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Structure of the $[SbI_4\{Me_2P(CH_2)_2PMe_2\}]^-$ Anion: Structural Evidence for an Arrested Double S_N2 Substitution

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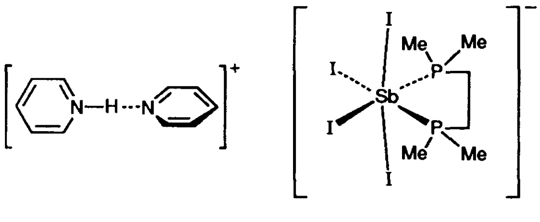
The antimony centre in the structurally characterised complex $[H(py)_2][SbI_4(dmpe)]$ [py = pyridine, dmpe = 1,2-bis(dimethylphosphino)ethane] shows significant distortions from octahedral geometry which are discussed in terms of an arrested double S_N2 transition state for the nucleophilic substitution of two iodide anions by dmpe.

Structurally characterised phosphine complexes of the heavier p-block elements are not well established[1] and, in the case of Group 15, the only complexes to have been described are $[\{Bi_2Br_7(PMe_3)_2\}_n]^{n-}$ **1**,[2] $[Bi_2Br_6(PMe_3)_4]$ **2**[3] and $[Bi_2Br_6(PMe_2Ph)_2(OPMe_2Ph)_2]$ **3**[3] for bismuth and $[SbBr_2(PMe_3)\{Fe(CO)(PMe_3)(\eta\text{-}C_5H_5)\}]$ **4**[4] and $[Sb(PPh_3)Me\{W(CO)_5\}_2]$ **5**[5] for antimony. Herein, we report the synthesis of an anionic 1,2-bis(dimethylphosphino)ethane (dmpe) complex of antimony $[H(py)_2][SbI_4(dmpe)]$ **6** (py = pyridine) and a description of the unusual structure in terms of an arrested transition state along a double S_N2 reaction coordinate.

Complex **6** was prepared serendipitously, although repeatably and in reasonable yield,† in a two step process. The reaction between SbI_3 and 1 equivalent of dmpe in tetrahydrofuran (thf) afforded a yellow powder which analysed† as the anticipated product $[SbI_3(dmpe)]$ **7**. The structure of **7** is likely to be dimeric and similar to those of **2** and **3**, but obtaining X-ray quality crystals was hampered by the fact that **7** is essentially insoluble in most common solvents. Compound **7** did, however, dissolve readily in pyridine to give a yellow solution from which yellow crystals were subsequently obtained,† but microanalytical data indicated that these crystals were not of **7** but of a new complex **6**. The identity of **6** was established by X-ray crystallography‡ as the salt $[H(py)_2][SbI_4(dmpe)]$, as shown in Fig. 1 and below, and its formation is probably the result of partial hydrolysis due to the presence of traces of water in the pyridine; we have encountered somewhat similar reactions previously.[2]



