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ORGANOBISMUTH COMPOUNDS
IV*. PREPARATION AND STRUCTURAL CHARACTERISTICS OF TRIPHENYLBISMUTH(V) COMPOUNDS CONTAINING A Bi–O–Bi BOND

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SUMMARY

Oxybis(triphenylbismuth) derivatives $(Ph_3Bi{-}O{-}BiPh_3)X_2$ where $X = ClO_4$, NO_3, Cl, Br, NCO and CF_3COO have been prepared and their structural characteristics have been determined by infrared spectroscopy and conductance measurements. In the solid state a non-ionic structure in which the X groups act as monodentate ligands, is indicated for these compounds. Conductance studies show that the non-ionic structure is maintained in acetonitrile except for $X = ClO_4$. The diperchlorate forms a dihydrate which also appears to have an ionic structure in the solid state as well as in acetonitrile. Conductance and infrared spectroscopic data for the anhydrous as well as the hydrated diperchlorate in dichloromethane suggest the presence of ion-pairs or non-ionic species. Triphenylbismuth oxide has also been isolated and its infrared spectrum indicates that it has a polymeric structure containing –Bi–O–Bi– units. The Bi–O–Bi stretching frequencies for these compounds have been assigned.

INTRODUCTION

Organoantimony(V) derivatives of the type R_3SbX_2, where R = methyl or phenyl and X = an anion group, are converted into compounds of the type $(R_3Sb{-}O{-}SbR_3)X_2$ upon hydrolysis. Several $(R_3Sb{-}O{-}SbR_3)X_2$ derivatives such as dihalides[2,3], dipseudohalides[4], dinitrates[5,6], diperchlorates[2,3] and dicarboxylates[7] have been now studied. With the exception of the perchlorates, these compounds are considered to be non-ionic, and to contain five-coordinate antimony. The perchlorates[2,3] have been reported to be ionic containing the $(R_3Sb{-}O{-}SbR_3)^{2+}$ cation. Recent studies of the triphenylbismuth(V) derivatives, Ph_3BiX_2[8], such as dihalides, dicyanate, dinitrate and dicarboxylates show that these compounds are structurally similar to the analogous triphenylantimony(V) compounds Ph_3SbX_2. However, tertiary organobismuth(V) compounds containing the Bi–O–Bi group have hitherto been unknown. In fact, with the exception of triphenylbismuth(V) derivatives of oxy-anions (which have been shown to contain Bi–O bonds), the organobismuth compounds containing bismuth–oxygen bonds have not been well characterized.

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* For Part III see ref. 1.

The organoantimony oxy compounds, $(R_3Sb{-}O{-}SbR_3)X_2$, such as diperchlorates[2,3], dinitrates[6], diisocyanates[4], diazides[4] and ditrifluoroacetates[7] are conveniently prepared by a metathetical reaction of trimethyl- or triphenylantimony dichloride with the appropriate silver salt if the reaction is carried out in a wet organic solvent such as acetone, alcohol or acetonitrile. Surprisingly, the metathetical reaction between an acetone solution of triphenylbismuth dichloride and an alcoholic solution of silver perchlorate has been found[9] to result in the formation of tetraphenylbismuthonium perchlorate. In view of this report we studied the metathetical reactions of triphenylbismuth dichloride with silver salts and found that the reaction of triphenylbismuth dichloride with silver perchlorate or tetrafluoroborate, using acetone as solvent, resulted in the formation of acetonyltriphenylbismuthonium perchlorate or tetrafluoroborate, $[Ph_3Bi(CH_2COCH_3)]X$[10], $X = ClO_4$ or BF_4. On the basis of further studies on the metathetical and the hydrolytic reactions of triphenylbismuth dihalides we now report on the preparation and structural characterization of oxybis(triphenylbismuth) derivatives $(Ph_3Bi{-}O{-}BiPh_3)X_2$ as well as the previously unknown triphenylbismuth oxide, Ph_3BiO.

