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PHENYLBISMUTH(III) AND TRIPHENYLBISMUTH(V) COMPLEXES WITH OXINE DERIVATIVES. THE CRYSTAL STRUCTURE OF CHLORO(2-METHYL-8-QUINOLINOLATO)TRIPHENYLBISMUTH(V)

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Summary

The complexes $Ph_3Bi(MeOx)X$ (MeOx = 2-methyl-8-quinolinolato; X = Cl, Br), $PhBi(MeOx)_2$ and $PhBiOx_2$ (Ox = 8-quinolinolato) have been prepared and characterized by electronic, IR and ^1H NMR spectra. The crystal structure of $Ph_3Bi(MeOx)Cl$ was determined by single-crystal X-ray diffraction from diffractometer data. Crystal data: $C_{28}H_{23}NOClBi$, monoclinic, space group $P2_1/n$, a 17.05(1), b 13.89(1), c 10.51(1) Å, β 97.30(3)°, V 2468 Å^3, $Z = 4$, D_{calcd} 1.70 g cm^{-3}; $R = 0.078$, 3048 observed reflections. The complex is monomeric, and the molecules are well separated, with the metal atom in a distorted octahedral coordination environment. The metal atom makes with the bidentate ligand a Bi–O bond of 2.19(2) Å and a relatively weak Bi–N bond of 2.71(2) Å.

Introduction

The 8-quinolinol (HOx) derivatives containing the Ph_3Bi^V moiety, of the type Ph_3BiOxX (X = Cl, Br), were prepared several years ago [1]; six-coordination by the O,N-chelating oxinato group and the halogen atom was suggested in the solid state from IR and electronic spectra.

Recent organobismuth reviews [2,3] contain little information about Ph_3Bi^V complexes, and this is limited essentially to the five-coordinate species $[Ph_3BiL_2]Y_2$ (where L is a monodentate oxygen donor and Y is a non-coordinating anion) [4] and Ph_3BiA_2 (where A is an acetato or thioacetato group acting as monodentate) [5,6]. Several papers deal with organo-antimony(V) oxinates [7 and ref. therein], but the behaviour of the oxinato group (monodentate or bidentate) in R_3SbOxX (R = phenyl or alkyl; X = Cl, Br, OH) has not been unequivocally established and, as far as we

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know, no X-ray structure has been reported.

In order to confirm the possibility of hexacoordination in the Ph_3Bi^V complexes we prepared the 2-methyl-8-quinolinol, H(MeOx), derivatives of formula $Ph_3Bi(MeOx)X$ (X = Cl, Br), which gave crystals suitable for structural studies. We extended the study also to the $PhBi^{III}$ species, obtaining complexes of formula $PhBiL_2$ ($L = Ox^-$, $MeOx^-$).

Experimental

Ph_3Bi (Alfa product) was purified by filtration of a concentrated solution in anhydrous Et_2O and removal of the solvent under reduced pressure. The organobismuth halides were prepared as follows [2]: (a) Ph_3BiCl_2 was made by reaction of Ph_3Bi with chlorine in $CHCl_3$ (dried over anhydrous $MgSO_4$), removal of the Cl_2 excess with a flow of nitrogen and precipitation with anhydrous MeOH; (b) Ph_3BiBr_2 was made by treating Ph_3Bi, dissolved in anhydrous n-hexane (containing a small amount of Et_2O) with a n-hexane solution of bromine; (c) $PhBiI_2$ was obtained from Ph_3Bi and iodine in anhydrous Et_2O. The sodium salts, NaOx and Na(MeOx), were prepared by dissolving HOx and H(MeOx) in aqueous NaOH (85°C), and recrystallized from absolute EtOH. Benzene (Na), n-hexane (Na/K), Et_2O (Na/K), acetone (Na_2CO_3), and MeOH (Mg) were dried by standard methods.

Preparation of the complexes

$Ph_3Bi(MeOx)X$

Equimolar amounts of Ph_3BiCl_2 and Na(MeOx) (2.5 mmol) were allowed to react in 15 ml of Et_2O. The suspension was stirred for 45 min, then the orange solid was separated from the orange solution and dissolved in benzene; The NaCl was filtered off, then n-hexane was added to the deep orange benzene solution. Orange crystals separated overnight (yield 70%); recrystallization from benzene-n-hexane gave fine crystalline $Ph_3Bi(MeOx)Cl$ suitable for X-ray study.

