidal unit EX_3 we can account for the geometry acording to VSEPR (Valence Shell Electron Pair Repulsion) theory. If the acceptor orbitals which give rise to the Lewis acidity are indeed the E–X σ^*-orbitals, we may represent the structure as shown in Figure 4. Addition of one ligand, L_1, then results in a four-coordinate structure with the expected equatorially-vacant, trigonal bipyramidal structure. Addition of two ligands, L_1 and L_2, leads to a square-based pyramidal geometry as seen in **1** - **3**, whereas three ligands, L_1 - L_3, result in an octahedral geometry. Moreover, this latter situation will result in a regular octahedral geometry when the lengths of the primary and secondary bonds are equal as is found in the BiI_3 structure and a range of bismuth and antimony halogenoanion structures (when X and L are the same, i.e. $L = X^-$ formally).[4]

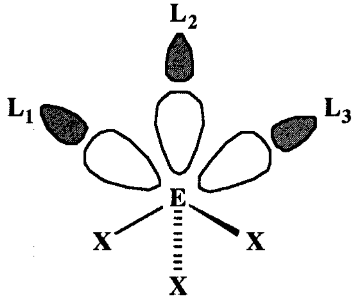

Figure 4. An EX_3 unit showing the three E–X σ^*-orbitals and the three ligands L_1 - L_3.

The four and five coordinate structures which derive from this model are also expected from VSEPR, but in the case of six-coordination, the two models are somewhat at odds. VSEPR has difficulty with six-coordination and seven electron pairs in terms of whether or not the structures are distorted (stereochemical activity or not of the lone pair), whereas the simple coordination ideas based on σ^*-orbitals lead directly to an octahedral arrangement where the presence of the non-bonded pair of electrons is not an issue (to a first approximation at least).

As mentioned above, in the majority of cases of six-coordination for seven electron pairs (six bonding pairs and one non-bonding) the observed structures are close to octahedral. There are, however, some interesting distortions from a regular geometry in some coordination complexes and it is these to which we shall now turn.

In the anionic complex $[SbI_4(dmpe)]^-$ **6** shown in Figure 5, it is found that the angle between one pair of *cis* iodines (α in Figure 5) is 123.92(2)° and that the corresponding Sb–I distances, r_1, are significantly longer (av. 3.291 Å) than those, r_2, to the other two iodines (av. 2.983 Å).[8]

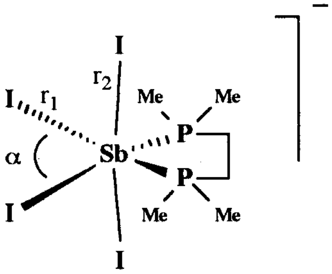

Figure 5. The structure of the anion $[SbI_4(dmpe)]^-$ **6**.

If we consider the two longer bonded iodines and the two phosphorus atoms as an equatorial plane with the remaining iodines in axial sites, it is clear that the lone pair shows a significant degree of stereochemical activity and that, specifically, it is becoming localised along the I·····I edge of the equatorial plane. Factors affecting the distortion of seven-electron pair octahedra have been discussed recently for a number of halides and halogenoanions of the group 15 elements in terms of orbital mixing and second order Jahn-Teller distortions[9] although we will not go into details here. We can, however, view the distortion in terms of a reaction coordinate involving a double S_N2 substitution at the antimony centre, as illustrated in Figure 6, where σ^*-orbitals are again useful.

If we consider the left hand side of Figure 6, i.e. structure **A**, we may view this as a situation in which the dmpe ligand approaches a $[SbI_4]^-$ anion which has the expected equatorially-vacant, trigonal bipyramidal structure. The lone pair associated with the antimony centre is indicated as the shaded orbital occupying the remaining equatorial site, and the acceptor orbitals, i.e. the two equatorial Sb–I σ^*-orbitals, are also shown (not shaded). If the dmpe approaches in the equatorial plane, each phosphorus atom will interact with one of the σ^*-orbitals as shown. Moreover, as this interaction becomes stronger, in other words, as the Sb–P distance decreases, this will have the result of lengthening these equatorial Sb–I bonds. In the extreme, we can imagine a complete double nucleophilic substitution of these two iodides by the two phosphorus atoms of the dmpe to give the $[SbI_2(dmpe)]^+$ cation **B**. Complex **6** can therefore be viewed as an intermediate along this reaction coordinate. Furthermore, it is clear that on going from **A** to **B**, the lone pair at the antimony centre effectively switches sides as indicated by the shaded orbital in **A** and **B**, and so as the iodides start to be displaced, the lone pair is becoming localised in the region between them. This model thus accounts both for the observed lengthening of the equatorial Sb–I bonds and the increase in angle above that which would be expected for a regular octahedron (by approx 35°).

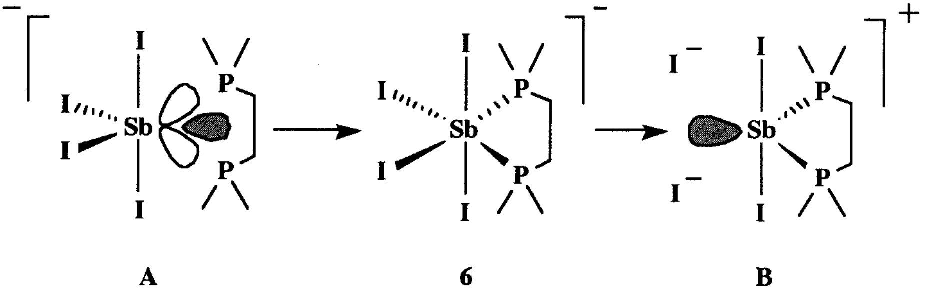

Figure 6. A reaction coordinate for the double nucleophilic substitution of two iodides by dmpe at an antimony centre.

In Figure 6, we can imagine the midpoint of this reaction coordinate to be a fairly regular octahedron and that **6** therefore lies more towards **B** than **A**. As a final example, in the bismuth complex anion $[BiI_4(PMe_2Ph)_2]^-$ with two mutually *cis* monodentate phosphines, a distortion is observed[7] such that the complex is more towards the **A** side, i.e. where the phosphorus atoms are still some distance from the element centre. In this case the Bi–P distances are long and the P–Bi–P angle is 112.33(6)° whilst the I–Bi–I angle for the two iodines in the equatorial plane (those *trans* to P) is 89.86(3)°, i.e. very close to 90°.

A related example of lone pair localization along an octahedral edge in a coordination complex is also found in the tellurium(IV) complex [$TeCl_4$(tmt)] (tmt = tetramethylthiourea)[10] although unlike in **6**, the ligands (here tmt) are *trans* and the distortion occurs along a Cl·····S edge.

In conclusion we can see that the σ^*-model is useful in understanding a number of features of the coordination chemistry of antimony and bismuth and of the heavier p-block elements in general, although as with all models, we must be aware of its limitations.

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