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SYNTHESIS AND MOLECULAR STRUCTURES OF COMPLEXES OF BISMUTH(III) NITRATE WITH TRIDENTATE LIGANDS: 2,6-BIS(—CH_2—P(=O)R_2) SUBSTITUTED PYRIDINE-*N*-OXIDES

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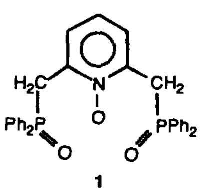
Abstract—The two trifunctional ligands 2,6-(Ph_2P(=O)—CH_2)$_2C_5H_3NO$ (**1**) and 2,6-[$(EtO)_2P$(=O)—CH_2]$_2C_5H_3NO$ (**2**) were prepared by Arbuzov reactions on 2,6-bis (chloromethyl)pyridine with Ph_2POMe and triethylphosphite, respectively, and characterized by spectroscopic methods and X-ray structural analysis (**1**). Their coordination chemistry with $Bi(NO_3)_3$ was studied. The complexes $Bi(NO_3)_3\cdot$**1**$\cdot$DMF and Bi $(NO_3)_3\cdot$**2** were isolated and their X-ray structures determined. In both cases, the ligands bind in a tridentate fashion to Bi^{III}, and the nitrate ions remain in the inner coordination sphere. Structural features of the unbound and bound ligand **1** are discussed.

Studies of the coordination chemistry of bismuth have recently been stimulated by several technologically important issues. In particular, Bi^{III} is a component in a number of high T_c superconducting oxide compositions, and several of its coordination complexes are useful solution-processible chemical precursors for solid-state materials.[1] Further, Bi^{III} is an important constituent in a number of nuclear waste streams. In this regard, it is very important to understand solution speciation and develop methods for bismuth-specific separations from aqueous solutions.

The coordination chemistry of Bi^{III} is largely governed by its large charge-to-radius ratio.[2] The ion is oxophilic, and it prefers to bind to anionic or neutral oxide donor ligands. In this regard, the ion has some similarities to the lanthanide (III) ions, and it is expected that chelating oxo-donor ligands will form very stable complexes with Bi^{III}. We have recently described the synthesis of a neutral trifunctional oxo-donor ligand, $[Ph_2P(O)CH_2]_2$ C_5H_3NO (**1**), that forms strong 2 : 1 stoichiometry



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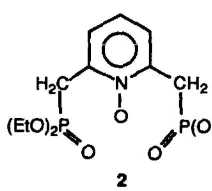

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coordination complexes with Ln^{III} and Th^{IV} ions.[3] In each case examined to date, the ligand binds in tridentate fashion.

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Further, in the presence of two or more equivalents of **1**, two nitrate counterions are displaced from the metal's inner coordination sphere. Unfortunately, **1** is not particularly soluble in hydrocarbon solvents. This limits its use as a practical liquid–liquid extractant. This shortcoming has led us to explore the feasibility of obtaining more soluble analogues of **1**. We report here an improved synthesis of **1**, the synthesis of the ethylphosphonate analogue **2**, and the coordination chemistry of both **1** and **2** with Bi $(NO_3)_3$.

EXPERIMENTAL

Thionyl chloride tech., 2,6-pyridinedimethanol (98%), *m*-chloroperbenzoic acid and triethyl phosphite were purchased from Aldrich Chemical Co. Bismuth nitrate was obtained from Ventron and 30% hydrogen peroxide was purchased from Fischer Chemical Co. The active peroxide content of the *m*-chloroperbenzoic acid was determined to be about 70% by titration[4] immediately prior to use. The Ph_2POMe was prepared from Ph_2PCl (Aldrich) and absolute methanol (Baker) according to a published procedure,[5] and it was vacuum distilled (b.p. 91–94°C, 10^{-3} Torr). The ligand syntheses were performed with rigorously dried solvents under a dry nitrogen atmosphere unless noted otherwise. IR spectra were recorded on a Matteson 2020 FT-IR spectrometer, and NMR spectra were obtained from Bruker WP-250 and JEOL GSX-400 spectrometers. NMR standards were Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). The mass spectra were obtained by FAB-MS techniques at the Midwest Center for Mass Spectrometry, and elemental analyses were performed by R. Ju of the University of New Mexico microanalytical facility.

Syntheses

2,6-*Bis*(*chloromethyl*)*pyridine*. Although the synthesis used here is closely related to that described earlier,[3,6,7] some important additional details are provided. Thionyl chloride was distilled under an atmosphere of dry nitrogen through a 150 mm Vigreux column (b.p. 70.5°C/630 mm). An initial deep yellow fraction was discarded. A 25 g (0.18 mol) sample of 2,6-pyridinedimethanol was added in small portions with stirring to 150 cm^3 of thionyl chloride cooled by an ice bath under a countercurrent of dry nitrogen (exothermic reaction with evolution of SO_2 and HCl). After the addition was complete, the solution was refluxed for 4 h under nitrogen. The excess thionyl chloride was then removed by vacuum evaporation at ambient temperature, leaving a cream-coloured crystalline solid. A 200 cm^3 portion of water and a few cm^3 of concentrated HCl were added until all except a small amount of a greenish–brown oily residue dissolved. The solution was filtered through filter paper and then neutralized with aqueous saturated $NaHCO_3$. This produced a white precipitate of 2,6-bis(chloromethyl)pyridine.