$Ph_3Bi(MeOx)Br$ was prepared in the same way; the yield was poor (40%) because, along with the red-orange crystals of the complex, a greenish powderly solid (unidentified) was formed; this was, however, easily separated from the complex by flotation in n-hexane.

Both complexes are soluble in benzene, CH_2Cl_2 and acetone, slightly soluble in Et_2O and MeOH and insoluble in H_2O and n-hexane.

Attempts to prepare the analogous iodo-derivative by metathesis from $Ph_3Bi(MeOx)Cl$ and KI in Et_2O or acetone, and to replace both the halogen atoms of Ph_3BiCl_2 by reaction with Na(MeOx) or NaOx in a 1/2 molar ratio (Et_2O or acetone) were unsuccessful. In both cases the residual oily solids were a mixture of decomposition products.

$PhBiL_2$($L = Ox^-$, $MeOx^-$)

The iodide $PhBiI_2$ (1.0 mmol) was dissolved in the minimum volume of anhydrous acetone, then a solution of the ligand sodium salt (molar ratio 1/2) in absolute EtOH was added. The yellow complex separated slowly; it was filtered off, washed with EtOH and n-hexane, and dried in vacuo. The compounds are slightly soluble in

TABLE 1

POSITIONAL PARAMETERS WITH ESD'S IN PARENTHESES

Atom	x	y	z
Bi	0.49378(5)	0.28101(6)	0.22335(8)
Cl	0.3792(5)	0.1508(6)	0.2271(7)
O	0.5822(8)	0.3965(11)	0.2330(15)
N	0.6278(13)	0.2307(17)	0.1269(21)
C(1)	0.4190(11)	0.3905(16)	0.2907(19)
C(2)	0.3619(14)	0.4384(16)	0.2059(23)
C(3)	0.3170(16)	0.5109(20)	0.2485(26)
C(4)	0.3254(14)	0.5405(18)	0.3776(28)
C(5)	0.3844(15)	0.4943(19)	0.4634(26)
C(6)	0.4300(13)	0.4212(17)	0.4205(20)
C(7)	0.5579(15)	0.2060(16)	0.4007(22)
C(8)	0.6376(18)	0.2372(21)	0.4351(28)
C(9)	0.6716(20)	0.1951(22)	0.5563(34)
C(10)	0.6311(30)	0.1359(32)	0.6230(34)
C(11)	0.5554(25)	0.1064(35)	0.5846(44)
C(12)	0.5163(20)	0.1462(30)	0.4668(32)
C(13)	0.4702(18)	0.2877(23)	0.0083(19)
C(14)	0.4963(16)	0.3629(17)	−0.0529(23)
C(15)	0.4809(19)	0.3676(21)	−0.1860(29)
C(16)	0.4369(25)	0.2937(29)	−0.2465(27)
C(17)	0.4081(25)	0.2192(27)	−0.1865(26)
C(18)	0.4194(21)	0.2102(23)	−0.0519(26)
C(19)	0.6485(13)	0.3966(19)	0.1799(22)
C(20)	0.6946(16)	0.4782(22)	0.1799(27)
C(21)	0.7619(19)	0.4799(29)	0.1120(36)
C(22)	0.7876(18)	0.4027(36)	0.0525(35)
C(23)	0.7597(22)	0.2336(39)	−0.0111(35)
C(24)	0.7141(24)	0.1510(33)	−0.0041(32)
C(25)	0.6489(18)	0.1505(25)	0.0695(31)
C(26)	0.6735(13)	0.3113(19)	0.1217(19)
C(27)	0.7412(18)	0.3186(30)	0.0524(25)
C(28)	0.5995(22)	0.0625(20)	0.0829(39)

