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COMPLEXES OF ORGANOMETALLIC COMPOUNDS

XXX. OXINATO TRIPHENYLBISMUTH HALIDES

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SUMMARY

The novel organobismuth(V) derivatives $Ph_3BiCl(Ox)$ and $Ph_3BiBr(Ox)$ (Ox^- = 8-quinolinate) have been synthesized, and their configuration investigated in the solid state and in solution. The complexes are assumed to be octahedral in the solid, with Ox^- acting as a chelating base and the halide atoms coordinating to bismuth. Tentative assignments of infrared bands in the 300–80 cm^{-1} region to Bi–Hal and other skeletal modes are proposed. The main effect of solvents appears to be the weakening and breaking of Bi–N-bonds.

INTRODUCTION

There is little published information on the coordination chemistry of organobismuth derivatives[1]. Complexes of $PhBi^{III}$ with mono- and bidentate nitrogen bases, and bidentate sulfur ligands, have recently been studied[2–4], and one of us (G.F.) has investigated anionic complexes of $PhBi^{III}$ ($PhBiX_3^-$; X = Cl, Br, I) and Ph_2Bi^{III} ($Ph_2BiX_2^-$; X = Cl, Br, I, SCN) in which the bismuth atom apparently attains four coordination[5]. In addition, the compounds 2,2′-biphenylylenetriphenylbismuth[6], triphenylbismuthonium tetraphenylcyclopentadienylide[7], and triphenylbismuth derivatives of the Group VIB metal carbonyls[8] have been described.

As a part of our program on coordination compounds of Group V organometal entities we have prepared the two complexes $Ph_3BiX(Ox)$ in which X = Cl or Br and HOx = 8-quinolinol, and have carried out configurational studies (mainly by vibrational and electronic spectra) on the solids and on solutions. These novel complexes appear to be the first examples of coordination compounds of organobismuth(V). 8-Quinolinol was selected as a ligand because of its ability to complex with metal ions and organometal moieties, and because of the ease of determination of the coordination behaviour of Ox^- by spectroscopy[9–18].

EXPERIMENTAL

Reagents from C. Erba (Milan) and Fluka (Buchs SG) were used, and were purified when necessary by standard procedures. Solvents were dried over molecular sieves. The compounds Ph_3BiCl_2 and Ph_3BiBr_2 were prepared by treating triphenylbismuth with Cl_2 and Br_2, respectively[19].

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TABLE 1

MELTING POINTS AND ANALYTICAL DATA FOR $Ph_3BiX(Ox)$ COMPLEXES

Compound	*M.p.* (°C)	*Analysis found (calcd.) (%)*			
		C	*H*	*N*	*Hal*
$Ph_3BiCl(Ox)$	115–117	52.00 (52.31)	3.25 (3.41)	2.22 (2.26)	5.39 (5.72)
$Ph_3BiBr(Ox)$	98–101	48.60 (48.81)	3.11 (3.19)	2.18 (2.11)	11.96 (12.03)

The compounds $Ph_3BiX(Ox)$ were prepared by adding ca. 0.5 mmole of Ph_3BiX_2, dissolved in a small volume of CH_2Cl_2 or $CHCl_3$, to ca. 0.5 mmole of NaOx in anhydrous CH_3OH. Yellow-orange crystals were obtained, and were purified by dissolution in CH_2Cl_2 and precipitation with CH_3OH; yield 80%. M.p. and analytical data are shown in Table 1.

Electronic spectra were recorded on Beckman DK-2A and Cary 7007 spectrophotometers; for solution spectra, 10 mm cells and anhydrous solvents were used, while spectra of solids were measured on Nujol mulls (made from finely powdered samples) spread on filter paper. IR spectra were recorded with Perkin–Elmer Mod. 457 and 621 and Beckman IR 11 spectrometers, on Nujol and hexachlorobutadiene mulls. PMR spectra were measured at 27° as 5–10% solutions in CH_2Cl_2 or C_6D_6 using Jeol C–60 and Varian HA–100 spectrometers, with TMS as internal standard. $Ph_3BiCl(Ox)$ was also studied at −80° in CH_2Cl_2 and toluene-d_8. The van 't Hoff "*i*" factors for solutions were determined at 37° using a Mechrolab Osmometer Mod. 301 A. Conductivity measurements were performed at 25° with an KBI conductolyzer Type 5300 B.