RESULTS AND DISCUSSION

$(Ph_3Bi{-}O{-}BiPh_3)X_2$ *derivatives*

The reaction of a benzene solution of triphenylbismuth dichloride with an aqueous solution of silver perchlorate afforded crystals of hydrated oxybis(triphenylbismuth) diperchlorate. The crystals are orthorhombic with a $P2_12_12_1$ space group and the unit cell contains four molecules. The measurements of the unit cell dimensions and the density gave a formula weight of 1137 which suggests that the product is a dihydrate. (The theoretical value for dihydrate is 1131). Upon drying the hydrated crystals in vacuo for about a week crystals of anhydrous $(Ph_3Bi{-}O{-}BiPh_3)(ClO_4)_2$ were obtained. Crystals of the anhydrous diperchlorate were also obtained by recrystallization of the dihydrate from absolute ethanol. The crystals of anhydrous diperchlorate are monoclinic with a $P2_1/C$ space group. The unit cell of the anhydrous compound also has four molecules. The crystallographic molecular weight for the anhydrous compound was found to be 1085 which is in close agreement with the theoretical value (1095).

The reaction of triphenylbismuth dichloride with silver tetrafluoroborate under similar conditions, however, did not afford oxybis(triphenylbismuth) ditetrafluoroborate; the main product of the reaction was found to be triphenylbismuth difluoride. The reaction between triphenylbismuth dichloride and silver nitrate under similar conditions gave a mixture containing mostly triphenylbismuth dinitrate and a small amount of oxybis(triphenylbismuth) dinitrate. Pure oxybis(triphenylbismuth) dinitrate was, however, obtained from the reaction of an acetone solution of triphenylbismuth dichloride with an aqueous solution of silver nitrate. The reactions of triphenylbismuth dichloride with silver cyanate and trifluoroacetate under similar conditions did not afford the oxy compounds. Triphenylbismuth dicyanate and ditrifluoroacetate were obtained instead. Analogous reactions[4,7] of triphenylantimony dichloride under similar conditions afford the oxy compounds.

Triorganoantimony dihalides are converted into the corresponding dihydroxides by treatment with two equivalents of alkali hydroxide, and, the reaction between equimolar portions of the dihalide and the alkali hydroxide results in the formation of the oxy dihalide. The hydrolysis of triphenylbismuth dichloride and dibromide has been studied by Challenger and Goddard[11]. These workers concluded that triphenylbismuth was the main product of the reaction of triphenylbismuth dichloride or dibromide with aqueous or alcoholic alkali metal hydroxide. However, by treating chloroform solutions of the dichloride and the dibromide with moist ammonia, these workers obtained products which they formulated as triphenylbismuth hydroxychloride and hydroxybromide. Our studies show that the reaction between equimolar portions of triphenylbismuth dichloride or dibromide and alcoholic sodium or potassium hydroxide affords oxybis(triphenylbismuth) dichloride or dibromide, $[(Ph_3Bi)_2O]X_2$. However, the action of alkali hydroxide on triphenylbismuth difluoride under similar conditions yielded triphenylbismuth and some uncharacterized material. The metathetical reactions of the oxybis(triphenylbismuth) dichloride with silver cyanate and silver trifluoroacetate afforded the oxy dicyanate and the oxy ditrifluoroacetate, respectively, but the oxy diacetate could not be obtained from a similar reaction with silver acetate. The main product of the reaction was found to be impure triphenylbismuth.

The analytical data and the melting points for the compounds studied in this investigation are recorded in Table 1. All the $(Ph_3Bi{-}O{-}BiPh_3)X_2$ compounds are white crystalline solids. They are unaffected by atmospheric moisture but decompose slowly on exposure to light. Samples stored in the dark at room temperature did not show any noticeable decomposition for several weeks. The compounds are soluble in polar organic solvents such as dichloromethane, ethanol and acetonitrile. With the exception of the diperchlorate and the dinitrate they are also soluble in chloroform and acetone. The diperchlorate is not appreciably soluble in chloroform or acetone;

