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BISMUTH(III) COMPLEXES WITH DIORGANODICHALCOGENO-PHOSPHINATO LIGANDS. SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION

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ABSTRACT. Metathesis reactions between $BiCl_3$ or OBiCl with alkali metal salts of diorganodichalcogenophosphinato ligands, in stoechiometric ratio, led to tris(diorganophosphinato)bismuth, $Bi(O_2PR_2)_3$ (R = Me, Ph, Cy, Pr^n, Bz), tris(diorganomonothiophosphinato)bismuth, $Bi(OSPPh_2)_3$, as well as the diphenyldithiophosphinato derivatives $Bi(S_2PPh_2)_3$ and $OBi(S_2PPh_2)$. The compounds were characterized by multinuclear NMR (^1H, ^{13}C, ^{31}P), IR and mass spectrometry. The spectroscopic data allowed us to predict a polymeric structure with anisobidentate ligands in case of the dioxo derivatives, while for the other species either monomeric or polymeric structures may be proposed.

Keywords: bismuth complexes, organophosphorus ligands, spectroscopic characterization

Introduction

Diorganophosphorus ligands of type $[R_2PXY]^-$ (R = alkyl or aryl, X, Y = O, S) and their metal complexes have attracted much interest for several years, due both to the diversity of their structural features and their potential applications (*i.e.* biological or catalytic activity). In compounds with such ligands different coordination patterns were observed, *i.e.* monodentate or bidentate (chelating or bridging two or more metal centers) as a consequence of *(i)* the ability of the ligand to involve one or both chalcogen atoms in interactions with metal centers, and *(ii)* the tendency of many Main Group or transition metals to increase their coordination number [1-4]. Several solid state structural types were established for different metal complexes by single-crystal X-ray diffraction studies. Related to the applications of these species, a special interest is concerned to their solution behavior and structure. Even if a large number of metal complexes with $[R_2PXY]^-$ (X, Y = O, S) ligands were already described, only few bismuth complexes containing dithiophosphinato groups were so far studied and structurally characterized by single-crystal X-ray diffraction, *i.e.* $Bi(S_2PMe_2)_3$ [5], $Bi(S_2PEt_2)_3$ [6], $Bi(S_2PPh_2)_3$ [7], and

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$MesBi(S_2PPh_2)_2$ [8]. Our studies, reported here, were focused on some bismuth(III) inorganic species with dioxo-, monothio- or dithiophosphinato ligands. Spectroscopic data (multinuclear NMR, MS) are also included for $Bi(S_2PPh_2)_3$, only IR data [9] and the crystal structure [7] being previously reported.

Experimental

Solvents were pre-dried over activated 4 Å molecular sieves and then distilled from potassium (THF), magnesium (methanol), calcium chloride (acetonitrile), Na_2CO_3 (acetone) under a continuous stream of argon. $BiCl_3$ and OBiCl were commercially products. All other starting materials were obtained according to literature methods: R_2PO_2Na (R = Me [10], Bz [11], Cy [12], Ph, Pr^n [13]), $Ph_2PS_2NH_4$, Ph_2PSONH_4 [13].

^1H, ^{13}C and ^{31}P NMR spectra were recorded on a VARIAN GEMINI instrument operating at 300, 75.4 and 121.4 MHz respectively, relative to TMS (^1H and ^{13}C) and H_3PO_4 85 % (^{31}P). Mass spectra were obtained using either a VARIAN CH7 (A) MAT instrument (EI) or a JEOL SX-102A spectrometer (FAB). IR spectra were recorded either as KBr pellets or Nujol mulls on a SPECORD IR UR 20 instrument.