CAUTION: neutralization and the following steps handling 2,6-bis(chloromethyl)pyridine should be done in a well-ventilated hood. Skin or eye contact with the solid, and especially with organic solutions of this compound, should be carefully avoided since the compound is a vigorous irritant and apparently has some vapour pressure at ambient temperature.

The solid was collected by filtration, washed with water and vacuum dried. In order to speed up the drying process, the solid was ground into a fine powder, vacuum dried and ground again. The solid was then dissolved in 100 cm^3 of hot heptane and the solution was decanted from a small amount of green sludge. Upon cooling the solution to room temperature and then to $-20°C$, large crystals of 2,6-bis(chloromethyl)pyridine formed. They were collected by filtration, washed with 3×10 cm^3 pentane and vacuum dried. Yield: 22.07 g (69.7%). Concentrating the filtrate and washing the solution to ~ 25 cm^3 gave another 0.66 g of product. Overall yield: 22.73 g (71.7%), m.p. 75–77 (lit.[8] 74–75°C).

Characterization data: MS (70 eV), *m*/*z*: 179 (11%), 177 (62%), 175 (100%, M^+, 2Cl), 142 (21%), 140 (67%, M^+-Cl), 104 (73%, $M^+-2Cl-H$), 77 (62%, $M^+-2\times CH_2Cl$), 63 (33%, $M^+-2\times CH_2Cl-N$), 51 (26%, $C_4H_3^+$). IR (KBr, cm^{-1}): 3063 (vw), 3011 (w), 2965 (w), 2857 (vw), 1991 (vw), 1912 (vw), 1829 (vw), 1738 (vw), 1589 (s), 1578 (s), 1433 (m), 1256 (m), 1163 (w), 1092 (w), 995 (w), 972 (w), 891 (w), 824 (m), 750 (s), 677 (vs), 615 (m), 557 (m). ^1H NMR ($CDCl_3$): δ 4.64 (4H, CH_2), 7.41 [d, $J = 7.8$ Hz, 2H, H(3/5) pyridine], 7.74 [t, $J = 7.8$ Hz, 1H, H(4) pyridine]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 46.43, 122.09, 138.13.

2,6-*Bis*[(*diphenylphosphino*)*methyl*]*pyridine*-P,P′-*dioxide* (**4**). A 65.85 g (0.305 mol) sample of *o*-methyldiphenylphosphinite was transferred under nitrogen via a cannula to a 500 cm^3 round-bottomed flask containing 100 cm^3 of dry triglyme [refluxed over benzophenone/sodium and distilled (b.p. 52.5°C/10^{-3} Torr)] and a stir bar. A 26.81 g (0.152 mol) sample of 2,6-bis(chloromethyl)pyridine dissolved in 100 cm^3 of triglyme was added via a pressure-equalized dropping funnel to the stirred solution of the phosphinite heated to 150°C. The pressure in the reaction flask was reduced to 20 mm through a reflux condenser and a trap cooled with liquid nitrogen. The mixture boiled gently and methyl chloride collected in the trap. When the addition was almost complete, a precipitate of the reaction product formed. After reagent addition was complete, the mixture was allowed to stir for an additional 3 h at 150°C under reduced pressure. It was allowed to cool to room temperature and then to −20°C. The mixture was filtered and the collected residue washed with cool ether (4 × 20 cm^3) and vacuum dried. A 61.57 g sample of a white solid remained. Concentration of the filtrate and washings by vacuum distillation to about 100 cm^3 gave another 6.76 g. Overall yield: 68.33 g (88.4%).

Characterization data: MS (70 eV), *m*/*z*: 507.5 (M^+, 100%), 201 (Ph_2PO^+, 70%). IR (KBr, cm^{-1}): 3047 (w), 3012 (vw), 2947 (vw), 2891 (w), 1591 (m), 1574 (m), 1501 (w), 1435 (s), 1398 (m), 1194 (vs), 1109 (s), 826 (m), 721 (s), 691 (vs), 525 (s), 469 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.5. ^1H NMR ($CDCl_3$): δ 3.77 (d, $J = 14.4$ Hz, CH_2), 7.10 [d, $J = 7.8$ Hz, H(3/5) pyridine], 7.31 [t, partly overlapped, $J = 7.8$ Hz, H(4) pyridine], 7.32–7.52 and 7.62–7.74 (m, C_6H_5 rings). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 40.55 (d, $J = 65$ Hz), 122.78, 128.36 (d, $J = 12.0$ Hz), 131.15 (d, $J = 9.6$ Hz), 131.68, 133.77, 136.71, 152.19 (d, $J = 5$ Hz). Found: C, 73.2; H, 5.5; N, 2.8. Calc. for $C_{31}H_{27}NO_2P_2$: C, 73.4; H, 5.4; N, 2.8%.

2,6 - *Bis*[(*diphenylphosphino*)*methyl*]*pyridine* - N, P,P′-*trioxide* (**1**). A 10.85 g (0.0214 mol) sample of 2,6-bis[(diphenylphosphino)methyl]pyridine-P,P′-dioxide was dissolved in 25 cm^3 of glacial acetic acid, and 4 cm^3 of H_2O_2 (30%) were added at 20°C. The solution was stirred for 2 days, and then an additional 3 cm^3 of H_2O_2 were added. This solution was then stirred for another 2 days. The mixture was vacuum evaporated and the white precipitate was exposed to an oil pump vacuum overnight. The residue was dissolved in 75 cm^3 of chloroform and extracted with water (7 × 40 cm^3). The chloroform solution was dried over molecular sieves (4 Å) and then distilled at ambient pressure (630 mm), leaving a white solid. Yield: 10.8 g (96.4%). Recrystallization was achieved by redissolving the solid in chloroform under reflux, concentrating the solution to about 50 cm^3 and adding pentane (50 cm^3) in small portions.