RESULTS AND DISCUSSION

The occurrence of absorption bands, centered around 360 nm, in the electronic spectra of solid $Ph_3BiX(Ox)$ (Fig. 1) suggests that Ox^- coordinates to Bi atoms

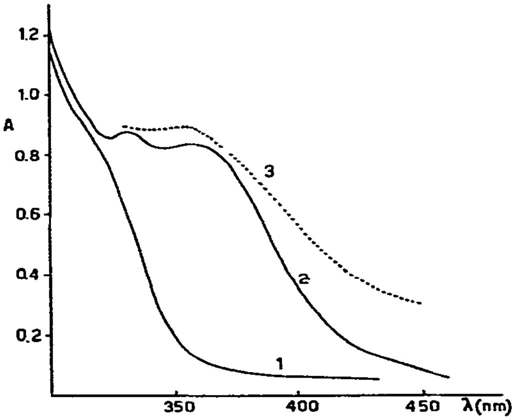
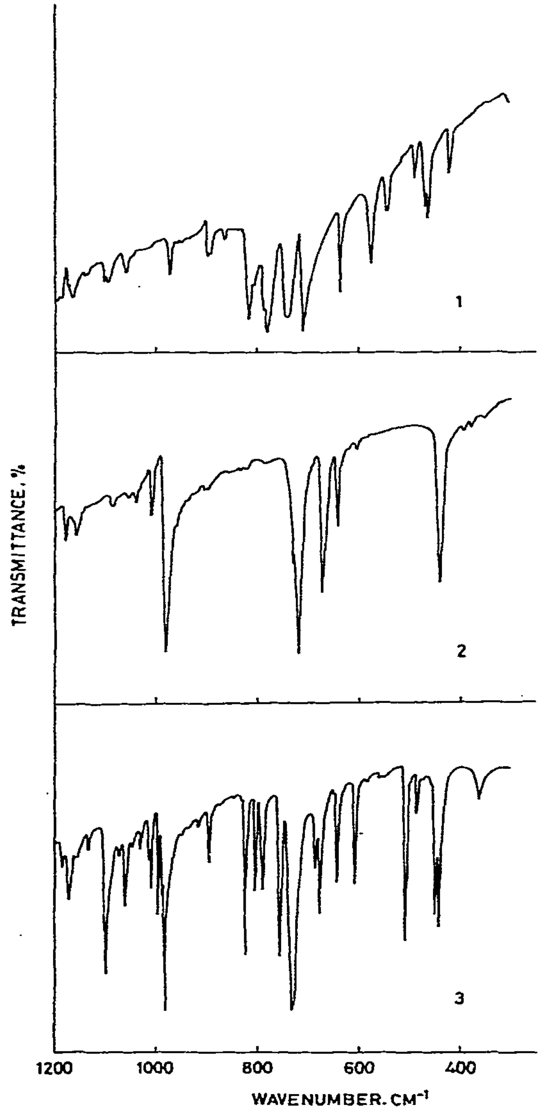


Fig. 1. The electronic absorption spectra of $Ph_3BiCl(Ox)$ in anhydrous methanol (curve 1) and benzene (curve 2) (Conc. 3×10^{-4} *M*; temp. 25°), and in the solid (curve 3; the absorbance, A, in arbitrary units). The spectrum of solid $Ph_3BiBr(Ox)$ roughly corresponds to that of curve 3.