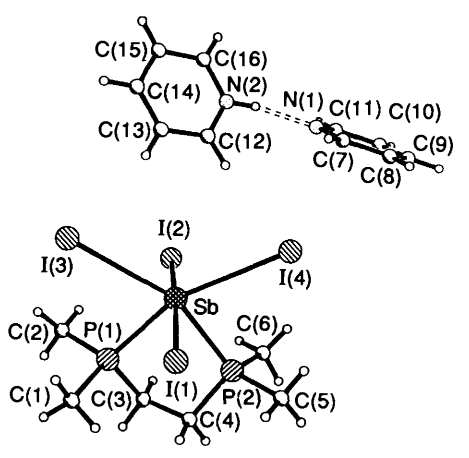


Fig. 1 A view of the structure of complex **6** showing the cation, $[H(py)_2]^+$, and the anion, $[SbI_4(dmpe)]^-$ together with the atom numbering scheme. Selected bond lengths (Å) and angles (°): Sb–P(1) 2.6658(14), Sb–P(2) 2.6437(14), Sb–I(1) 2.9665(9), Sb–I(2) 3.0006(9), Sb–I(3) 3.3152(10), Sb–I(4) 3.2670(10); P(1)–Sb–P(2) 78.59(4), P(1)–Sb–I(1) 89.15(3), P(1)–Sb–I(2) 82.51(3), P(1)–Sb–I(3) 79.92(3), P(1)–Sb–I(4) 155.20(3), P(2)–Sb–I(1) 84.62(3), P(2)–Sb–I(2) 89.20(3), P(2)–Sb–I(3) 157.80(3), P(2)–Sb–I(4) 78.13(3), I(1)–Sb–I(2) 170.475(15), I(1)–Sb–I(3) 89.59(2), I(1)–Sb–I(4) 97.04(2), I(2)–Sb–I(3) 93.46(2), I(2)–Sb–I(4) 88.74(2), I(3)–Sb–I(4) 123.92(2)

The $[H(py)_2]^+$ cation in **6** comprises a protonated pyridine which is hydrogen bonded to a second pyridine in a nearly linear fashion [N(1) • • • H(2)–N(2) 160°].

The $[SbI_4(dmpe)]^-$ anion adopts a structure in which the antimony centre is approximately octahedrally co-ordinated by four iodines and the two phosphorus atoms of a dmpe ligand, but there are some significant and notable distortions from an

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† 1,2-Bis(dimethylphosphino)ethane (0.23 g, 1.534 mmol) was added to a stirred solution of SbI_3 (0.76 g, 1.534 mmol) in tetrahydrofuran (thf) (20 cm^3) which resulted in a yellow solution and the formation of a yellow precipitate. Stirring was continued overnight and the thf was then removed by vacuum which afforded $[SbI_3(dmpe)]$ **7** as an analytically pure yellow powder (Found: C, 11.40; H, 2.20. $C_6H_{16}I_3P_2Sb$ requires C, 11.05; H, 2.45%).

Addition of pyridine (10 cm^3) to solid **7** with stirring overnight afforded a yellow solution although much of **7** remained undissolved. The yellow solution was transferred to a separate flask and hexane (20 cm^3) was layered over it. Solvent diffusion at room temperature over a period of days afforded yellow crystals of **6** which were suitable for X-ray diffraction (Found: C, 20.70; H, 2.70; N, 3.25. $C_{16}H_{27}I_4N_2P_2Sb$ requires C, 20.45; H, 2.90; N, 3.00%). The bismuth analogue of **6** was prepared similarly (Found: C, 19.50; H, 2.60; N, 2.90. $C_{16}H_{27}BiI_4N_2P_2$ requires C, 18.75; H, 2.65; N, 2.75%).

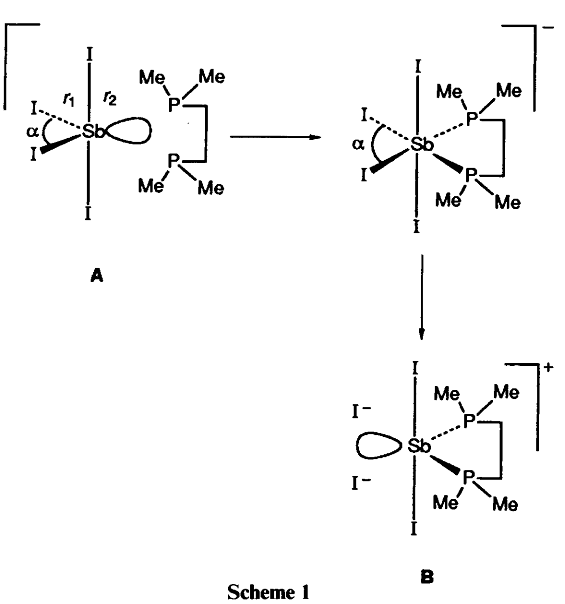
‡ *Crystal data*: $C_{16}H_{27}I_4N_2P_2Sb$, 0.50 × 0.22 × 0.18 mm, $M = 938.68$, monoclinic, space group $P2_1/n$, $a = 7.8486(11)$, $b = 17.271(3)$, $c = 20.438(3)$ Å, $\beta = 99.348(15)°$, $U = 2733.6(7)$ Å^3, $Z = 4$, $D_c = 2.281$ g cm^{-3}, $\mu = 5.648$ mm^{-1} (Mo-Kα radiation, $\lambda = 0.710\ 73$ Å), $F(000) = 1720$; $R' = 0.0743$ for 230 parameters, including anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for constrained H atoms, by refinement on F^2 from all 4792 measured unique data ($2\theta_{max}$ 50°) measured at 160 K on a Stoe–Siemens diffractometer and corrected semiempirically for absorption; weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0372p)^2 + 2.43p]$ where $p = (F_o^2 + 2F_c^2)/3$; conventional $R = 0.0267$ for F values of 4059 reflections with $F^2 > 2\sigma(F^2)$.[6,7] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Diffraction data collected for the bismuth analogue were not of sufficient quality to enable a complete structure solution but the observed positions of the heavy atoms were consistent with a structure similar to **6**.