Characterization data: MS (70 eV), *m*/*z*: 523 (M^+, < 1%), 201 (100%, Ph_2PO^+), 77 (50%, Ph^+). IR (KBr, cm^{-1}): 3055 (w), 3015 (vw), 2964 (w), 2868 (w), 1589 (vw), 1562 (w), 1483 (w), 1437 (m), 1403 (m), 1235 (m), 1190 (vs), 1123 (s), 831 (s), 750 (m), 719 (s), 694 (vs), 621 (w), 523 (s), 467 (s), 424 (w). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.4. ^1H NMR ($CDCl_3$): δ 4.12 (d, $J = 6.9$ Hz, CH_2 protons), 6.96 [t, $J = 3.9$ Hz, H(4) pyridine], 7.33–7.50 (m, C_6H_5), 7.56 [d, $J = 3.9$ Hz, H(3/5) pyridine], 7.61–7.85 (m, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.50 (d, $J = 67.0$ Hz), 124.46, 125.83, 128.55 (d, $J = 12.1$ Hz), 130.79 (d, $J = 9.9$ Hz), 131.25, 131.95, 132.96, 143.8.

2,6 - *Bis*[(*diethylphosphono*)*methyl*]*pyridine* (**3**) *and* 2,6-*bis*[(*diethylphosphono*)*methyl*]*pyridine*-N-*oxide* (**2**). A sample of 2,6-bis(chloromethyl-pyridine) (4.0 g, 23 mmol) was dissolved in 40 cm^3 of $(EtO)_3P$, and the solution was added to a dropping funnel in a nitrogen-filled glove bag. The funnel was then fitted to a reaction flask containing an additional 40 cm^3 of $(EtO)_3P$. The flask was also fitted with a water-cooled condenser capped with a nitrogen bubbler. The flask was heated with an oil bath at 140–150°C, and the solution in the addition funnel was added dropwise over 4 h. It is important to maintain the oil bath temperature above 140°C, or the reaction will not go to completion. The reaction vessel was then cooled to 25°C and a small amount of white solid was removed by filtration. The yellow filtrate was evaporated, leaving a dark yellow liquid. Yield: 7.90 g (88%). This was combined with a solution containing 100 cm^3 of dry $CHCl_3$ and 5.4 g (0.023 mol) of 3-chloroperbenzoic acid. The resulting mixture was heated with stirring at 70°C for 16 h. A slight excess of oxidant is required for a complete reaction, and the oxidation is sensitive to temperature. If heated above 75°C, the solution turns brown and the product isolated is the bis-phosphonic acid derivative of **2**. When done correctly, the initially yellow solution turns almost colourless. The solution was neutralized with equal volumes of saturated aqueous $NaHCO_3$ solution until gas evolution ceased. The organic layer was collected, filtered and dried over 4 Å molecular sieves. The $CHCl_3$ solution was then filtered and evaporated to dryness, leaving a brown solid. This was recrystallized from diethyl ether–pentane solution, resulting in a white solid. Yield: 3.9 g (47%), m.p. 65–66°C.

Characterization data: $[(EtO)_2P(O)CH_2]_2C_5H_3NO$. IR (KBr, cm^{-1}): 3057 (w), 2984 (m), 2930 (w), 2909 (w), 1566 (w), 1491 (m), 1429 (m), 1292 (m), 1250 (s), 1163 (w), 1055 (s), 1026 (s), 964 (s), 872 (w), 828 (w), 806 (m), 779 (m), 713 (w), 542 (m). FAB-MS (% intensity): 396 (M^+, 100), 380 (7), 350 (7), 259 (10), 243 (10), 215 (5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.7. ^1H NMR ($CDCl_3$): δ 1.26 (t, $J = 7.0$ Hz, 12H), 3.68 (d, $J = 22$ Hz, 4H), 4.11 (m, 8H), 7.13 (t, $J = 7.8$ Hz, 1H), 7.43 (d, $J = 7.8$ Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.3 (d, $J = 6.4$ Hz), 28.0 (d, $J = 141$ Hz), 62.5 (d, $J = 6.7$ Hz), 124.3, 125.5, 143.9 (d, $J = 7.1$ Hz). Found: C, 45.3; H, 7.1; N, 3.8. Calc. for $C_{15}H_{27}NO_7P_2$: C, 45.6; H, 6.9; N, 3.5%.

Preparation of the complexes

The complexes were prepared by addition of a solution of the ligands **1** or **2** (1 meq. in 10 cm^3 of $CHCl_3$/15 cm^3 of DMF) to a solution of Bi $(NO_3)_3$ (1 meq. in 25 cm^3 of DMF). The mixture was stirred for 1 h and the solvent evaporated. The residue was washed with pentane, filtered and dried. Suitable single crystals were obtained by allowing Et_2O to slowly vapour diffuse into a DMF solution of each complex.