TABLE 1

ANALYTICAL DATA

Compound	M.p. (°C)	Analysis found (calcd.) (%)	
		C	H
$\{[(C_6H_5)_3Bi]_2O\}(ClO_4)_2(H_2O)_2$	148[a]	38.63 (38.20)	3.06 (3.03)
$\{[(C_6H_5)_3Bi]_2O\}(ClO_4)_2$[b]	144[a]	39.28 (39.47)	2.86 (2.76)
$\{[(C_6H_5)_3Bi]_2O\}(NO_3)_2$[c]	155–156	42.34 (42.36)	3.04 (2.96)
$\{[(C_6H_5)_3Bi]_2O\}Cl_2$[d]	147[a]	44.55 (44.69)	2.50 (3.12)
$\{[(C_6H_5)_3Bi]_2O\}Br_2$	135[e]	41.41 (40.92)	3.19 (2.86)
$\{[(C_6H_5)_3Bi]_2O\}(NCO)_2$	139[e]	45.84 (46.54)	3.08 (3.08)
$\{[(C_6H_5)_3Bi]_2O\}(CF_3COO)_2$[f]	156–157	42.70 (42.70)	2.88 (2.70)
$(C_6H_5)_3BiO$	155	48.40 (47.50)	3.69 (3.31)

[a] Decomposed without melting. [b] Found: Cl, 6.54. Calcd.: Cl, 6.47%. [c] Found: N, 3.04. Calcd.: N, 2.74%. [d] Found: Cl, 7.33. Calcd.: Cl, 7.32%. [e] Decomposed on melting. [f] Found: F, 10.17. Calcd.: 10.76%.

TABLE 2

CONDUCTANCE DATA[a]

Compound	Λe ($ohm^{-1} \cdot cm^2 \cdot eq^{-1}$)
$\{[(C_6H_5)_3Bi]_2O\}(ClO_4)_2(H_2O)_2$	117.0
$\{[(C_6H_5)_3Bi]_2O\}(ClO_4)_2$	141.0
$\{[(C_6H_5)_3Bi]_2O\}(NO_3)_2$	9.9
$\{[(C_6H_5)_3Bi]_2O\}Cl_2$	2.8
$\{[(C_6H_5)_3Bi]_2O\}Br_2$	6.7
$\{[(C_6H_5)_3Bi]_2O\}(NCO)_2$	1.3
$\{[(C_6H_5)_3Bi]_2O\}(CF_3COO)_2$	3.2
$(C_6H_5)_3BiO$	1.5

[a] At 2×10^{-3} M conc. in acetonitrile at 25°. The specific conductance of the solvent was $1.17 \times 10^{-6} \cdot ohm^{-1} \cdot cm^{-1}$.

the dinitrate is moderately soluble in chloroform but is only very sparingly soluble in acetone. The equivalent conductances of these compounds were determined in acetonitrile and the observed conductances are recorded in Table 2. The conductance data show that both the hydrated and the anhydrous diperchlorate behave as 1/2 electrolytes in acetonitrile but that the other compounds are not significantly ionized. For solutions of the anhydrous as well as the hydrated diperchlorate in dichloromethane (10^{-3} M) the conductance was found to be ~ 0.7 $ohm^{-1} \cdot cm^2 \cdot eq^{-1}$. The conductance of a 10^{-3} M solution of tetraethylammonium perchlorate in this solvent was found to be ~ 22.8 $ohm^{-1} \cdot cm^2 \cdot eq^{-1}$. Therefore both the hydrated and the anhydrous diperchlorate appear to be unionized in dichloromethane.

The infrared spectra of these compounds were studied in the solid state in the region 4000 to 200 cm^{-1}. The spectra of all the compounds show very similar absorption bands due to the phenyl groups and these bands do not differ significantly from those observed for triphenylbismuth dihalides[8]. One of the important features in the spectrum of each compound is the presence of a strong band at ca. 630–620 cm^{-1}. Since no strong band is observed in this region for triphenylbismuth[12] or triphenylbismuth dihalides[8] the 630–620 cm^{-1} band is assigned to the Bi–O–Bi antisymmetric stretching vibration. This assignment is consistent with those reported for other M–O–M antisymmetric stretching frequencies. The Sb–O–Sb antisymmetric stretching frequency for the $(Ph_3Sb{-}O{-}SbPh_3)X_2$ compounds[3,13,14] is observed at ca. 750 cm^{-1}. The Sn–O–Sn antisymmetric stretching frequency[15] for the $(R_3Sn)_2O$ compounds has been reported in the region 775–740 cm^{-1} and the Ge–O–Ge asymmetric stretching frequency[16] for $(H_3Ge)_2O$ has been assigned at ca. 870 cm^{-1}.