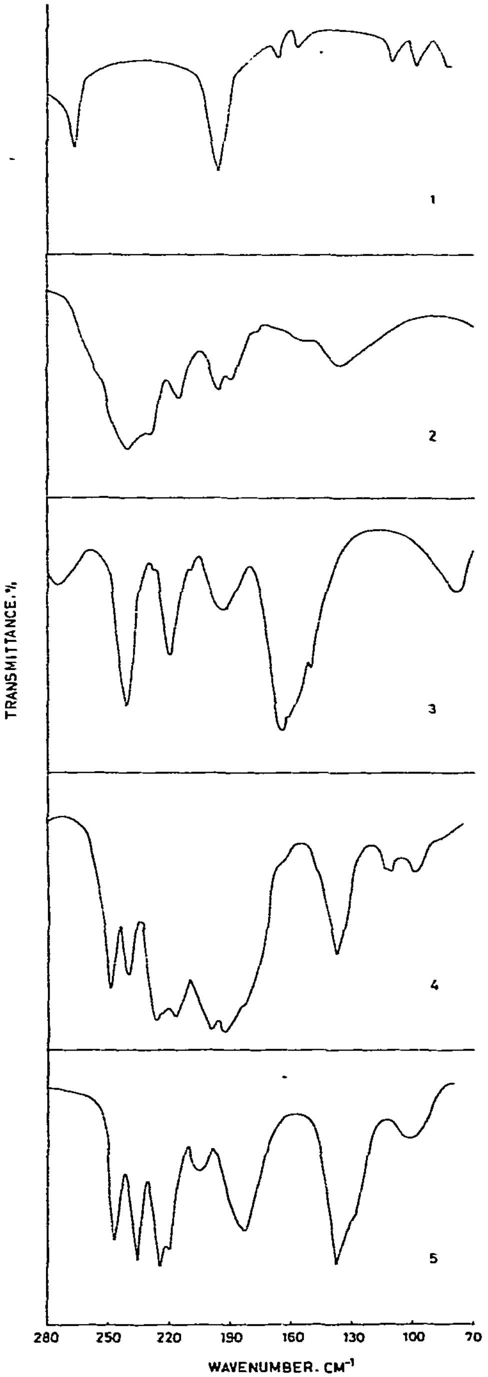


Fig. 2. Infrared spectra in the range 1200–400 cm^{-1}, Nujol mulls. Curve 1 : 8-quinolinol; curve 2: Ph_3BiX_2; curve 3: $Ph_3BiX(Ox)$.

Fig. 3. Low energy infrared spectra of 8-quinolinol (curve 1), Ph_3BiCl_2 (curve 2), Ph_3BiBr_2 (curve 3), $Ph_3BiCl(Ox)$ (curve 4) and $Ph_3BiBr(Ox)$ (curve 5), in nujol mulls.

through its *O,N*-donor atoms[9-18]. Chelation of Ox^- with Bi in the solid is also indicated by the infrared spectra in the 4000–250 cm^{-1} range (which are essentially alike). The broad ν(OH) band in the 3500–2700 cm^{-1} region, which is present in the vibrational spectra of HOx and its adducts[20], is obviously missing in solid $Ph_3BiX(Ox)$. The band of $Ph_3BiX(Ox)$ at 1100 cm^{-1} appears to be displaced (10 cm^{-1}) with respect to the corresponding band of HOx (Fig. 2) assigned to aryl–oxygen vibrations[21]. The oxine band at 465 cm^{-1}, assigned to an in-plane C–O bend[12], appears to be displaced to 505 cm^{-1} in $Ph_3BiX(Ox)$ (Fig. 2). Shifts of this type have been observed in a large number of chelate metal–oxine complexes[12,22].

Information on coordination of bismuth by halide and donor ligand atoms may, in principle, be derived from the low energy spectra of Fig. 3, but this can be difficult because of the phenyl–bismuth vibrations[23,24]. The strong band at 138 cm^{-1}, common to both complexes, could be due to a bismuth–ligand atom skeletal vibration possibly associated with a Bi–O bond; but it could also arise from lattice vibrations. From inspection of Fig. 3 it seems likely that Bi–Cl vibrational modes occur around 225–250 cm^{-1} in Ph_3BiCl_2, and are shifted to around 180–230 cm^{-1} in $Ph_3BiCl(Ox)$. Vibrational modes for $BiCl_3$, assumed to belong to the C_{3v} point group, were assigned to bands occurring at 288 cm^{-1}. (ν_1, approximately a symmetric $BiCl_3$ stretch) and 242 cm^{-1} (ν_3)[25]; analogous assignments have been proposed for a series of Bi^{III} complexes[26,27]. Tentative band assignments to bismuth–bromide vibrations appear to be even less reliable, but Bi–Br stretchings could contribute to the band located at 164 cm^{-1} in Ph_3BiBr_2 (in contrast to a previous assignment[23]) and at 138 cm^{-1} in $Ph_3BiBr(Ox)$; this would be reasonably consistent with previously reported data for Bi–Br vibrational modes[27], since a shift to lower energies of Bi–Hal vibrations with the increasing coordination number of the metal is expected from the parallel increase of the ionic character of Bi–Hal bonds[25].