Characterization data: Bi $(NO_3)_3\cdot\mathbf{1}\cdot$DMF. IR (KBr, cm^{-1}): 3061 (w), 2982 (w), 2945 (w), 2932 (w), 1669 (m), 1643 (m), 1578 (w), 1485 (s), 1472 (s), 1437 (s), 1385 (s), 1267 (s), 1204 (s), 1128 (s), 1067 (s), 1020 (s), 997 (w), 858 (m), 822 (m), 745 (s), 727 (s). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 36.1. Found: C, 40.9; H, 3.4; N, 7.2. Calc. for $C_{34}H_{34}N_5O_{13}P_2Bi$: C, 41.2; H, 3.5; N, 7.1%. Bi $(NO_3)_3\cdot\mathbf{2}$. IR (KBr, cm^{-1}): 3084 (w), 2984 (w), 2934 (w), 1489 (w), 1385 (s), 1290 (m), 1259 (m), 1233 (s), 1211 (s), 1161 (m), 1096 (m), 1049 (s), 1024 (s), 962 (m), 866 (m), 825 (m), 808 (m), 779 (m).

Crystallographic analysis

Suitable crystals were mounted in sealed glass capillaries. Pertinent data collection and refinement parameters are summarized in Table 1. Data were collected in the ω scan mode on a Siemens (R3m/V) automated diffractometer equipped with a graphite monochromator and Mo-K_α radiation (λ = 0.71073 Å). All calculations were performed with SHELXTL PLUS (VMS version; G. Sheldrick, Siemens Corp., Madison, WI, U.S.A.). The structures were solved by direct methods and refined by using full-matrix least squares techniques. The quantity minimized was $\Sigma w(|F_0| - |F_c|)^2$. Some individual details for the refinements are provided. The non-hydrogen atom positions in $[Ph_2P(O)CH_2]_2C_5H_3NO$ were refined anisotropically, and the hydrogen atoms were placed in idealized positions (riding model) with $U_{iso} = 1.25U_{eq}$ of the parent atom. The data for the complexes were treated similarly except that the DMF solvent molecule in Bi $(NO_3)_3\{[Ph_2P(O)CH_2]_2C_5H_3NO\}\cdot(C_3H_7NO)$ was positionally disordered, and it was only refined isotropically. Selected bond distances are summarized in Table 2, and views of the molecules are shown in Figs 1–3. Supplementary material is available from the Cambridge Crystallographic Database.

RESULTS AND DISCUSSION

2,6 - Bis[(diethylphosphono)methyl]pyridine - *N*-oxide (**2**) was prepared as summarized in Scheme 1. For simplicity, an Arbuzov reaction between 2,6-bis(chloromethyl)pyridine and $(EtO)_3P$ was employed. A Michaelis reaction scheme may also be used as described for the synthesis of the difunctional compound 2-(diethylphosphonomethyl)

Table 1. Summary of crystallographic data

	1	Bi $(NO_3)_3\cdot\mathbf{1}\cdot$DMF	Bi $(NO_3)_3\cdot\mathbf{2}$
Chemical formula	$C_{31}H_{27}NO_3P_2$	$C_{34}H_{34}N_5O_{13}P_2Bi$	$C_{15}H_{27}N_4O_{16}P_2Bi$
Formula weight	523.5	991.6	790.3
Colour, habit	colourless rod	pale yellow block	pale yellow plate
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$Cmc2_1$	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	29.613(11)	15.610(5)	10.401(2)
b (Å)	10.783(5)	15.570(5)	22.381(4)
c (Å)	8.055(2)	16.553(6)	12.208(2)
β (°)		108.61(2)	91.63(1)
Volume ($Å^3$)	2571.9(16)	3812.7(12)	2840.6(7)
Z	4	4	4
Temperature (°C)	20	20	20
Density (g cm^{-3})	1.352	1.727	1.848
Absorption coeff. (cm^{-1})	0.197	4.759	6.369
Transmission (min/max)	0.8965/0.9714	0.7168/0.9940	0.2270/1.000
Independent reflections	1720	6710	3699
Observed reflections	1631 [$F > 2\sigma(F)$]	4819 [$F > 2\sigma(F)$]	2649 [$F > 2\sigma(F)$]
R(*F*) (%)	4.57	6.03	6.94
$R_w(F)$ (%)	3.94	5.25	3.32

Table 2. Selected bond distances (Å)