ANISOTROPIC THERMAL PARAMETERS ($\times 10^2$)[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	5.46(5)	5.01(5)	4.31(5)	−0.11(5)	−0.47(3)	−0.38(5)
Cl	10.6(6)	9.4(5)	7.3(5)	−4.4(5)	0.3(4)	0.3(4)
O	5.6(9)	5.6(1.0)	5.7(1.0)	−0.9(8)	−0.3(8)	−1.3(8)
N	7.8(1.4)	6.9(1.5)	6.6(1.4)	0.6(1.3)	−2.7(1.2)	−2.6(1.3)
C(1)	4.1(1.1)	6.3(1.4)	4.0(1.2)	0.5(1.0)	−0.9(0.9)	−0.9(1.1)
C(2)	7.4(1.6)	4.8(1.3)	6.2(1.6)	1.9(1.2)	−1.3(1.3)	−0.2(1.2)
C(3)	8.4(1.9)	7.7(1.8)	6.7(1.8)	2.2(1.5)	−0.8(1.5)	−0.4(1.5)
C(4)	5.5(1.4)	6.4(1.6)	9.2(2.0)	−0.5(1.2)	0.1(1.4)	−1.1(1.5)
C(5)	6.1(1.5)	7.5(1.7)	7.6(1.8)	−0.5(1.3)	0.1(1.4)	−1.5(1.5)
C(6)	6.2(1.4)	6.5(1.5)	3.8(1.2)	0.2(1.2)	0.1(1.1)	−0.7(1.1)
C(7)	8.9(1.7)	4.2(1.3)	5.7(1.5)	1.4(1.3)	−0.8(1.3)	1.0(1.2)
C(8)	10.8(2.2)	7.9(2.0)	8.8(2.0)	1.5(1.7)	−3.9(1.8)	−0.5(1.7)
C(9)	12.8(2.6)	7.6(2.1)	9.7(2.4)	3.0(1.8)	−7.3(2.1)	−3.1(1.8)
C(10)	18.0(4.2)	13.1(3.5)	7.3(2.3)	4.8(3.1)	0.6(2.6)	2.6(2.3)
C(11)	11.1(3.0)	21.1(4.4)	14.5(3.7)	2.7(3.1)	1.5(2.8)	8.5(3.3)
C(12)	11.3(2.6)	18.5(3.6)	8.7(2.4)	1.3(2.5)	1.7(2.0)	8.2(2.6)

TABLE 1 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(13)	15.8(2.5)	10.4(2.2)	1.1(1.0)	−2.8(2.1)	1.5(1.2)	−1.4(1.3)
C(14)	9.6(1.9)	5.4(1.4)	5.3(1.6)	−0.8(1.3)	0.2(1.4)	0.8(1.2)
C(15)	12.5(2.5)	7.2(1.9)	7.5(2.1)	−1.0(1.7)	−2.3(1.8)	2.0(1.6)
C(16)	21.2(3.9)	13.3(3.0)	4.0(1.7)	−2.3(2.9)	−0.5(2.0)	2.4(2.0)
C(17)	26.5(4.2)	11.1(2.5)	4.0(1.6)	−6.7(2.9)	−4.8(2.1)	0.1(1.9)
C(18)	18.2(3.2)	8.7(2.1)	5.6(1.7)	−4.9(2.2)	−2.8(1.9)	−2.5(1.6)
C(19)	4.3(1.3)	8.1(1.8)	4.2(1.3)	−0.1(1.3)	−0.7(1.1)	−0.3(1.3)
C(20)	6.4(1.7)	9.6(2.1)	7.2(1.9)	−1.4(1.6)	−1.5(1.5)	2.3(1.6)
C(21)	6.9(2.2)	12.7(3.0)	10.1(2.7)	0.9(2.0)	−3.0(1.9)	6.5(2.4)
C(22)	4.8(1.8)	17.6(3.7)	10.0(2.7)	0.5(2.3)	−0.9(1.7)	7.6(2.7)
C(23)	10.5(2.9)	21.1(4.6)	6.6(2.3)	5.6(3.1)	−3.0(2.2)	−0.3(3.0)
C(24)	11.7(3.0)	16.3(3.6)	7.1(2.1)	8.5(2.7)	−4.2(2.1)	−5.6(2.5)
C(25)	7.5(1.9)	10.3(2.4)	8.1(2.1)	4.0(1.9)	−3.5(1.7)	−2.6(2.0)
C(26)	5.2(1.3)	8.5(1.9)	2.1(1.1)	2.1(1.3)	−1.5(1.0)	0.2(1.1)
C(27)	6.9(2.0)	17.1(3.4)	3.5(1.5)	4.7(2.2)	−1.0(1.4)	0.9(1.8)
C(28)	14.9(3.0)	4.1(1.7)	16.3(3.4)	2.8(1.8)	−4.0(2.6)	−3.7(1.9)

CALCULATED POSITIONAL PARAMETERS OF THE HYDROGEN ATOMS[b]