It may be concluded that the solids $Ph_3BiX(Ox)$ contain Bi atoms coordinated by *O,N*-8-quinolinate atoms and by one halogen atom. Bismuth would then be six-coordinated, and the idealized geometry of the complexes would be octahedral.

The configuration of $Ph_3BiX(Ox)$ in solution is considerably influenced by the solvent. The electronic spectrum of $Ph_3BiCl(Ox)$ (absorption maxima around 353 and 330 nm in C_6H_6, (Fig. 1) and CH_2Cl_2) is consistent with chelation of Bi by Ox^- [9-18]. On the other hand, $Ph_3BiCl(Ox)$ in CH_3OH (Fig. 1) and $CHCl_3$, and $Ph_3BiBrOx$ in C_6H_6, CH_2Cl_2, $CHCl_3$ and CH_3OH, do not show any band around 350 nm (spectra are essentially similar to curve 1 of Fig. 1), which could imply that the Bi–N bonds have been broken[15,16]. Furthermore, the 330–353 nm band of $Ph_3BiCl(Ox)$ in C_6H_6 and CH_2Cl_2 slowly disappears with time (*e.g.*, 1 h after the preparation of a benzene solution, only a shoulder was present at ca. 360 nm), suggesting a gradual dissociation of Bi–N bonds even in these solvents. This may be interpreted in terms of competition for the bismuth atom between ligand nitrogen and solvent donor atoms (the oxygen of CH_3OH), or with basic impurities, such as water, present in the solvents. The spectrum of $Ph_3BiCl(Ox)$ in wet benzene does in fact closely correspond to curve 1 of Fig. 1.

Osmometry (in C_6H_6) and conductivity (in CH_3OH) measurements indicate that dissociation of $Ph_3BiX(Ox)$ would eventually occur to a limited extent. Values in benzene solution of the van 't Hoff factor *i* 1.40 and *i* 1.27 were obtained for $[Ph_3BiCl(Ox)]$, 3.3×10^{-3} and 5.2×10^{-3} *M* respectively, and *i* 1.35 and *i* 1.18 for $[Ph_3$-

BiBr(Ox)], 4.9×10^{-3} and 5.7×10^{-3} M, respectively. On the other hand, variable osmometric results were obtained in successive experiments, which is consistent with gradual changes occurring in the solution (perhaps due to hydrolysis in the wet solvent). Molar conductivities of $Ph_3BiCl(Ox)$ and $Ph_3BiBr(Ox)$, 10^{-3} M were $\Lambda_M = 12$ and $\Lambda_M = 8$ $\Omega^{-1} \cdot cm^2 \cdot mole^{-1}$, respectively; values for NaCl and Ph_4AsCl in the same experimental conditions were $\Lambda_M = 100$ and $\Lambda_M = 86$ $\Omega^{-1} \cdot cm^2 \cdot mole^{-1}$, respectively.

PMR spectra of $Ph_3BiX(Ox)$ show a complex structure, with broad signals in the range δ 6.7–8.7 ppm, and no assignment can be made. These spectra are quite different from those for $Ph_3SbCl(Ox)$ and related compounds, which show well-resolved oxinate proton signals comparable to those observed for alkylmetal complexes[18]. Poorly resolved PMR spectra were previously reported for (oxinato)aryltin complexes, and ascribed to anisotropic effects due to aryl groups bound to tin[28].

It may be concluded that $Ph_3BiX(Ox)$ exist in solution as essentially monomeric undissociated species, in which the halogen is firmly bound to the metal, and 8-quinolinol is linked to bismuth mainly through oxygen. The Bi–N bonds are weakened in solution with respect to the solid state, and tend to undergo cleavage, behaviour analogous to that previously observed with $Ph_3Pb(Ox)$ and Ph_3SnOx[15,16]. This effect is more pronounced for $Ph_3BiBr(Ox)$, in keeping with the lower acidic Lewis character of the metal for halides due to the decrease of electronegativity from Cl to Br.

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