Preparation of tris(dimethylphosphinato)bismuth(III), $Bi(O_2PMe_2)_3$ (1)

A mixture of 0.5 g (1.6 mmol) $BiCl_3$ and 0.68 g (4.8 mmol) $Me_2PO_2Na\cdot 1.5\ H_2O$ in acetonitrile (50 ml) was refluxed for 2 hours under argon atmosphere. The resulted NaCl was filtered off and the solvent was removed in vacuum, leaving the title compound as a white solid. Yield 0.54 g (70%). M.p. 71-73°C. IR:(KBr, cm^{-1}): 1295s, 1255m, 1150vs (asym PO_2); 960vs (sym PO_2); 870vs ($P-CH_3$); 750m, 700s (P-C). ^1H NMR ($CDCl_3$): 1.42 (d, 18H, CH_3, $^2J_{PH}$ 16.7 Hz). ^{13}C NMR ($CDCl_3$): 16.50 (d, $^1J_{PC}$ 102.5 Hz). ^{31}P NMR ($CDCl_3$): 51.9 (s). FAB+ MS [*m/z* (%)]: 1371 (5) $[Bi_3(O_2PMe_2)_8^+]$, 976 (8) $[Bi_2(O_2PMe_2)_6^+]$, 488 (17) $[Bi(O_2PMe_2)_3^+]$, 395 (58) $[Bi(O_2PMe_2)_2^+]$, 302 (10) $[Bi(O_2PMe_2)^+]$, 93 (100) $[O_2PMe_2^+]$, 77 (7) $[OPMe_2^+]$.

Preparation of tris(diphenylphosphinato)bismuth(III), $Bi(O_2PPh_2)_3$ (2)

A mixture of 0.98 g (3.1 mmol) $BiCl_3$ and 2.23 g (9.3 mmol) $Ph_2PO_2Na\cdot$in methanol (100 ml) was stirred under argon atmosphere, for 2 hours, at room temperature. The white precipitate containing NaCl and the desired product was filtered off and washed with water to remove NaCl. The unsoluble white solid was dried to yield 2.07 g (77%) of the title compound. M.p. 237°C. IR (KBr, cm^{-1}): 1435vs (P-Ph); 1135s, 1085vs, 1065m (asym PO_2); 1030m, 1010vs, 990vs (sym PO_2); 745vs, 725vs, 690vs (PC). ^1H NMR (Me_2CO-d_6): 7.52 (m, 18H, C_6H_5-*meta+para*); 7.84 (m, 12H, C_6H_5-*ortho*). For ^{31}P NMR, see subsequent discussion.

General method for the NMR tube scale reactions

$BiCl_3$ and the sodium salt of the appropriate diorganophosphinic acid were mixed in a 1:3 molar ratio in $CDCl_3$, directly in the NMR tube, at room temperature, according to the data in Table 1, and the NMR spectra were recorded.

*Tris(di-n-propylphosphinato)bismuth(III), $Bi(O_2PPr^n{}_2)_3$ (**3**)*: ^{1}H NMR ($CDCl_3$): 1.02 (m, 18H, C*H*$_3$); 1.64 (m, 24H, C*H*$_2$-C*H*$_2$). ^{13}C NMR ($CDCl_3$): 15.46 (s, C_α); 15.59 (d, C_β, $^2J_{PC}$ 19.2 Hz); 31.22 (d, C_γ, $^1J_{PC}$ 90.6 Hz). ^{31}P NMR ($CDCl_3$): 58.4 (s).

*Tris(dicyclohexylphosphinato)bismuth(III), $Bi(O_2PCy_2)_3$ (**4**)*: ^{1}H NMR ($CDCl_3$): 1.22-1.82 (m, 33H, C_6H_{11}). ^{13}C NMR ($CDCl_3$): 24.61 (s, C_4); 25.92 (s, C_3); 26.19 (d, C_2, $^2J_{PC}$ 13.5 Hz); 34.99 (d, C_1, $^1J_{PC}$ 90.6 Hz); ^{31}P NMR ($CDCl_3$): 62.3 (s).