[Ph$_2$P(O)CH$_2$]$_2$C$_5$H$_3$NO (**1**)		Bi(NO$_3$)$_3$·**1**·DMF		Bi(NO$_3$)$_3$·**2**	
P—O(2)	1.480(3)	P(1)—O(2)	1.509(6)	P(1)—O(2)	1.483(11)
P—C(4)	1.813(4)	P(2)—O(3)	1.522(7)	P(1)—O(4)	1.538(10)
P—C(5)	1.801(4)	P(1)—C(6)	1.835(12)	P(1)—O(5)	1.533(13)
P—C(11)	1.803(4)	P(2)—C(7)	1.810(11)	P(1)—C(6)	1.802(13)
N—O(1)	1.315(6)	N(1)—O(1)	1.335(8)	P(2)—O(3)	1.507(9)
N—C(1)	1.377(4)	N(1)—C(1)	1.371(12)	P(2)—O(6)	1.528(10)
C(1)—C(4)	1.495(5)	N(1)—C(5)	1.347(11)	P(2)—O(7)	1.512(13)
		C(1)—C(7)	1.507(12)	P(2)—C(7)	1.801(14)
		C(5)—C(6)	1.490(14)	N(1)—O(1)	1.345(12)
		Bi—O(1)	2.375(6)	Bi—O(1)	2.386(8)
		Bi—O(2)	2.337(6)	Bi—O(2)	2.325(9)
		Bi—O(3)	2.306(6)	Bi—O(3)	2.354(8)
		Bi—O(4)	2.503(7)	Bi—O(8)	2.547(11)
		Bi—O(5)	2.561(7)	Bi—O(9)	2.536(11)
		Bi—O(7)	2.452(9)	Bi—O(11)	2.572(12)
		Bi—O(9)	2.594(10)	Bi—O(12)	2.614(11)
		Bi—O(10)	2.577(13)	Bi—O(14)	2.426(10)
				Bi—O(15)	2.606(14)

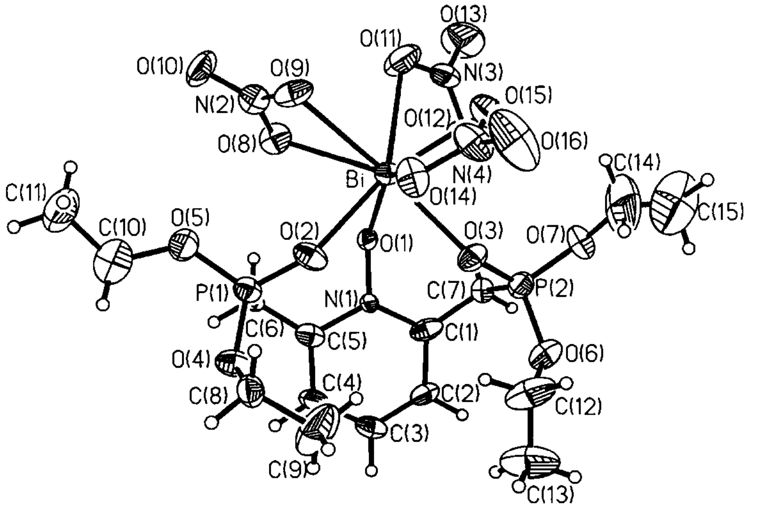


Fig. 1. ORTEP view of Bi(NO$_3$)$_3$·**2**.

pyridine, [(EtO)$_2$P(O)CH$_2$]C$_5$H$_4$N.[9,10] The intermediate phosphonopyridine compound (**3**) is obtained as a yellow oil in good yield. Subsequent oxidation of **3** with *m*-chloroperbenzoic acid in CHCl$_3$ gives the target compound **2** as a white solid in 47% overall yield. The final oxidation step is sensitive to reaction conditions, but the accompanying undesired oxidation by-products are readily separated from **2**. The compound displays a strong parent ion in the FAB-MS, and it contains IR stretching frequencies at 1292 and 1250 cm^{-1} that are tentatively assigned to ν(PO) and ν(NO), respectively. The ^{31}P{^{1}H} NMR spectrum shows a single resonance at δ 23.7, and the fully assigned ^{1}H and ^{13}C{^{1}H} NMR spectra are consistent with the proposed structure.

We have previously reported a synthesis of the related phosphine oxide ligand **1** that employs a metathesis reaction between Ph$_2$PK and 2,6-bis(chloromethyl)pyridine, followed by sequential oxidation of the two phosphorus atoms and then the nitrogen atom with hydrogen peroxide and peracetic acid, respectively.[3] Although **1** is obtained in moderate yield (56%), the reaction sequence is laborious. A simpler alternative route is provided by the sequence outlined in Scheme 2. The Arbuzov

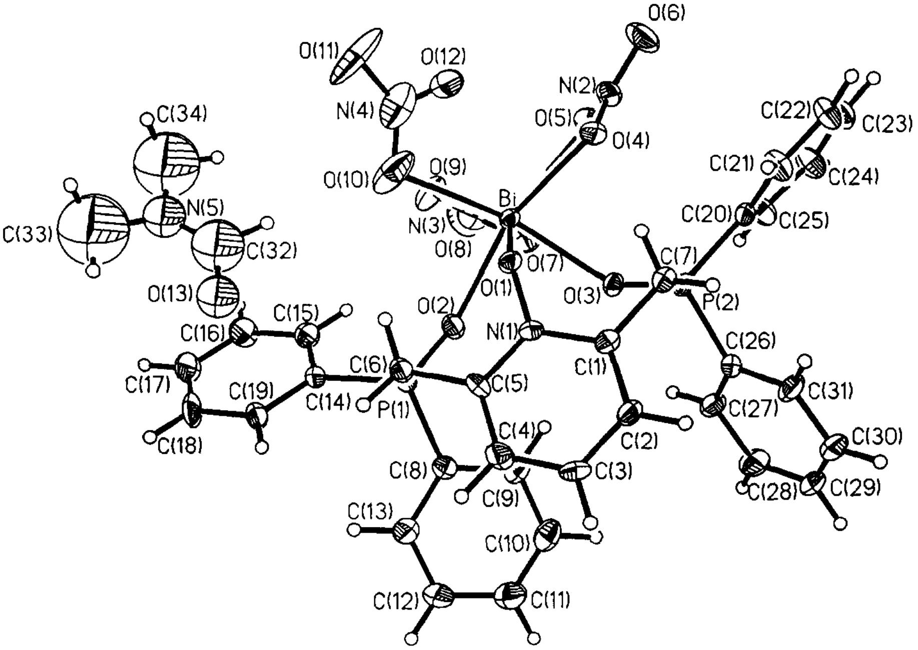


Fig. 2. ORTEP view of $Bi(NO_3)_3 \cdot \mathbf{1} \cdot DMF$.

