Structure of Organometallic Derivatives of Quinquevalent Antimony and Bismuth containing Metal–Oxygen–Metal Bonds

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Summary $(Ph_3SbN_3)_2O$ and $(Ph_3BiClO_4)_2O$ have metal–oxygen–metal bridges with angle M–O–M close to 141° and a trigonal bipyramidal configuration at the metal atoms.

$$\underset{(I)}{R_3YX_2} \rightarrow \underset{(II)}{X{\cdot}R_3Y\text{–}O\text{–}YR_3{\cdot}X}$$

R = Ph, Me
Y = Sb, Bi
X = Halide, Nitrate
Pseudohalide

HYDROLYSIS of triorgano-antimony and -bismuth derivatives (I) yield compounds of general formulae (II)[1,2] for which i.r. spectra and conductance data have been interpreted in favour of non-ionic structures containing five-co-ordinated antimony and bismuth. On the other hand, a tetrahedral antimony configuration with ionic ClO_4^-

groups has been claimed from i.r. studies for $(Me_3SbClO_4)_2O$ [3] and $(Ph_3SbClO_4)_2O$.[2] Re-investigation of the spectra of hydrated and anhydrous forms of $(Ph_3SbClO_4)_2O$ led us to conclude that spectral data previously reported[2] are more appropriate to a hydrated form of this compound. Our i.r. data are summarised in the Table from which we inferred that anhydrous $(Ph_3SbClO_4)_2O$ and $(Ph_3BiClO_4)_2O$ would have structures rather similar to those postulated for (II) above with five-co-ordinate metal atoms. To elucidate the structures and the nature of the bonding in such systems we have determined the crystal structures of a representative of (II), $(Ph_3SbN_3)_2O$, and of $(Ph_3BiClO_4)_2O$† and find that the preferred molecular configuration at the metal atoms is a slightly distorted trigonal bipyramid.

TABLE

Perchlorate i.r. frequencies (cm^{-1}) *for* $[Ph_3Sb(ClO_4)]_2O$, $[Ph_3Bi(ClO_4)]_2O$, *and their hydrates*

$[Ph_3Sb(ClO_4)]_2O$	$[Ph_3Sb(ClO_4)]_2O,(H_2O)_2$
1155 s	1120 s
1015 s	1056—1038 b,s
868	928 m
625 m	625 m
400 w	418 m

$[Ph_3Bi(ClO_4)]_2O$	$[Ph_3Bi(ClO_4)]_2O,(H_2O)_2$
1128 s	1110 s
1028 s	1050—1034 b,s
920—900 m	930 m
705 m	628 m
640 m	

b = broad; m = medium; s = strong; w = weak.

The analysis of $(Ph_3SbN_3)_2O$ reveals that the molecule has a (crystallographic) twofold (C_{2v}) axis through the oxygen atom. The antimony atom in the asymmetric unit is in a slightly distorted trigonal bipyramidal environment with the bridging oxygen at one vertex and the azide group at the other (Figure 1). The Sb–O bond length [1·985(3) Å] is significantly shorter than that found in methoxytetraphenylantimony [2·061(7) Å,[4] dimethoxytriphenylantimony [2·039(8), 2·027(8) Å],[5] and in tetraphenylantimony hydroxide [2·048(7) Å].[6]

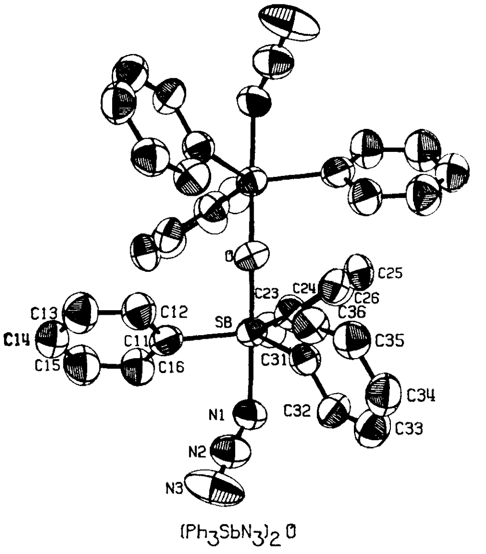

FIGURE 1. *An ORTEP prepared view of* $(Ph_3SbN_3)_2O$ *showing our numbering scheme.*

The Sb–O–Sb angle [139·8(4)°] is much larger than tetrahedral as a consequence of phenyl · · · phenyl intramolecular interaction between the two halves of the molecule. The mean Sb–C(phenyl) distance is 2·115(8) Å in good agreement with *e.g.* the mean distance in methoxytetraphenylantimony [2·119(8) Å].[4] The O–Sb–N(1) angle is essentially linear [178·3(3)°] but the phenyl carbon atoms are distorted slightly out of the equatorial plane away from the bridging oxygen atom in such a way that the antimony atom is 0·11 Å above the plane of C(11) C(21) C(31), resulting in a mean O–Sb–C(phenyl) angle of 92·1(3)°. The azide group, which is nearly linear [N(1)–N(2)–N(3) is 176·8(9)°] is oriented *trans* with respect to the O–Sb′ bond in the symmetry related portion of the molecule and the angle Sb–N(1)–N(2) is 118·3(6)°; relevant bond lengths are Sb–N(1) 2·236(8) Å, N(1)–N(2) 1·213(12) Å, N(2)–N(3) 1·116(16) Å.