*Tris(dibenzylphosphinato)bismuth(III), $Bi(O_2PBz_2)_3$ (**5**)*: ^{1}H NMR ($CDCl_3$): 2.84 (s, br, 12H, C*H*$_2$); 7.17 (s, br, 30H, C_6H_5). ^{13}C NMR ($CDCl_3$): 36.21 (d, *C*H$_2$, $^1J_{PC}$ 88.6 Hz); 126.68 (s, C_p); 128.49 (s, C_m); 130.01s (C_o); 131.78 (d, C_i, $^2J_{PC}$ 6.6 Hz). ^{31}P NMR ($CDCl_3$): 48.5 (s).

Table 1.

Preparation details for $Bi(O_2PR_2)_3$ (NMR tube scale reactions).

$BiCl_3$ g (mmol)	NaO_2PR_2 g (mmol)	
0.0305 (0.1)	R = Pr^n	0.0499 (0.3)
0.0228 (0.07)	R = Cy	0.0547 (0.21)
0.0228 (0.07)	R = Bz	0.0551 (0.21)

Preparation of tris(diphenylmonothiophosphinato)bismuth(III), $Bi(OSPPh_2)_3$ (6)

A mixture of 0.31 g (1.0 mmol) $BiCl_3$ and 2.26 g (3.0 mmol) $Ph_2P(S)ONH_4$·in acetone (50 ml) was refluxed under argon atmosphere for 2 hours. NH_4Cl was filtered off and the solvent was removed in vacuum. The resulting colorless solid was recrystalized from benzene. Yield 0.5 g (55%). M.p. 180°C. IR (KBr, cm^{-1}): 1437vs (P-Ph); 1128s, 1109s; 1033m, 1013m, 994m (P-O) 656m (P=S); 770s, 748s, 732s, 693s (PC). ^{1}H-NMR ($CDCl_3$): 7.36 (m, 12H, C_6H_5-*meta*); 7.46 (m, 6H, C_6H_5-*para*); 7.83 (m, 12H, C_6H_5-*ortho*). ^{13}C NMR ($CDCl_3$): 128.31 (m, C_m,$^3J_{PC}$ 13.9 Hz); 131.45 (m, C_o, $^2J_{PC}$ 12.8 Hz) 132.10 (s, C_p); 134.10 (d, C_i, $^1J_{PC}$ 113.1 Hz). ^{31}P NMR ($CDCl_3$): 80.9 (s). EI MS [*m/z* (%)]: 908 (5) [M^+], 675 (10) [$Bi(OSPPh_2)_2{}^+$], 442 (17) [$Bi(OSPPh_2)^+$], 233 (5) [$SOPPh_2{}^+$], 217 (59) [$SPPh_2{}^+$], 201 (17) [$OPPh_2{}^+$], 154 (100) [$Ph_2{}^+$].

Preparation of tris(diphenyldithiophosphinato)bismuth(III), $Bi(S_2PPh_2)_3$ (7)

A mixture of 0.63 g (2 mmol) $BiCl_3$ and 1.6 g (6 mmol) $Ph_2PS_2NH_4$·in THF (50 ml) was stirred under argon atmosphere, for 3 hours, at room temperature. The solvent was removed in vacuum and the remained solid was treated with chloroform. NH_4Cl was filtered off and the solvent was removed in vacuum to give a yellow crystalline product. Yield 1.37 g (72%). M.p. 127°C. ^{1}H NMR ($CDCl_3$): 7.38 (m, 18H, C_6H_5-*meta+para*); 7.87 (ddd, 12H, C_6H_5-*ortho*, $^3J_{PH}$ 14.5, $^3J_{HH}$ 8.0, $^4J_{HH}$ 1.2 Hz); ^{13}C NMR ($CDCl_3$): 128.19 (d, C_m, $^3J_{PC}$ 13.3 Hz); 130.55 (d, C_o, $^2J_{PC}$ 12.1 Hz); 131.06 (s, C_p); 139.29 (d, C_i, $^1J_{PC}$ 83 Hz); ^{31}P NMR ($CDCl_3$): 60.1 (s). EI MS [*m/z* (%)]:707 (96) [$Bi(S_2PPh_2)_2{}^+$], 458 (22) [$Bi(S_2PPh_2)^+$], 249 (55) [$S_2PPh_2{}^+$], 217 (100) [$SPPh_2{}^+$], 154 (5) [$Ph_2{}^+$], 77 (5) [Ph^+].