For the hydrated oxybis(triphenylbismuth) diperchlorate weak bands are observed at ca. 3300, 3180 and 1620 cm^{-1} which can be attributed to the H–O–H stretching and bending vibrations. The absorption bands due to the internal vibrations of the ClO_4, NO_3, NCO and CF_3COO groups were identified by comparing the spectra of these derivatives with the spectra of the oxybis(triphenylbismuth) dichloride or dibromide. The anion group frequencies as well as the Bi–O–Bi antisymmetric stretching frequency observed for each compound are listed in Table 3.

For a perchlorate ion of T_d symmetry[17] only the asymmetric Cl–O stretching (ν_3) and bending (ν_4) modes, each of which is triply degenerate, are infrared active.

TABLE 3

INFRARED SPECTROSCOPIC DATA (cm^{-1}) IN THE HIGH FREQUENCY REGION[a]

Compound	Bi–O–Bi Asym. str. frequency	Anion group frequencies
$\{[(C_6H_5)_3Bi]_2O\}(ClO_4)_2(H_2O)_2$	632–628 s	1110 s, 1042 s, 930 m, 628 (sh)
$\{[(C_6H_5)_3Bi]_2O\}(ClO_4)_2$	620 s	1128 s, 1028 s, 920–900 s, 705 m, 640 m
$\{[(C_6H_5)_3Bi]_2O\}(NO_3)_2$	636 s	1470 s, 1290 s, 1012 m, 816 w, 712 w
$\{[(C_6H_5)_3Bi]_2O\}Cl_2$	632 s	
$\{[(C_6H_5)_3Bi]_2O\}Br_2$	630 s	
$\{[(C_6H_5)_3Bi]_2O\}(NCO)_2$	628 s	2180 s
$\{[(C_6H_5)_3Bi]_2O\}(CF_3COO)_2$	630 s	1700 s, 1412 m
$(C_6H_5)_3BiO$	625 s	

[a] m = Medium; s = strong; sh = shoulder; w = weak.

For the hydrated diperchlorate two strong bands at 1110 and 1042 cm^{-1} are observed in the Cl–O asymmetric stretching frequency region. The infrared forbidden Cl–O symmetric stretching frequency (ν_1) is also observed as a medium band at 930 cm^{-1}. The absorption due to the Cl–O bending frequncy is apparently masked by the strong band due to the Bi–O–Bi stretching frequency which shows a shoulder at 628 cm^{-1}. Since the observed splitting of the ν_3 mode and the appearance of the infrared inactive mode ν_1 can be caused by the lowering of the perchlorate symmetry due to hydrogen bonding as well as solid state effects, the observed spectrum of the hydrated diperchlorate can be interpreted in terms of an ionic structure containing the hydrated cation $[Ph_3Bi(H_2O)]_2O^{2+}$. Indirect support for the proposed structure is provided by the isolation of the cationic complexes of the type $[(Ph_3BiL)_2O](ClO_4)_2$, where L is an O-donor ligand such as triphenylarsine oxide. Further studies on such complexes are in progress and the results of these studies will be discussed in a separate communication.

The perchlorate frequencies observed for the anhydrous oxy diperchlorate are, however, comparable to the perchlorate frequencies reported for the complexes $Co(Ph_2MeAsO)_4(ClO)_2$[18] and $Co[CH_3S(CH_2)_2SCH_3]_2(ClO_4)_2$[19,20] which have been shown by X-ray crystallography to contain monodentate perchlorate groups. Two strong well resolved bands at 1128 and 1028 cm^{-1} and a medium band at 920–900 cm^{-1} are observed for the anhydrous diperchlorate and these can be assigned as the A_1, E, and A_1 modes of the unidentate perchlorate group of C_{3v} symmetry[17]. Two weaker but well resolved perchlorate bands are also observed at 705 and 640 cm^{-1} and these can be assigned to the ClO_3 bending modes[17]. The infrared spectrum of oxybis(triphenylantimony) diperchlorate[3] has been interpreted in terms of an ionic structure. It is worth noting that the perchlorate frequencies[3] reported for the oxybis(triphenylantimony) diperchlorate are almost identical to those observed for the hydrated oxybis(triphenylbismuth) diperchlorate. We, therefore, repeated the reported work on oxybis(triphenylantimony) diperchlorate and our results[21] show that the spectrum reported for the oxybis(triphenylantimony) diperchlorate is in fact due to the hydrated oxybis(triphenylantimony) diperchlorate. The spectrum which we obtained for the anhydrous oxybis(triphenylantimony) diperchlorate[21] is indeed best interpreted in terms of a non-ionic structure containing monodentate perchlorate groups. Accordingly, we believe that in the solid state the anhydrous oxybis(triphenylbismuth) diperchlorate as well as the analogous antimony compound have a five coordinate non-ionic structure containing monodentate perchlorate groups.