idealised geometry. Thus, the pseudo-axial iodines, I(1) and I(2), are tipped towards the dmpe ligand [I(1)–Sb–I(2) 170.475(15)°] and the angle between the pseudo-equatorial iodines, I(3) and I(4), is unusually large [I(3)–Sb–I(4) 123.92(2)°] (see below). Moreover, the antimony to axial iodine distances (av. 2.984 Å) are shorter than the corresponding distances to the equatorial iodines (av. 3.291 Å) by approximately 0.3 Å; values comparable, respectively, to the three shorter primary [2.868(10) Å] and the three longer secondary (3.32 Å) Sb–I bonds in crystalline SbI_3.[8]

These distortions cannot readily be accounted for by steric arguments but the latter two observations may be rationalised by a model illustrated in Scheme 1 based on a nucleophilic substitution reaction pathway. Thus we can view $[SbI_4(dmpe)]^-$ as a complex of $[SbI_4]^-$ and dmpe, an initial encounter geometry for which is illustrated in **A**. The structure of the monomeric $[SbI_4]^-$ anion, although not independently established, would be expected to be disphenoidal, on the basis of valence shell electron pair repulsion arguments,[9] with the axial Sb–I bonds longer than the equatorial Sb–I bonds[9] (r_1 and r_2 in Scheme 1), and with an inter-equatorial angle (α in Scheme 1) of close to 100°.[10] Moreover, the Lewis acidity of this species is likely to be associated with the two unoccupied, equatorial Sb–I σ* orbitals, $2b_1$ and $4a_1$ in C_{2v} symmetry,[*,11] such that the two phosphorus atoms would be expected to approach the antimony centre *trans* to these equatorial Sb–I bonds. Population of these orbitals will lead to a lengthening of the equatorial Sb–I bonds as observed, the extent of the lengthening depending on the strength of the Sb–P interaction. This latter point is difficult to gauge in this case since few Sb–P bonds have been structurally characterised;[2] the observed Sb–P bond lengths in $[SbI_4(dmpe)]^-$ (av. 2.655 Å) are only slightly longer than those found in **4** [2.596(4) Å][4] and **5** [2.594(6) Å][5] both of which are also co-ordinate P ⟶ Sb bonds.

The effect on the equatorial I–Sb–I angle can be appreciated if we consider a complete substitution of two iodide anions by the dmpe ligand to give the cation $[SbI_2(dmpe)]^+$ **B** {complexes of this general type, *i.e.* $[EX_2L_2]^+$, have not been structurally characterised but there is a report of a related complex $[BiPh_2(OAsPh_3)_2]^+$ [12]}. Thus as the substitution of the two iodides by the dmpe ligand proceeds (*i.e.* **A** ⟶ **B**), the antimony lone pair effectively switches sides and a stereochemical consequence of this should be that the equatorial I–Sb–I angle increases during substitution as the lone pair becomes localised in this region. The structural data are, therefore, consistent with a view of the structure of $[SbI_4(dmpe)]^-$ as a point along a reaction coordinate involving a double nucleophilic substitution at antimony of two iodide anions by a dmpe ligand, *i.e.* as an arrested transition state.