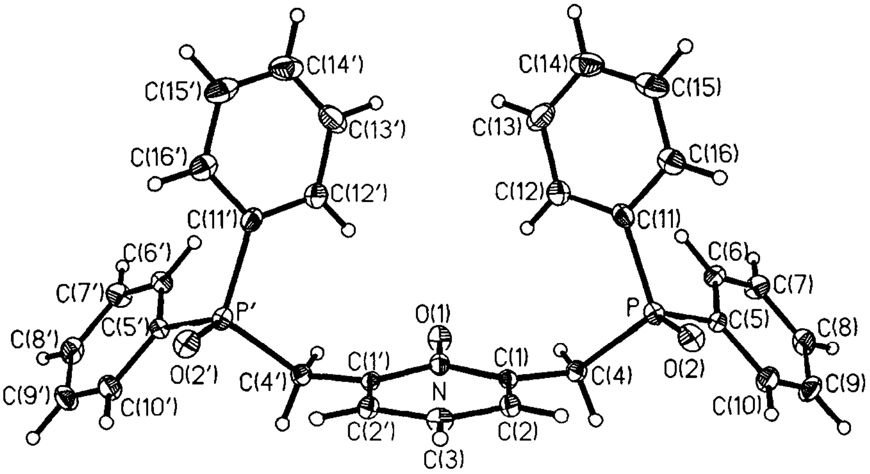
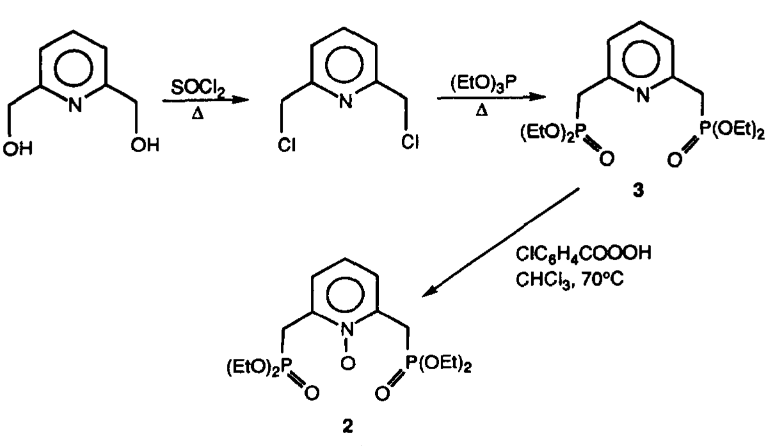
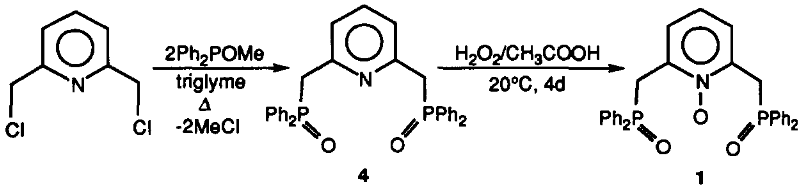


Fig. 3. ORTEP view of $[Ph_2P(O)CH_2]_2C_5H_3NO$ (**1**).



Scheme 1.



Scheme 2.

reaction is straightforward, and it proceeds with good yield (88%) to give the intermediate ligand **4**. The oxidation of **4** was performed at ambient temperature with peracetic acid (H_2O_2–CH_3COOH), with a conversion of better than 96% in this step. Both compounds were fully characterized by mass spectrometry and IR and NMR spectroscopy. For the most part, the data are in close agreement with those reported earlier;[3] however, a few important differences are noteworthy. The $^{31}P\{^1H\}$ NMR resonance for **4** in the present study is found as a singlet at δ 30.5, and this value corrects a misprinted value of δ 34 reported earlier.[3] The $^{31}P\{^1H\}$ NMR resonance for **1** appears as a singlet at δ 31.4, as described earlier.[3] The IR spectrum of **4** obtained here on a more highly purified sample shows some important differences from the spectrum described previously.[3] Several weak and a few strong bands (1451, 1272, 1119 and 753 cm^{-1}) are no longer observed, and these may indicate the presence of an impurity compound in the original samples of **4**. In pure samples of **4**, a strong band at 1194 cm^{-1} is assigned to the P=O stretching frequency. The IR spectrum of **1** obtained here is similar to that of **4**, except that the ν(PO) region contains two strong adsorptions at 1190 and 1123 cm^{-1}. The ν(NO) band appears at 1235 cm^{-1}. If the Arbuzov reaction is not carried out under reduced pressure as described, the methyl chloride remaining in the reaction mixture reacts with the *O*-methyldiphenyl phosphinite to form methyldiphenylphosphine oxide, $Ph_2(Me)P(O)$, as a side product. This shows a strong absorption of 1274 cm^{-1} in the IR spectrum. Further, this compound displays a doublet at δ 1.99 ($J = 13.2$ Hz) in the ^1H NMR spectrum due to the protons of the methyl group directly attached to phosphorus. The phenyl proton multiplet overlaps with that of the main product **4**.