The infrared spectra of the hydrated and the anhydrous diperchlorate were also recorded in dichloromethane and acetonitrile in the frequency range 1200 to 950 cm^{-1}. In dichloromethane the spectra for both compounds were identical and showed two strong well resolved perchlorate bands at 1142 and 1028 cm^{-1}. The symmetric Cl–O stretching frequency could not be determined in solution due to the overlap with the solvent bands. Under similar conditions the infrared spectrum of a dichloromethane solution of tetraethylammonium perchlorate showed only a single perchlorate band at 1100 cm^{-1}. Thus the spectroscopic as well as the conductance data indicate that in dichloromethane both the hydrated and the anhydrous diperchlorate exist either as ion-pairs or as non-ionic species. In acetonitrile satisfactory spectra could not be obtained due to the strong absorption by the solvent at ca. 1100 cm^{-1}. Still the spectra of both the compounds indicated the presence of only one perchlorate band at ca. 1120 cm^{-1}.

The absorption frequencies due to the anion groups observed for the oxybis(triphenylbismuth) dinitrate, dicyanate and the ditrifluoroacetate also indicate that the anion groups in each of these compounds act as monodentate ligands. For the dinitrate the strong nitrate bands at 1470 and 1290 cm^{-1} correspond to the $-NO_2$ asymmetric (ν_4) and symmetric (ν_1) stretching vibrations of the $-ONO_2$ group[22]. The moderately strong band at 1012 cm^{-1} corresponds to the NO stretching mode (ν_2) and the weak bands at 816 and 712 cm^{-1} can be assigned to the out-of-plane rocking (ν_6) and the NO_2 bending (ν_3 or ν_5) modes. The nitrate bands at 1470 and 1290 cm^{-1} were unchanged when the spectrum was recorded in chloroform solution, therefore, the observed infrared spectroscopic features cannot be attributed to the solid state effects.

For the oxybis(triphenylbismuth) dicyanate only the N–C–O asymmetric stretching frequency[23] can be assigned and this frequency is observed at 2190 cm^{-1} in the solid state as well as in chloroform solution. The N–C–O symmetric stretching frequency[23] is masked by the phenyl bands; the N–C–O bending frequency[23] which is expected to occur at ca. 620 cm^{-1} is masked by the strong Bi–O–Bi asymmetric stretching band. Although the observed N–C–O asymmetric stretching frequency for this compound is in the same range as reported for several organometallic isocyanates we consider that the mode of bonding of NCO to bismuth (nitrogen *versus* oxygen) cannot be ascertained from the present data and the term cyanate is being used here without such implications. The asymmetric and symmetric (O=C–O) stretching frequencies for the oxybis(triphenylbismuth) ditrifluoroacetate are observed at 1700 and 1412 cm^{-1} in the solid state. In chloroform solution the 1700 cm^{-1} band is shifted to 1678 cm^{-1} but the symmetric (O=C–O) stretching frequency remains unchanged.

The infrared absorption bands for these compounds in the 600 to 200 cm^{-1} region are listed in Table 4. For the ditrifluoroacetate the bands due to the trifluoroacetate group have not been included. The other anion groups do not show any absorption in this region. A comparison of the spectra of $(Ph_3Bi–O–BiPh_3)X_2$ derivatives with the spectra of Ph_3Bi[12] and Ph_3BiX_2 derivatives[8] shows that the strong band at ca. 450 cm^{-1} and the medium to weak bands at ca. 250–220 cm^{-1} for the $(Ph_3Bi–O–Bi-$

TABLE 4

INFRARED SPECTROSCOPIC DATA (cm^{-1}) IN THE LOW FREQUENCY REGION[a]