H(2)	0.3537	0.4196	0.1133
H(3)	0.2769	0.5438	0.1855
H(4)	0.2911	0.5921	0.4075
H(5)	0.3933	0.5145	0.5555
H(6)	0.4715	0.3895	0.4824
H(8)	0.6663	0.2821	0.3827
H(9)	0.7274	0.2112	0.5907
H(10)	0.6579	0.1113	0.7069
H(11)	0.5283	0.0592	0.6361
H(12)	0.4601	0.1298	0.4353
H(14)	0.5267	0.4154	−0.0037
H(15)	0.5008	0.4220	−0.2354
H(16)	0.4257	0.2960	−0.3422
H(17)	0.3776	0.1683	−0.2388
H(18)	0.3959	0.1579	−0.0034
H(20)	0.6808	0.5366	0.2281
H(21)	0.7915	0.5418	0.1085
H(22)	0.8370	0.4047	0.0105
H(23)	0.8057	0.2327	−0.0613
H(24)	0.7269	0.0914	−0.0507

[a] The form of the expression is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] The numeration of the hydrogen atoms follows that of the carbon atom to which they are bonded.

benzene, acetone and CH_2Cl_2; insoluble in MeOH and n-hexane.

The IR spectra were recorded on a Beckman IR 11 Spectrophotometer (Nujol mulls) the ^1H NMR Spectra on a Varian FT 80A Spectrometer ($T = 27$°C) and the electronic spectra on a Beckman DK 2A Spectrophotometer (the spectra of solid samples were recorded with Nujol mulls spread on paper). Molecular weights were measured at 37°C on a Knauer Model 11 Vapor Pressure Osmometer.

TABLE 2

BOND[a] AND CONTACT DISTANCES (Å)

Bond distances			
Coordination			
Bi-Cl	2.67(1)	Bi-C(1)	2.16(2)
Bi-O	2.19(2)	Bi-C(7)	2.29(2)
Bi-N	2.71(2)	Bi-C(13)	2.25(2)
Ligand			
O(1)-C(19)	1.32(3)	C(23)-C(24)	1.39(6)
C(19)-C(20)	1.38(4)	C(24)-C(25)	1.43(5)
C(20)-C(21)	1.43(5)	C(25)-C(28)	1.50(5)
C(21)-C(22)	1.34(6)	C(25)-N	1.34(4)
C(22)-C(27)	1.41(6)	C(26)-N	1.37(3)
C(27)-C(23)	1.41(6)	C(26)-C(27)	1.44(4)
		C(26)-C(19)	1.42(4)
Contact distances (< 4 Å)			
O···N	2.71(2)	Cl···C(7)	3.43(2)
O···C(1)	2.92(2)	Cl···C(13)	3.50(3)
O···C(7)	3.24(2)	Cl···C(1)	3.45(2)
O···C(13)	3.22(2)	C(1)···C(7)	3.58(3)
N···C(7)	3.27(2)	C(1)···C(13)	3.50(3)
N···C(13)	2.92(3)		

[a] The C-C (Ph) bond distances are normal.

TABLE 3

SELECTED BOND ANGLES (°) ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Coordination		Ligand	
N-Bi-O	66.3(6)	Bi-O-C(19)	127(1)
N-Bi-Cl	119.0(5)	Bi-N-C(25)	132(2)
N-Bi-C(7)	81.5(4)	Bi-N-C(26)	108(2)
N-Bi-C(13)	73.1(4)	O-C(19)-C(20)	121(2)
N-Bi-C(1)	150.5(5)	O-C(19)-C(26)	120(2)
O-Bi-Cl	174.5(4)	C(20)-C(19)-C(26)	119(2)
O-Bi-C(1)	84.7(4)	C(19)-C(20)-C(21)	120(3)
O-Bi-C(7)	92.3(4)	C(20)-C(21)-C(22)	123(3)
O-Bi-C(13)	91.9(4)	C(21)-C(22)-C(27)	116(3)
C(1)-Bi-C(7)	106.0(1)	C(19)-C(26)-C(27)	117(3)
C(1)-Bi-C(13)	104.0(1)	C(22)-C(27)-C(26)	123(3)
C(1)-Bi-Cl	90.0(2)	C(25)-N-C(26)	118(2)
C(7)-Bi-C(13)	150.0(1)	N-C(26)-C(27)	125(3)
C(7)-Bi-Cl	87.3(2)	N-C(25)-C(24)	121(3)
C(13)-Bi-Cl	91.0(2)	N-C(25)-C(28)	117(3)
		C(24)-C(25)-C(28)	122(3)
		C(25)-C(24)-C(23)	121(4)
		C(24)-C(23)-C(27)	120(4)
		C(22)-C(27)-C(23)	122(3)
		C(26)-C(27)-C(23)	115(3)
		C(19)-C(26)-N	117(2)