Preparation of oxo(diphenyldithiophosphinato)bismuth(III), OBi(S$_2$PPh$_2$) **(8)**

A mixture of 1.3 g (5.0 mmol) OBiCl and 1.335 g (5.0 mmol) $Ph_2PS_2NH_4$ in acetone (50 ml) was refluxed for 2 hours. NH_4Cl was filtered off and the yellow solution was concentrated in vacuum. The resulting yellow solid was recrystalized from acetic acid. Yield 2.2 g (93%). M.p. 76°C. IR (KBr, cm^{-1}): 1436s (P-Ph); 610s, 660s (asym PS_2); 555vs (sym PS_2). ^1H NMR ($CDCl_3$): 7.32 (m, 4H, C_6H_5-*meta*); 7.40 (m, 2H, C_6H_5-*para*); 7.78 (dm, 4H, C_6H_5-*ortho*, $^2J_{PH}$ 14.4 Hz). ^{13}C NMR ($CDCl_3$): 128.46 (d, C_m, $^3J_{PC}$ 13.9 Hz), 131.95 (d, C_o, $^2J_{PC}$ 10.8 Hz), 132.23 (s, C_p), 132.88 (d, C_i, $^1J_{PC}$ 76.1 Hz). ^{31}P NMR ($CDCl_3$): 71.0 (s).

Results and Discussion

Synthesis

Inorganic bismuth derivatives of type $Bi(X_2PR_2)_3$ (X = O, R = Me, Ph, Pr^n, Cy, Bz; X = S, R = Ph), $Bi(OSPPh_2)_3$ and $OBi(S_2PPh_2)$ were obtained by salt metathesis reactions between either $BiCl_3$ or OBiCl and an alkali metal or ammonium salt of the appropriate phosphorus-containing acid, according to equations (1) – (4):

$$\mathrm{BiCl_3 + 3\ NaO_2PR_2 \longrightarrow Bi(O_2PR_2)_3 + 3\ NaCl} \qquad (1)$$

R = Me (**1**), R = Ph (**2**)
R = Pr^n (**3**), R = Cy (**4**)
R = Bz (**5**)

$$\mathrm{BiCl_3 + 3\ NH_4OSPPh_2 \longrightarrow \underset{\mathbf{6}}{Bi(OSPPh_2)_3} + 3\ NH_4Cl} \qquad (2)$$

$$\mathrm{BiCl_3 + 3\ NH_4S_2PPh_2 \longrightarrow \underset{\mathbf{7}}{Bi(S_2PPh_2)_3} + 3\ NH_4Cl} \qquad (3)$$

$$\mathrm{OBiCl + NH_4S_2PPh_2 \longrightarrow \underset{\mathbf{8}}{OBi(S_2PPh_2)} + NH_4Cl} \qquad (4)$$

Compounds **1**, **2** and **6**–**8** were isolated as solid products, while compounds **3**–**5** were generated in solution, directly in the NMR tube, and investigated spectroscopically without further isolation.

Some data concerning the new compounds and related bismuth(III) dithiophosphinates, already described in literature, are given in Table 2.

All compounds were investigated by NMR spectroscopy. Compounds **1**, **2** and **6**–**8** were also characterized by infrared spectroscopy and mass spectrometry (EI or FAB).