Compound	Frequencies							
$\{[(C_6H_5)_3Bi]_2O\}(ClO_4)_2(H_2O)_2$		445 s		382 m	300 w	254 m		222 w
$\{[(C_6H_5)_3Bi]_2O\}(ClO_4)_2$		445 s	380 vw	349 m	300 w	252 s		224 w
$\{[(C_6H_5)_3Bi]_2O\}(NO_3)_2$		449 s	400 vw	369 m	300 w	248 m		222 w
$\{[(C_6H_5)_3Bi]_2O\}Cl_2$	560 vw	454 s	400 vw	344 m	300 w	251 m		224 w
$\{[(C_6H_5)_3Bi]_2O\}Br_2$		448 s		346 m	298 vw	246 m		220 w
$\{[(C_6H_5)_3Bi]_2O\}(NCO)_2$		452 s	402 vw	338 m	298 vw	252–242 m		220 w
$\{[(C_6H_5)_3Bi]_2O\}(CF_3COO)_2$		448 s		356 m		250 m	232 vw	222 m
$(C_6H_5)_3BiO$		448 s		340 m		250 m		220 m

[a] m = Medium; s = strong; v = very; w = weak.

$Ph_3)X_2$ derivatives are similar to those observed for Ph_3Bi and Ph_3BiX_2 derivatives. These bands can, therefore, be assigned to the *y*- and *t*-vibrations[24] respectively. The medium band observed for the $(Ph_3Bi-O-BiPh_3)X_2$ derivatives in the 332 to 338 cm^{-1} region appears to be associated with the vibration of the Bi–O–Bi group, since no absorption is observed in this region for Ph_3Bi or Ph_3BiX_2 derivatives. This band is therefore tentatively assigned to the Bi–O–Bi symmetric stretching frequency. Although the Sb–O–Sb symmetric stretching frequency for the $(R_3Sb-O-SbR_3)X_2$ derivatives has not been established, the proposed assignment is consistent with the assignments for the Sn–O–Sn[15] and Ge–O–Ge[16] symmetric stretching frequencies.

For the Ph_3BiX_2 derivatives[8] where X = Cl, NO_3, NCO and CH_3COO the Bi–X stretching frequency occurs at ca. 240, 250, 275 and 254 cm^{-1} respectively. Therefore the Bi–X stretching frequency for the $(Ph_3Bi-O-BiPh_3)X_2$ derivatives is expected to occur in the region 250 cm^{-1} or below.

The X-ray powder photographs of oxybis(triphenylbismuth) dichloride, dibromide, dicyanate and ditrifluoroacetate were compared with those of the corresponding Ph_3BiX_2 derivatives as well as with that of Ph_3BiO. On this basis the possibility of the oxy compounds being mixtures of Ph_3BiX_2 and Ph_3BiO can be ruled out.

Triphenylbismuth oxide

Preparation of triphenylbismuth dihydroxide[25] from the reaction of triphenylbismuth dichloride and aqueous silver oxide has been described in the literature. We have isolated triphenylbismuth oxide, Ph_3BiO, in small yield by treatment of a benzene solution of triphenylbismuth dichloride with the solid or an aqueous solution of silver oxide. Triphenylbismuth oxide is a white solid which is unaffected by atmospheric moisture and appears to be stable at room temperature. It is moderately soluble in benzene and is also slightly soluble in acetonitrile but is insoluble in chloroform or diethyl ether. In acetone or alcohol it is reduced to triphenylbismuth. It also decomposes slowly in benzene but the decomposition is slow enough to allow the isolation of a relatively pure compound. The equivalent conductance of a 2×10^{-3} *M* solution in acetonitrile at 25° was found to be 1.5 $ohm^{-1} \cdot cm^2 \cdot eq^{-1}$. The molecular weight could not be determined due to its decomposition in solution.