X-ray data for $Ph_3Bi(MeOx)Cl$

A well formed fragment of approximate dimensions 0.10 × 0.15 × 0.12 mm mounted on a glass fibre with epoxy adhesive was used for the X-ray study. Crystal data are: $C_{28}H_{23}NOClBi$, $Ph_3Bi(MeOx)Cl$, FW = 634, a 17.05(1), b 13.89(1), c 10.51(1) Å, β 97.30(3)°, V 2468 Å^3, $D_x = 1.70$ g cm^{-3} for $Z = 4$, μ(Mo-K_α) 83 cm^{-1}; monoclinic, space group $P2_1/n$, from systematic absences $h0l$ when l is odd, and $0k0$ when k is odd, general positions $\pm(x, y, z;\ 1/2 + x,\ 1/2 - y,\ 1/2 + z)$.

The intensities were measured on a Philips PW 1100 diffractometer with the θ–2θ scan technique. Using graphite-monochromatized Mo-K_α radiation (λ 0.7107 Å), 4223 reflexions up to θ 25° were collected at a scan speed of 0.03° s^{-1}. Reference reflexions recorded at regular intervals during the data collection showed no significant change in intensity. The measured intensities were corrected for Lorentz and polarization factors and for absorption, and 3048 independent reflections with $I > 3\sigma(I)$ were obtained and used in subsequent calculations.

The structure was solved by the heavy atom method. The hydrogen atoms were introduced in calculated positions (C–H 1 Å; U_{iso} 0.06 Å^2). Refinement of scale factor, positional parameters and anisotropic temperature factors for all non-hydrogen atoms converged with the conventional R factor of 0.078. The quantity minimized in the refinement was $\Sigma w\Delta^2$ with $w = 1$. A final difference Fourier map showed no significant feature. Scattering factors for C, N, O and Cl were supplied internally by the X-RAY system [8], for Bi and H were those of ref. [9] and [10] respectively. A correction for the anomalous dispersion of Bi was also applied [11]. Atomic parameters are listed in Table 1, and distances and angles in Tables 2 and 3. Tables of structure factors may be obtained from the authors.

Results and discussion

Crystal structure of $Ph_3Bi(MeOx)Cl$

As shown in Fig. 1, the metal atom is six-coordinate in a distorted octahedral coordination geometry. The major distortions can apparently be ascribed to the geometric constraints of the chelated ligand and to the fact that the nitrogen atom is only weakly bonded to the metal. Thus, the Cl–Bi–O axis is quasi linear, and the Cl–Bi–C angles are orthogonal within the error limits, whereas the nitrogen atom is markedly displaced from the ideal octahedral site, and the N–Bi–O angle has a value of only 66°. As a consequence the two *trans* phenyl rings are bent towards the empty space and the C–Bi–C angles of the contiguous groups are about 15° larger than expected for a regular octahedral arrangement. Bonding of the chelated ligand is essentially through the oxygen atom. The weakness of the Bi–N bond is indicated by three effects: (i) the Bi–N distance of 2.71(2) Å is very long compared with the sum of the atomic radii (2.25 Å) [12] or with the mean of the other metal–ligand distances; (ii) the Bi–N–C angles are 108 and 132°, so that the Bi–N bond deviates by about 10° from the direction of the nitrogen σ-bonding orbital; (iii) the Bi–C(1) bond distance of 2.16 Å is significantly shorter than the Bi–C(7) and Bi–C(13) bond distances (mean 2.27 Å), possibly owing to the weak competition by the *trans* nitrogen atom. Apart from the short Bi–C(1) value, the Bi–C distances are in agreement with the sum of the atomic radii (2.30 Å) [12]. The C–O bond of 1.32(3) Å is a partial double bond, as expected upon the influence of the aromatic ring, whereas the Bi–O distance of 2.19(2) Å is very close to the sum of the atomic radii