Scheme 1

The use of crystal structure data in delineating the stereochemical consequences of a particular reaction coordinate has been discussed in general by Bürgi and Dunitz[13,14] and specifically for four-co-ordinate phosphorus, antimony and bismuth systems by Schmidpeter and co-workers,[15] Sowerby[16] and ourselves[10,17] respectively. The most relevant study with regard to the present work concerns a double substitution at four-co-ordinate tin(IV)[18] although in this case there is no stereochemically active lone pair. In this study, we have demonstrated that unusual structures adopted by acid–base complexes of the heavier p-block elements can be understood both in terms of a particular reaction coordinate, in conjunction with a partially stereochemical active lone pair, and σ* orbitals as the relevant acceptor orbitals.

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References

1 W. Levason and C. A. McAuliffe, *Coord. Chem. Rev.*, 1976, **19**, 173.
2 W. Clegg, R. J. Errington, G. A. Fisher, M. E. Green, D. C. R. Hockless and N. C. Norman, *Chem. Ber.*, 1991, **124**, 2457.
3 W. Clegg, R. J. Errington, R. J. Flynn, M. E. Green, D. C. R. Hockless, N. C. Norman, V. C. Gibson and K. Tavakkoli, *J. Chem. Soc., Dalton Trans.*, 1992, 1753.
4 H. A. Kaul, D. Greissinger, W. Malisch, H. P. Klein and U. Thewalt, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 60.
5 B. Sigwarth, U. Weber, L. Zsolnai and G. Huttner, *Chem. Ber.*, 1985, **118**, 3114.
6 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
7 G. M. Sheldrick, SHELXS-86 and SHELXL-92, programs for crystal structure determination and refinement, University of Göttingen, 1986 and 1992.
8 J. Trotter and T. Zobel, *Z. Kristallogr.*, 1966, **123**, 67.
9 R. J. Gillespie and I. Hargittai, *The VSEPR Model of Molecular Geometry*, Allyn and Bacon, Boston, MA, 1991.
10 W. Clegg, R. J. Errington, G. A. Fisher, D. C. R. Hockless, N. C. Norman, A. G. Orpen and S. E. Stratford, *J. Chem. Soc., Dalton Trans.*, 1992, 1967 and refs. therein.
11 T. A. Albright, J. K. Burdett and M. H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, 1985.
12 T. Allman, R. G. Goel and H. S. Prasad, *J. Organomet. Chem.*, 1979, **166**, 365.
13 H.-B. Bürgi, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 460.
14 H.-B. Bürgi and J. D. Dunitz, *Acc. Chem. Res.*, 1983, **16**, 153.
15 K. B. Dillon, A. W. G. Platt, A. Schmidpeter, F. Zwaschka and W. S. Sheldrick, *Z. Anorg. Allg. Chem.*, 1982, **488**, 7.
16 D. B. Sowerby, personal communication.
17 W. Clegg, N. A. Compton, R. J. Errington, G. A. Fisher, D. C. R. Hockless, N. C. Norman, N. A. L. Williams, S. E. Stratford, S. J. Nichols, P. S. Jarrett and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1992, 193.
18 D. Britton and J. D. Dunitz, *J. Am. Chem. Soc.*, 1981, **103**, 2971.

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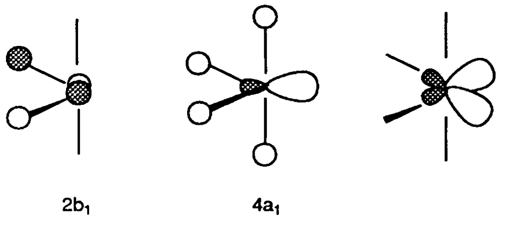
[*] The two equatorial Sb–I σ* orbitals, $2b_1$ and $4a_1$, for a disphenoidal AB_4E structure are shown below[11] together with a diagram of the relevant and alternative Sb–I σ* bond orbitals which are derived from an effective hydridisation of $2b_1$ and $4a_1$; the bond orbital picture[11] more clearly illustrates the origin of the expected *trans* disposition of the Lewis bases to the equatorial A–B bonds.



$2b_1$ $4a_1$