Combination of ligands **1** and **2** with $Bi(NO_3)_3$ in a 1 : 1 ratio in DMF–$CHCl_3$ solution, followed by solvent evaporation, led to the formation of crystalline complexes, $Bi(NO_3)_3\cdot\mathbf{1}\cdot DMF$ and $Bi(NO_3)_3\cdot\mathbf{2}$. The IR spectra of the complexes are sufficiently complex in the region 1300–1000 cm^{-1} that it is inappropriate to assign ν(NO) and ν(PO) and to compute the coordination shifts relative to the free ligand. Single-crystal X-ray diffraction analyses, however, provide confirmation of the compositions and structures of these complexes. All attempts to prepare complexes with a 2 : 1 ligand/metal ratio by using excess ligand in the syntheses were unsuccessful.

The molecular structure for $Bi(NO_3)_3\cdot\mathbf{2}$ is shown in Fig. 1. The Bi^{III} ion is nine-coordinate, and the inner sphere coordination polyhedron is generated by one tridentate ligand and three bidentate nitrate groups. The average Bi—O distance, 2.340 Å, associated with the neutral phosphoryl donor centres, O(2) and O(3), is shorter than the Bi—O distance, 2.386(8) Å, generated by the pyridine-*N*-oxide oxygen atom O(1). A similar trend in bond distances was seen in the coordination of **1** with Yb^{III}.[3] For comparison, these Bi—O distances are intermediate between the average Bi—O(alkoxide) distance, 2.24 Å, and the average Bi—O(ether) distance, 2.6–2.8 Å, in a series of $Bi(NO_3)_3$ (polyethyleneglycol) complexes.[1] The oxygen atom donor centres of **2** define a triangular coordination face with non-bonding edge lengths, O(1)---O(2) 2.986 Å, O(1)---O(3) 2.978 Å and O(2)---O(3) 3.118 Å. It is interesting that the edge length separating the two P=O groups is identical to the corresponding non-bonded distance in $Yb(NO_3)_3\cdot\mathbf{2}\cdot MeOH$, while the two edge lengths involving the N—O---O=P non-bonded distances are significantly longer than in the ytterbium complex (average 2.863 Å).[3] This expansion of the ligand "footprint" on the metal coordination polyhedron is consistent with the greater ionic radius for Bi^{III} compared to Yb^{III}. The Bi—O (nitrate) distances vary over the range 2.426(10)–2.614(10) Å (average value 2.550 Å). This average distance compares favourably with the values found in $Bi(NO_3)_3$(PEG) complexes.[1]

The structure of $Bi(NO_3)_3\cdot\mathbf{1}\cdot DMF$ is closely related to the structure of $Bi(NO_3)_3\cdot\mathbf{2}$; a view of the molecule is shown in Fig. 2. The solvate molecule DMF is not bonded to the bismuth ion, and it does not appear to have unusually close contacts with any atoms in the central core of the structure. As anticipated, the ligand **1** is bonded to the Bi^{III} in a tridentate fashion. The Bi—O(N) distance and one of the Bi—O(P) distances are similar to those found in Bi(NO$_3$)$_3$·**2**; however, the second Bi—O(P) distance is significantly shorter, 2.306(6) Å. Nonetheless, the non-bonded O---O edge distances on the triangular coordination face generated by **1** are identical to those in Bi(NO$_3$)$_3$·**2**: O(1)---O(2) 2.986 Å, O(1)---O(3) 2.978 Å and O(2)---O(3) 3.118 Å. Surprisingly, only two of the three nitrate groups are bonded in a bidentate fashion, while the third NO$_3^-$ is bonded in a monodentate mode. The non-bonded O(12)---Bi distance is 2.766 Å, while the bonded distance O(10)—Bi is 2.577(13) Å. It is worth noting that this bond is approximately *trans* to the short Bi—O(P) vector.

The molecular structure of the free ligand **1** has also been determined, and a view of the molecule is shown in Fig. 3. Comparison of bond distances with its Bi^{III} complex shows, as expected, that the P═O and N—O distances elongate with coordination, although the change involving the N—O group may not be statistically significant given the accuracy of the data for the complex. Comparison of the structural parameters for **1** with the parameters for the P,P′-oxidized form of the ligand,[11] [Ph$_2$P(O)CH$_2$]$_2$C$_5$H$_3$N, suggests that N-oxidation leads to slight lengthening of the pyridine ring distance N—C(1) and the distances involving the methylene carbon, C(1)—C(4) and C(4)—P; however, these trends may also be insignificant due to the large e.s.d.s on the bond distance for [Ph$_2$P(O)CH$_2$]$_2$C$_5$H$_3$N.