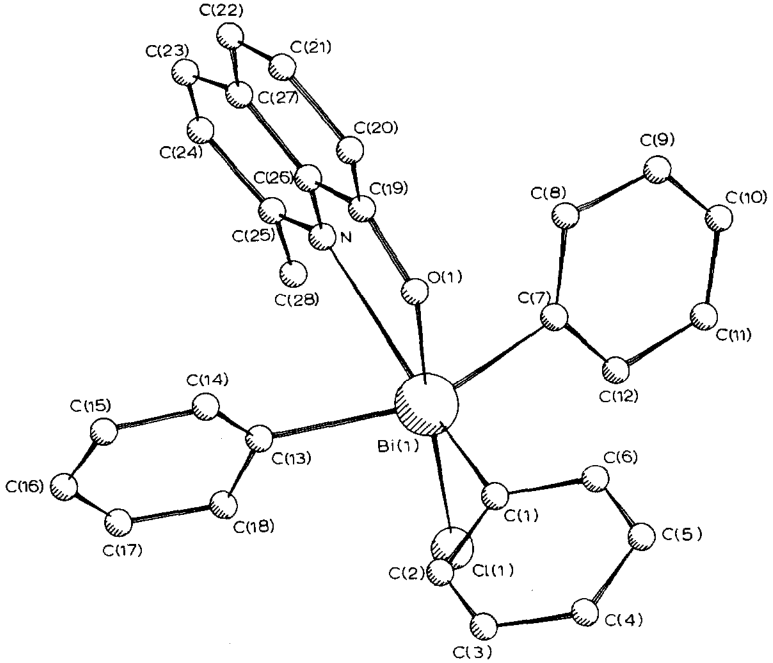


Fig. 1. Crystal structure of chloro(2-methyl-8-quinolinolato)triphenylbismuth(V).

(2.20 Å) [12]. The Bi–Cl bond distance of 2.67(1) Å (sum of the atomic radii for Bi–Cl 2.60 Å) is longer than a mean of 2.57(2) Å found in Ph_3BiCl_2 [13]; Bi–Cl bond distances in the range 2.61–2.87 Å were found in the $BiCl_5^{2-}$ ion [14].

Compounds

The analytical data for the prepared compounds are reported in Table 4 along with the absorption maxima of the electronic spectra. The absorption around 355 nm in the electronic spectra of solid $Ph_3Bi(MeOx)X$ (Fig. 2(a); 360 nm in the

TABLE 4

ANALYTICAL DATA AND ELECTRONIC SPECTRA (λ_{max} (nm); $\varepsilon_{mol} \times 10^{-3}$ in parentheses)

Compound	Colour	M.p. (°C)	Analyses (Found (cald.)(%))				λ_{max}	
			C	H	N	Hal	solid	benzene
$Ph_3Bi(MeOx)Cl$	orange	130	52.8	3.5	2.2	5.6	≃ 355sh	355(2.3)
			(53.0)	(3.7)	(2.2)	(5.6)		
$Ph_3Bi(MeOx)Br$	red-orange	115	48.9	3.3	2.0	11.3	≃ 355sh	355sh(3.4)
			(49.6)	(3.4)	(2.0)	(11.8)		
$PhBi(MeOx)_2$	yellow	> 270	52.2	3.7	4.5		370	370(5.0)
			(51.8)	(3.5)	(4.6)			
$PhBi(Ox)_2$	yellow	> 270	49.9	2.8	4.8		390	385(4.8)
			(50.2)	(3.0)	(4.9)			

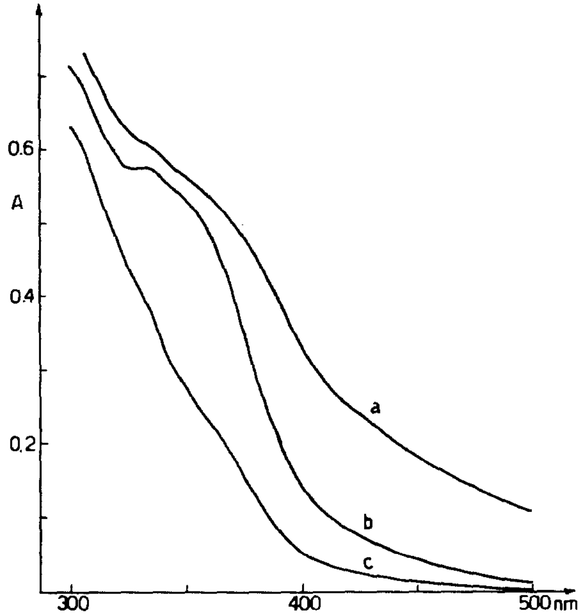


Fig. 2. Electronic spectra of $Ph_3Bi(MeOx)Cl$: (a) solid; (b) 2.3×10^{-4} *M* in benzene; (c) 1.7×10^{-4} *M* in dichloroethane.

oxinato analogues [1]), depends on the chelated ligand. In fact H(MeOx), or HOx, have a maximum at 315 nm ($\varepsilon_{mol} \simeq 2.4 \times 10^3$); when the methyloxinato or oxinato groups coordinate through the oxygen and nitrogen atoms, the absorption maximum