The infrared spectrum of solid triphenylbismuth oxide was studied in 4000 to 200 cm^{-1} region. No bands are observed in the spectrum which can be attributed to the O–H stretching or Bi–OH bending frequencies. Therefore, the possibility of this compound being a hydroxide can be ruled out. The observed spectrum for the oxide is very similar to that of the oxybis(triphenylbismuth) dichloride or dibromide. The infrared absorption bands for the triphenylbismuth oxide in the 600 to 200 cm^{-1} region are listed in Table 4. The strong band due to the Bi–O–Bi asymmetric stretching vibration observed for the oxy dichloride or other oxy compounds at ca. 620 cm^{-1} is also observed for the oxide at 630 cm^{-1}. The band of medium intensity observed for the oxy compounds in the region 382–338 cm^{-1} is observed for the oxide at 340 cm^{-1}. The bands at ca. 450 and 250 cm^{-1} observed for the oxide can be assigned to the *y*- and *t*-vibrations respectively. The presence of the Bi–O–Bi stretching frequencies and the marked similarity of the spectrum of triphenylbismuth oxide with the spectra of the oxybis(triphenylbismuth) derivatives suggests that triphenylbismuth oxide has a five coordinate polymeric structure involving –Bi–O–Bi– units. The polymeric structure is also in accord with the low solubility of this compound in organic solvents.

EXPERIMENTAL

Materials

Triphenylbismuth dichloride and other Ph_3BiX_2 derivatives were prepared as described previously[8]. Acetonitrile was purified by treatment with calcium hydride and subsequent distillation under reduced pressure. Other solvents and chemicals were reagent grade and were used without further purification.

Analyses

Elemental analyses were performed by A. B. Gygli, Microanalytical Laboratory, Toronto, or by Schwarzkopf Microanalytical Laboratory, New York.

Physical measurements

Infrared spectra were recorded on a Beckman Model IR-12 spectrophotometer. Samples were prepared as mulls in Nujol or halocarbon oil and the spectra were recorded using KRS-5 and polyethylene windows. Solution spectra were obtained using 0.1 mm pathlength sealed sodium chloride cells. The electrical conductivities were measured with a Beckman Model RC-18A conductivity bridge. The X-ray powder photographs were taken with a Philips Model PW 1024/10 Debye–Scherrer camera using Cu-K_α radiation with a nickel filter. Unit cell and space group data were obtained by photographic methods using single crystals. Densities were determined by floating the crystals in a mixture of carbon tetrachloride and bromoform. Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected.

Oxybis(triphenylbismuth) diperchlorate (hydrated)

A benzene solution of triphenylbismuth dichloride (1.6 g in 25 ml of benzene) and an aqueous solution of silver perchlorate (1.3822 g in 25 ml of water) were mixed together and stirred for three hours at room temperature. The benzene layer was separated and the remaining mixture was filtered. The residue which contained silver chloride and most of the oxybis(triphenylbismuth) diperchlorate was treated with 50 ml of 95% ethanol. The mixture was filtered and the filtrate was concentrated under vacuum. The compound was finally crystallised as white crystals by adding diethyl ether slowly and cooling it down to 5°. Yield 50%.

Oxybis(triphenylbismuth) diperchlorate (anhydrous)

This compound was obtained by either drying a finely powdered sample of hydrated oxybis(triphenylbismuth) diperchlorate under vacuum at room temperature for about a week or by recrystallising the hydrated sample from absolute ethanol and anhydrous diethyl ether. Yield 100%.

Oxybis(triphenylbismuth) dinitrate

An aqueous solution of silver nitrate (1.1324 g, 0.0066 mole) was added to an acetone solution of triphenylbismuth dichloride (1.703 g, 0.0033 mole) and the mixture was stirred for 3–4 h at room temperature. It was then filtered and the filtrate was concentrated under vacuum. To the concentrated solution diethyl ether was added slowly till the solution became turbid. Upon cooling the turbid solution, crystals of oxybis(triphenylbismuth) dinitrate separated out. The crystals were filtered off and were dried under vacuum at room temperature. Yield 60–70%.

Oxybis(triphenylbismuth) dichloride

An acetone solution of triphenylbismuth dichloride (5.11 g, 0.01 mole) was mixed with a methanol solution of sodium hydroxide (0.4 g, 0.01 mole) and stirred for 2 h at room temperature. The mixture was then filtered and the filtrate was concentrated under vacuum until white crystals of oxybis(triphenylbismuth) dichloride started to come out of the solution. The compound was finally precipitated by adding water to the mixture and recrystallised twice from chloroform and petroleum ether. Yield 60–70%.

Oxybis(triphenylbismuth) dibromide

This compound was obtained by the method as described above using triphenylbismuth dibromide instead of dichloride. Yield 60–70%.