No crystallographic symmetry is demanded for $(Ph_3BiClO_4)_2O$ and, despite the differences in σ-donor capacity of azide and perchlorate, the molecular geometry is similar to that of $(Ph_3SbN_3)_2O$. Thus the Bi–O–Bi angle is 142·4(7)° and the two independent halves of the molecule adopt slightly distorted trigonal bipyramidal configurations with the bridging oxygen at one vertex and a perchlorate oxygen at the other (Figure 2). The average O–Bi–O angle is 171·0(6)° and mean oxygen–metal distances are Bi–O(bridge) 2·07(1) Å and Bi–O(perchlorate) 2·65(1) Å; the mean Bi–C(phenyl) distance is 2·19(2) Å, not significantly different from the value [2·12(8) Å] found in triphenylbismuth dichloride.[7]

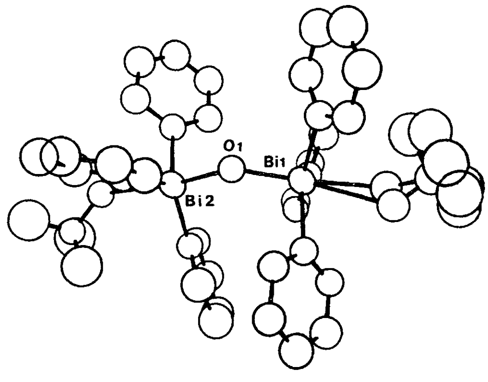

FIGURE 2. *General view of* $(Ph_3BiClO_4)_2O$ *showing the disordered perchlorate group.*

One of the two perchlorates in the asymmetric unit is disordered between two sites which are not completely resolved, consequently bond length information from this group is not reliable [the mean Cl–O distance is 1·39(6) Å.] In the ordered perchlorate group the Cl–O(bismuth) bond [1·48(2) Å] is longer than the mean of the remaining three Cl–O bonds [1·38(3) Å]. The O(perchlorate)–Bi distance [2·65(1) Å] is too long to be a normal single bond [*cf.* Bi–O(bridge) 2·07 Å] and, with the perchlorate distances above, implies that in this instance the Bi–O(perchlorate)

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† Crystals of the anhydrous antimony derivative could not be obtained at this time in a satisfactory form for structure studies.

bond is partially covalent, intermediate in character between Cl^{-}–O · · · Bi^{+} and Cl–O–Bi. The phenyl carbon atoms lie nearly 0·3 Å off the equatorial planes through the bismuth atoms and the mean O(bridge)–Bi–C(phenyl) angle is 97·1(7)°, significantly larger than in $(Ph_3SbN_3)_2O$ [92·1(3)°] reflecting the weaker co-ordination between perchlorate and bismuth *vis à vis* azide and antimony.

Crystals of $(Ph_3SbN_3)_2O$ are monoclinic, space group $C2/c$ (C_{2h}^{6}) with four molecules in a unit cell of dimensions $a = 12{\cdot}633(2)$, $b = 19{\cdot}374(4)$, and $c = 14{\cdot}178(5)$ Å, $\beta = 105{\cdot}40(1)°$, molecular symmetry = 2.

$(Ph_3BiClO_4)_2O$ crystallised in space group $P2_1/c(C_{2h}^{5})$ with four molecules in a unit cell of dimensions $a = 18{\cdot}750(3)$, $b = 10{\cdot}108(2)$, $c = 18{\cdot}927(3)$ Å, $\beta = 92{\cdot}19(2)°$.

Data for both materials were collected with a Hilger and Watts computer-controlled four-circle diffractometer. Both structures were solved by way of the heavy atom and refined by least-squares methods. For $(Ph_3SbN_3)_2O$ all non-hydrogen atoms were refined anisotropically and hydrogen atoms, located from a difference synthesis, were allowed for but not refined. At the conclusion of refinement R is 0·044 for some 2000 observed data. Some 3100 observed data were used in refinement of the $(Ph_3BiClO_4)_2O$ structure. With bismuth allowed anisotropic motion, and carbon, oxygen, and chlorine atoms restricted to isotropic motion, R at the conclusion of refinement is 0·070.

We are grateful to the National Research Council of Canada for a post-graduate scholarship (to D.R.R.), a crystallographic computing grant (to G.F.), and operating grants (to G.F. and R.G.G.).

(*Received, October 12th*, 1971; *Com.* 1773.)

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