NMR Spectroscopy

The dioxo derivatives exhibit a poor solubility in $CDCl_3$. For compound **2** the NMR spectra could be obtained only in presence of more polar solvents, *i.e.* acetone-d_6 or DMSO-d_6. This suggests a possible polymeric structure for these compounds.

Table 2.

Analitical data for the new Bi(III) compounds and related derivatives.

Compound	M.p. [°C]	^{31}P NMR ($CDCl_3$)	Structure data
$Bi(O_2PMe_2)_3$ (**1**)	71-73	51.9	NMR, MS, IR[a]
$Bi(O_2PPh_2)_3$ (**2**)	237	12.5[b]	NMR, MS, IR[a]
$Bi(O_2PPr^n{}_2)_3$ (**3**)		58.4	NMR[a]
$Bi(O_2PCy_2)_3$ (**4**)		62.3	NMR[a]
$Bi(O_2PBz_2)_3$ (**5**)		48.5	NMR[a]
$Bi(OSPPh_2)_3$ (**6**)	180	80.9	NMR, IR[a]
$Bi(S_2PPh_2)_3$ (**7**)	127	60.1	NMR, MS,[a] IR [9], X-ray [7]
$OBi(S_2PPh_2)$ (**8**)	76	71.0	NMR, IR[a]
$Bi(S_2PMe_2)_3$	242	60.4 (C_6D_6)	NMR, X-ray [5]
$Bi(S_2PEt_2)_3$			NMR, X-ray [6]
$MesBi(S_2PPh_2)_2$	180 (dec)	-	NMR, MS, X-ray [8]

[a] This work; [b] In DMSO-d_6.

In a mixture of $CDCl_3$ – DMSO-d_6, the ^{31}P NMR spectrum of **2** exhibits two resonances, at δ 28.4 and 24.8 ppm, respectively. The resonance at lower field (δ 28.4 ppm) is very close to that observed for the free acid in $CDCl_3$ (δ 28.6 ppm). However, the ^{31}P NMR spectrum in pure DMSO-d_6 for compound **2** contains only one resonance (δ 12.5 ppm), different from the values observed in the same solvent for $Ph_2P(O)OH$, (δ 24.7 ppm) or Ph_2PO_2Na (δ 17.4 ppm), which clearly suggests the formation of a Bi(III) species, probably a DMSO adduct, with a monomeric structure. The strong coordination ability of DMSO to the bismuth atom is well known [14,15].

In order to investigate the influence of the organic group attached to phosphorus upon the solubility of bismuth derivatives, some related species, *i.e.* $Bi(O_2PR_2)_3$ (R = Pr^n, Cy, Bz), were generated directly in the NMR tube, in $CDCl_3$. For all dioxo derivatives the ^1H and ^{13}C resonances are not significantly shifted compared to the free acids, but in all cases the ^1H resonance for the O*H* group, characteristic for the free acids, is absent, as well as the corresponding OH stretching vibration in the region 2600 - 1600 cm^{-1}, in the IR spectra (for compounds **1** and **2**). In contrast to the free acids, the proton resonances for the dioxo derivatives exhibit a broad aspect and the proton-proton and phosphorus-proton couplings are not resolved. The ^{31}P resonances for the Me and Bz substituted derivatives are enough shifted to conclude the formation of the desired complexes [*i.e.* δ 48.5 ppm for $Bi(O_2PBz_2)_3$ in contrast to δ 51.4 ppm for $Bz_2P(O)OH$, and δ 51.9 ppm for $Bi(O_2PMe_2)_3$ in contrast to δ 48.6 ppm for $Me_2P(O)OH$].

The Bi(III) compounds containing monothio or dithio ligands are soluble in common organic solvents and the NMR spectra in $CDCl_3$ solution are consistent with the formation of the desired compounds (**6**–**8**). The ^1H and ^{13}C NMR spectra exhibit the expected resonances for the organic groups attached to phosphorus, split by the proton-proton and phosphorus-proton couplings, and phosphorus-carbon couplings, respectively. The ^{31}P NMR spectra show only one sharp resonance.