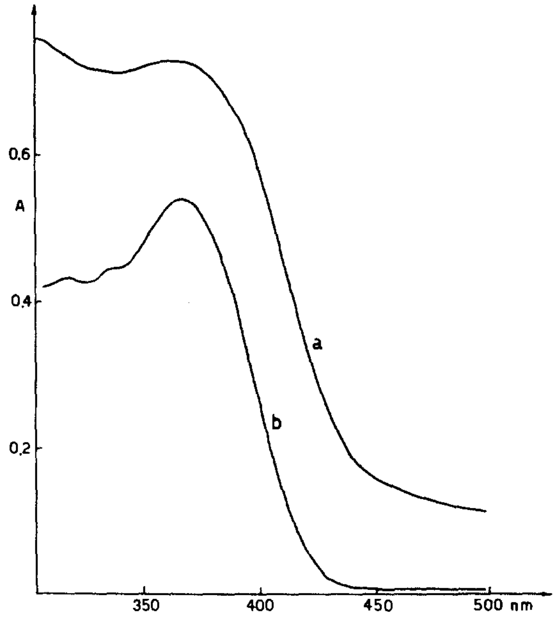


Fig. 3. Electronic spectra of $PhBi(MeOx)_2$: (a) solid; (b) 1.2×10^{-4} *M* in dichloroethane.

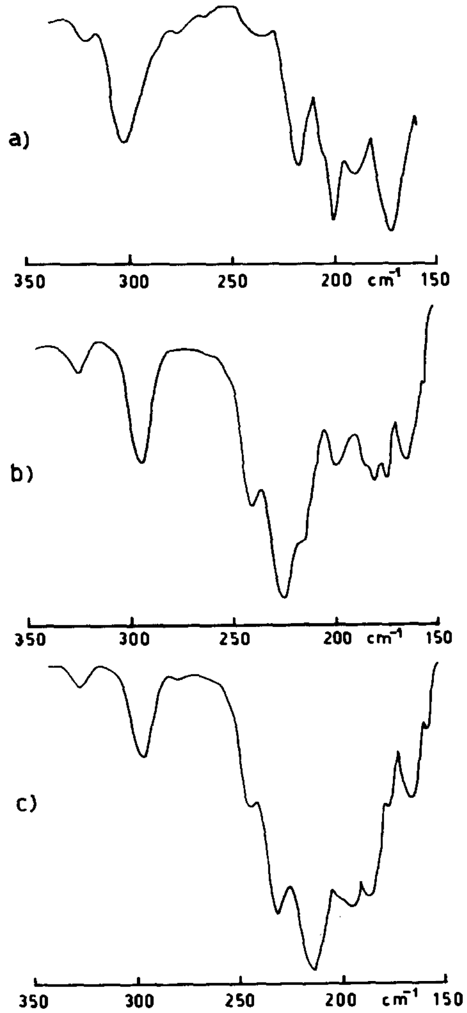


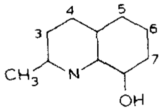
Fig. 4. Infrared spectra: (a) $PhBi(MeOx)_2$; (b) $Ph_3Bi(MeOx)Br$; (c) $Ph_3Bi(MeOx)Cl$.

shifts towards 350–420 nm with an ε_{mol} of the same order [1 and ref. therein]. The spectra of $Ph_3Bi(MeOx)X$ ($X = Cl$, Br) in anhydrous benzene (Fig. 2(b)) do not change with time, differing from that of Ph_3BiOx [1]; in dichloromethane the extinction coefficient at ca. 350–360 nm is lower than in benzene, and in methanol the absorption due to chelation is absent, as is the case for the analogous oxinato complexes. The electronic spectra of $PhBi(MeOx)_2$ (Fig. 3) and $PhBiOx_2$ have the same shape in solid, benzene and dichloroethane; the ε_{mol} values in these solvents are in accord with chelation, whereas in MeOH the chelated structure is broken. $Ph_3Bi(MeOx)Cl$, $PhBi(MeOx)_2$ and $PhBiOx_2$ are essentially monomers in benzene; the experimental molecular weight of $Ph_3Bi(MeOx)Br$ (1×10^{-2} *M* in benzene) is about 20% below the theoretical value, probably owing to a partial decomposition in the osmometric apparatus from which moisture is not excluded.

