The Crystal Structure of the $[Sb(C_2O_4)_3]^{3-}$ Ion. A Sterically Active Lone Pair in Six-co-ordination

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Summary The crystal structures of potassium and ammonium trisoxalatoantimonate(III) tetrahydrates have shown that the structure of the $[Sb(C_2O_4)_3]^{3-}$ ion is based on a pentagonal bipyramid, with a lone pair presumably occupying an axial position.

THE molecular structure of XeF_6,[1] and the structures of isoelectronic anions $[TeCl_6]^{2-}$, $[TeBr_6]^{2-}$, and $[SbBr_6]^{3-}$ [2] are generally regarded as examples of the breakdown of the valence-shell electron-pair-repulsion (VSEPR) approach[3] to the explanation of molecular stereochemistry. The apparent lack of any appreciable distortion away from O_h symmetry due to the lone pair of electrons has been rationalised on the basis of the difficulty of including more than six bulky ligands in the central atom co-ordination sphere. In the case of XeF_6,[1] the electron-diffraction data have been interpreted in terms of a distorted (approximately C_{3v}) octahedron undergoing large vibrations. It is possible that similar anomalies occur in the lattices of the isoelectronic anions, causing the X-ray diffraction data to show an averaged, higher symmetry. We have examined the crystal structure of the isoelectronic complex anion $[Sb(C_2O_4)_3]^{3-}$, to see whether the more rigid bidentate oxalate group has "frozen out" a statically distorted structure.

Crystals of $(NH_4)_3Sb(C_2O_4)_3,4H_2O$ are orthorhombic, $a = 20{\cdot}88$, $b = 6{\cdot}890$, $c = 11{\cdot}75$ Å, *Pnam*, $U = 1690$ Å^3, $Z = 4$, $D_m = 1{\cdot}93$, $D_c = 1{\cdot}95$. 1211 independent reflections were measured (Cu-K_α radiation) using a Stoe Automated Weissenberg Diffractometer, and the structure solved and refined by standard methods to an R-value of 0·088. Crystals of $K_3Sb(C_2O_4)_3,4H_2O$ are isomorphous, $a = 20{\cdot}94$, $b = 6{\cdot}90$, $c = 11{\cdot}69$ Å. 629 independent reflection intensities, collected by Weissenberg and precession photography (Mo-K_α radiation) and measured by an integrating microdensitometer, have refined to an R of 0·12.

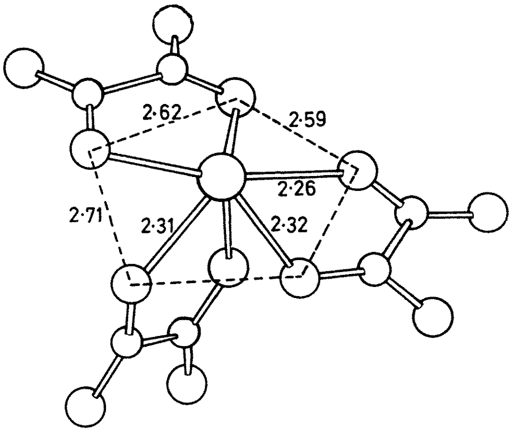

FIGURE 1. *A perspective view of the* $[Sb(C_2O_4)_3]^{3-}$ *ion. Interatomic distances* (Å) *are averaged values from the two structures. E.s.d.'s are* Sb–O ± 0·01, O–O ± 0·02 Å.

The structure of the $[Sb(C_2O_4)_3]^{3-}$ anion in both compounds is very similar (Figures 1 and 2). The anion has *m* (C_s) symmetry and is clearly based on a pentagonal bipyramid with one vacant axial site. One oxalate group lies in the mirror plane, with its two co-ordinated oxygen atoms bridging one equatorial and one axial site. The other two oxalate groups are mirror-related and lie approximately in the equatorial plane. Figure 1 is a perspective view of the anion. Five of the six co-ordinated oxygen atoms are almost coplanar and form a slightly distorted pentagon (equatorial bond angles at antimony are all in the range 70—72°). The antimony is displaced 0·35 Å out of the equatorial plane away from the axial oxygen atom. Figure 2 is a projection approximately perpendicular to the equatorial plane, and shows clearly how all six co-ordinated oxygen atoms lie on one side of the antimony atom, a situation which has been observed in other antimony(III) compounds with lower co-ordination numbers.[4] Since the next nearest atom to antimony (an oxalate oxygen from a neighbouring anion) is 3·42 Å away, the unusual stereochemistry is presumably due to the repulsive effect of a lone pair of electrons occupying an axial site of a pentagonal bipyramidal arrangement of valence orbitals. There is no reason to suppose that the oxalate groups alone are responsible for this stereochemistry. The structure of the corresponding tris(oxalato)-complex of chromium(III),[5] an ion with no sterically important non-bonding electrons, is close to octahedral symmetry. Thus in this particular example of a seven electron pair system, the VSEPR assumption of the stereochemical importance of non-bonding electron pairs is vindicated. It is also interesting to note that the axial Sb–O bond lengths of 2·06(2) and 2·10(1) Å for the potassium and ammonium salts, respectively, are significantly shorter than the equatorial values, a demonstration of the considerable repulsive effects of the lone pair and the Sb–O bonding electron pairs in the equatorial positions.

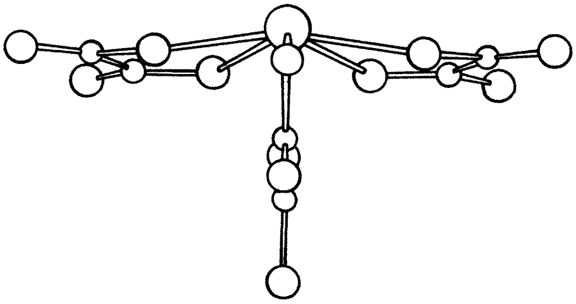

FIGURE 2. *A projection of the* $[Sb(C_2O_4)_3]^{3-}$ *ion approximately perpendicular to the equatorial plane.*

The pentagonal bipyramidal structure for a formally six-co-ordinate atom has also been recognised in the structure of $Pb[(Pr^iO)_2PS_2]_2$,[6] in this case the lone pair is assumed to occupy an equatorial position. A different structure having C_{3v} symmetry has been reported in a bidentate dithiocarbamate–arsenic(III) complex $(Et_2NCS_2)_3$-As.[7] The difficulties of predicting a unique structure for seven-co-ordination by minimising nuclear and electron repulsion energies have been described,[8] obviously in such a situation the individual steric requirements of the ligands become very important in controlling the overall geometry.

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