It is important to notice that the structure of the free ligand **1** contains a mirror plane that passes through C(3), N and O(1), and the two —CH$_2$P(O)Ph$_2$ arms are positioned above the plane of the pyridine-*N*-oxide ring. Further, the orientation of the open chelate chain O(2)—P—C(4)—C(1)—N(O)—C(1′)—C(4′)—P′—O(2′) places the N—O bond vector in an *anti* configuration relative to the two P═O bond vectors. Of course, tridentate chelation of **1** with Bi^{III} requires reorganization of the chelate chain. We have attempted to examine the energetics of this reorganization by using molecular mechanics calculations (CAChe, Personal Mechanics Version 3.0.4.1). The CAChe augmented force field was used except that the P═O and N—O r_0 values were modified to 1.48 and 1.315 Å, respectively. This more accurately reflects the structural features of the ligand **1** found in the X-ray crystallographic study. The only significant conformational change for the free ligand upon energy minimization of the X-ray structure involved a slight tipping of the pyridine-*N*-oxide ring. This corresponds to changes of ~25° in the N—C—C—P torsion angles and ~16° in the C—C—P—O torsion angles. These probably reflect the packing forces present in the solid-state structure. Attempts to study the energetics of the group rotation process(es) that bring the two P═O and the N—O bond vectors into a *syn* conformation, as found in the coordination complexes, were not particularly informative. The

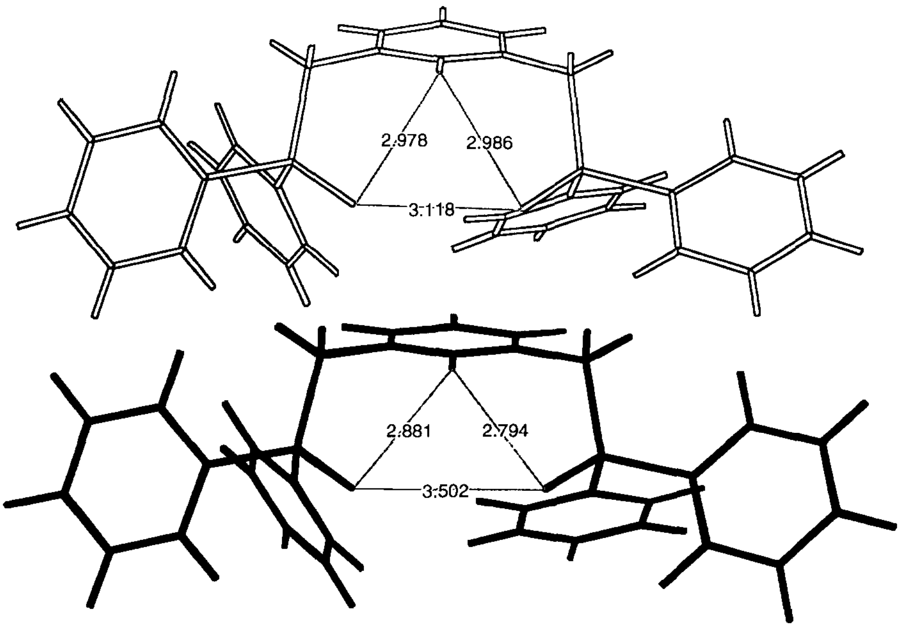


Fig. 4. Framework representations of **2**. Top: view of the ligand conformation as found in the complex Bi(NO$_3$)$_3$·**2**. Bottom: view of the ligand in the absence of the metal ion following energy minimization calculation.

results, within the current accuracy of the computations, suggest relatively flat barriers to reorganization, and this is qualitatively consistent with the high stability of the coordination complexes. It is interesting that energy minimization of the *syn* conformation without the metal present results in a much greater P═O---O═P non-bonded separation than the starting structure adopted from the footprint of the ligand on the Bi^{III} ion. These changes are depicted in Fig. 4.

CONCLUSIONS

As anticipated, the synthesis of ligand **2** provides a more soluble form of **1**, and the change in substituent groups does not significantly alter the type of coordination geometry displayed with Bi $(NO_3)_3$. Future studies will be directed at the preparation of analogue ligands with more lipophilic alkoxy groups that should further enhance the solvent extraction characteristics of **2**.

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REFERENCES

1. R. D. Rogers, A. H. Bond and S. Aguinaga, *J. Am. Chem. Soc.* 1992, **114**, 2960.
2. *Comprehensive Inorganic Chemistry.* Pergamon Press, Oxford (1973).
3. B. M. Rapko, E. N. Duesler, P. H. Smith, R. T. Paine and R. R. Ryan, *Inorg. Chem.* 1993, **32**, 2164.
4. D. J. Pasto and C. R. Johnson, *Organic Structure Determination.* Prentice-Hall, Englewood Cliffs, NJ (1969).
5. K. S. Colle and E. S. Lewis, *J. Org. Chem.* 1978, **43**, 571.
6. E. Buhleier, W. Wehner and F. Vögtle, *Justus Liebigs Ann. Chem.* 1978, 537.
7. W. Baker, K. M. Buggle, J. F. McOmie and D. A. M. Watkins, *J. Chem. Soc.* 1958, 3594.
8. W. V. Dahlhoff and S. M. Nelson, *J. Chem. Soc.* (*A*) 1971, 2184.
9. E. Maruszewska-Wieczorkowska and J. Michalski, *Roczniki Chem.* 1964, **38**, 625.
10. P. Page, M. R. Mazieres, J. Bellan and M. Sanchez, *Phosphorus, Sulfur and Silicon* 1992, **70**, 205.
11. E. Szbyk, Z. Y. Zhang, G. J. Palenik, R. C. Palenik and S. O. Colgate, *Acta Cryst.* 1989, **C45**, 1234.