Mass Spectra

The FAB+ MS spectrum of compound **1** contains the molecular ion in a relatively high abundance (12%), but peaks with higher mass are also present (*i.e. m/z* 1371 $[Bi_3(O_2PMe_2)_8^+]$, *m/z* 976 $[Bi_2(O_2PMe_2)_6^+]$), thus consistent with the formation of molecular associations, at least of a trimeric species $[Bi(O_2PMe_2)_3]_3$.

For the monothio and dithio derivatives, peaks of low intensity, corresponding to the molecular ions, were observed in the EI spectra, along with different other peaks corresponding to ions formed by fragmentation. For compound **7**, even if the single-crystal X-ray studies revealed a dimeric structure [7], no fragments with m/z values higher than corresponding to a monomeric species were observed in the EI MS spectrum, which is consistent with weak intermolecular Bi···S interactions.

Infrared Spectra

The infrared spectra of the dioxo derivatives **1** and **2** are consistent with a coordination of the phosphinato ligands through both oxygen atoms to the metal center (*e.g.* vasym(PO_2) 1135s, 1085vs, 1065m, and $v_{sym}(PO_2)$ 1030m, 1010vs, 990vs for **2** *vs.* vasym(PO_2) 1035m, 1010s, and $v_{sym}(PO_2)$ 1142vs, 1133vs for $Ph_2SbO_2PPh_2$, for which a polymeric structure, with *O,O'*-bridging ligand, was established by single-crystal X-ray diffraction [16]). Taking into account the low solubility of this type of bismuth compounds and the observation in mass spectrum of compound **1** of fragments with a higher mass than expected for a monomeric species, polymeric structures with bridging ligand units might be considered. The difference in solubility might be due to a higher association degree for the phenyl substituted compound.

The strong IR absorptions observed for the compound **6** in the region 1130-1000 cm^{-1} and at 656 cm^{-1} are indicative for single P-O and double P=S bonds in the monothiophosphinato ligand [c.f. $Ph_2P(S)OH$ [17]: v(P-O) 892vs, v(P=S) 633vs; $Ph_2SbOSPPh_2$ [16]: v(PO) 1061vs, 1050vs, v(PS) 593vs; for which a polymeric structure, with *O,O'*-bridging ligand, was established by single-crystal X-ray diffraction). This behaviour is consistent with the primary coordination of the monothio ligands to the metal centre through the oxygen atom, while the sulfur doubly bonded to phosphorus is probably involved in secondary intramolecular bonding, thus resulting in a distorted octahedral $Bi(O,S)_3$ core. Additional increase in coordination number of the metal centre through intermolecular bismuth chalcogen interactions, as observed in the related dimeric antimony derivative, $[Sb(OSPPh_2)_3]_2$ [18], cannot be excluded.

It was suggested that the difference Δ = vasym(PS_2) - vsym(PS_2) might be used for estimation of the coordination pattern of the dithiophosphorus ligands in metal complexes, *i.e.* Δ = 50-70 cm^{-1}, Δ = 70-90 cm^{-1} and Δ > 95 cm^{-1} indicates isobidentate, anisobidentate and monodentate coordination, respectively [18]. Indeed, for $Bi(S_2PPh_2)_3$ (**7**) the Δ = 75 cm^{-1} [9] is consistent with the bidentate pattern of the dithio ligand found by single-crystal X-ray diffraction studies [7]. For the bismutyl derivative $OBi(S_2PPh_2)$ (**8**) the difference Δ of 105 cm^{-1} would suggest a monodentate coordination of the dithio ligand. However, taking into account that in all bismuth(III) complexes investigated so far by single-crystal X-ray diffraction [5-8] the dithiophosphorus ligands are coordinated through both sulfur atoms thus resulting in higher coordination number of the metal centre, molecular associations in solid state for compound **8** can not be excluded.

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