The far IR spectra of the methyloxinato complexes (Fig. 4), in the 350–150 cm^{-1}

TABLE 5

^{1}H NMR DATA ($T \simeq 27°$C; chemical shifts in ppm)

Compound	Solvent	Phenyl		Ligand			
		o	$m + p$				
Ph_3BiCl_2	benzene-d_6	8.56	6.75–7.25				
	acetone-d_6	8.43	$\simeq$ 7.7				
	DMSO-d_6	8.37	$\simeq$ 7.7				
				H(4)	H(7)	CH_3	OH
H(MeOx)	benzene-d_6			7.42	6.61	2.31	8.40
	acetone-d_6			8.06	$\simeq$ 7.0	2.70	n.o.
	DMSO-d_6			8.06	$\simeq$ 6.9	2.62	9.25
$Ph_3Bi(MeOx)Cl$	benzene-d_6	8.56		7.28	6.27	2.47	
	acetone-d_6	8.30		7.91	7.06	2.62	
	DMSO-d_6	8.12		8.0		2.56	
$Ph_3Bi(MeTA)_2$ [a]	$CDCl_3$	8.24	7.60				

[a] Ref. 8; MeTA = methylthioacetato.

region show absorptions due to ligand, phenyl and Bi–X. The Bi–X absorptions in Ph_3BiX_2 fall at about 240 cm^{-1} for X = Cl [1,5] and 167 cm^{-1} for X = Br [1]; in $Ph_3Bi(MeOx)Cl$, as in the oxinato complex, the Bi–Cl band is shifted to 180–220 cm^{-1}. The Bi–Br absorption of $Ph_3BiOxBr$ appears at about 138 cm^{-1}, and so this band does not show up in the methyloxinate spectrum shown in Fig. 4.

The similar electronic and far IR spectra indicate that the same type of coordination is present in Ph_3BiOxX and $Ph_3Bi(MeOx)X$ in the solid state.

The ^{1}H NMR spectral data for of Ph_3BiCl_2 in various solvents are listed in Table 5. The phenyl protons give two groups of signals: a complex higher field pattern is due to the *meta* and *para* protons, the lower field doublet around 8.4–8.5 ppm ($J_{2,3}$ 8 Hz; $J_{2,4}$ 1.5 Hz) is assigned to the *ortho* protons on the basis of the data for $PhBiX_2$ (X = Cl, Br) [15,16] and Ph_3Bi^V derivatives [6,17]. Among the H(MeOx) protons the H(4) and H(7) signals are well distinguishable doublets, whereas the H(3), H(5), H(6) signals are superimposed upon each other [18]; for instance in benzene-d_6 (Table 5) the H(4) resonance is at 7.42 ppm ($J_{3,4}$ 8.5 Hz), the H(7) one at 6.61 ppm ($J_{6,7}$ 7.5 Hz) and the H(3), H(5), H(6) signals are in the 7.0–7.3 ppm region. In acetone-d_6 and DMSO-d_6 all the resonances are shifted downfield, and the H(3), H(5), H(6) signals are in the range 7.2–7.5 ppm. In the benzene-d_6 spectrum of $Ph_3Bi(MeOx)Cl$ the signals of the *ortho* protons are unchanged with respect to those of Ph_3BiCl_2, whereas the methyloxinato signals are significantly shifted upfield; the resonances of *m*, *p*, H(3), H(5), H(6) are superimposed in the region 6.5–7.4 ppm. The $Ph_3Bi(MeOx)Cl$ spectrum in acetone-d_6 is similar in terms of the number and position of the signals to that in benzene, apart for a general downfield shift; the spectrum in DMSO-d_6 shows a larger number of signals in the 7.0–7.7 ppm range, suggesting that there is some decomposition of the complex in this solvent.

This work confirms that in the complexes $Ph_3Bi(MeOx)X$ and Ph_3BiOxX (X = Cl, Br) the bidentate ligand is chelated and the halogen atom is directly bonded to Bi, which is six-coordinated. Such a coordination is generally maintained in benzene, in which the MeOx derivatives are the most stable, whereas polar solvents tend to break the Bi–N bond and, in some cases (i.e. MeOH, DMSO), to decompose the complexes. In $PhBi(MeOx)_2$ or $PhBiOx_2$ the presence of two O,N-chelated ligands leads to five-coordinated bismuth, as found in the Et_2DTC [19] and 1-oxopyridine-2-thiolato [20] derivatives. The Bi–N bond must be stronger than that in the Ph_3Bi^V complexes; thus the chelated structure is retained in benzene, dichloroethane, acetone, whereas in methanol the $PhBi^{III}$ complexes behave like the Ph_3Bi^V derivatives.

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