Oxybis(triphenylbismuth) dicyanate

Silver cyanate (0.3 g, 0.002 mole) was added to an acetone (50 ml) solution of oxybis(triphenylbismuth)dichloride (0.9669 g, 0.001 mole) and the mixture was stirred for 5 h at about 5°. It was then filtered and the filtrate was concentrated under vacuum. The compound was obtained as fine white powder by adding water to the solution. It was filtered and crystallised twice from dry acetone and diethyl ether. Yield 40%.

Oxybis(triphenylbismuth) ditrifluoroacetate

The compound was obtained by the metathetical reaction of an acetone solution of oxybis(triphenylbismuth) dichloride with an aqueous solution of silver trifluoroacetate under conditions similar to those described for the dicyanate. Yield 40%.

Triphenylbismuth oxide

Method I. A benzene solution of triphenylbismuth dichloride (1.7 g, 0.0033 mole) was mixed with an aqueous solution of freshly prepared silver oxide (0.7725 g, 0.0033 mole) and stirred for 5 h at room temperature in the dark. The benzene layer was separated by decantation and stored over molecular sieves for 12 h. It was then filtered and concentrated by evaporation of benzene. Triphenylbismuth oxide was obtained from the concentrated benzene solution by adding petroleum ether slowly. Yield 40%.

Method II. A benzene solution of triphenylbismuth dichloride (1.7 g, 0.0033 mole) was stirred with silver oxide for about 2 h and then filtered. The filtrate was concentrated under vacuum and then treated with petroleum ether when triphenylbismuth oxide was obtained as white powder. Yield 10%.

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REFERENCES

1 R. G. Goel and H. S. Prasad, *Can. J. Chem.*, 49 (1971) 2529.
2 G. G. Long, G. O. Doak and L. D. Freedman, *J. Amer. Chem. Soc.*, 86 (1964) 209.
3 G. O. Doak, G. G. Long and L. D. Freedman, *J. Organometal. Chem.*, 4 (1965) 92.
4 R. G. Goel and D. R. Ridley, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 21.
5 M. Shindo and R. Okawara, *J. Organometal. Chem.*, 5 (1966) 537.
6 G. C. Tranter, C. C. Addison and D. B. Sowerby, *J. Organometal. Chem.*, 12 (1968) 369.
7 R. G. Goel, unpublished results.
8 R. G. Goel and H. S. Prasad, *Can. J. Chem.*, 48 (1970) 2488, and references therein.
9 G. O. Doak, G. G. Long, S. K. Kakar and L. D. Freedman, *J. Amer. Chem. Soc.*, 88 (1966) 2342.
10 R. G. Goel and H. S. Prasad, *J. Chem. Soc. A*, (1971) 562.
11 F. Challenger and A. E. Goddard, *J. Chem. Soc.*, 118 (1920) 762.
12 K. Shobatake, C. Postmus, J. R. Ferraro and K. Nakamoto, *Appl. Spectrosc.*, 23 (1969) 12.
13 R. G. Goel, P. N. Joshi, D. R. Ridley and R. E. Beaumont, *Can. J. Chem.*, 47 (1969) 1423.
14 R. G. Goel and D. R. Ridley, *Inorg. Chem.*, submitted for publication.
15 T. Tanaka, *Organometal. Chem. Rev. A*, 5 (1970) 1, and references therein.
16 S. Cradock, *J. Chem. Soc. A*, (1968) 1426.
17 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, (1961) 2081.
18 G. A. Rodley and P. W. Smith, *J. Chem. Soc. A*, (1967) 1580.
19 F. A. Cotton and D. L. Weaver, *J. Amer. Chem. Soc.*, 87 (1965) 4189.
20 P. Pauling, G. B. Robertson and G. A. Rodley, *Nature*, 207 (1965) 73.
21 R. G. Goel and H. S. Prasad, to be submitted for publication.
22 C. C. Addison and N. Logan, *Advan. Inorg. Chem. Radiochem.*, 6 (1964) 98.
23 J. S. Thayer and R. West, *Advan. Organometal. Chem.*, 5 (1967) 115.
24 D. H. Whiffen, *J. Chem. Soc.*, (1956) 1350.
25 F. Challenger and O. V. Richards, *J. Chem. Soc.*, (1934) 405.