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Chelating Properties of 2-((Diphenylphosphino)methyl)pyridine *N,P*-Dioxide and 2,6-Bis((diphenylphosphino)methyl)pyridine *N,P,P'*-Trioxide toward f-Element Ions

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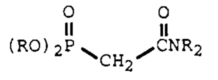
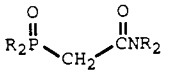
The bifunctional 2-((diphenylphosphino)methyl)pyridine *N,P*-dioxide, $2\text{-}[(C_6H_5)_2P(O)CH_2]C_5H_4NO$ (**4**), and trifunctional 2,6-bis((diphenylphosphino)methyl)pyridine *N,P,P'*-trioxide, $2,6\text{-}[(C_6H_5)_2P(O)CH_2]_2C_5H_3NO$ (**5**), ligands have been prepared, and their coordination chemistry has been surveyed with Pr(III), Tb(III), Yb(III), and Th(IV). Single-crystal X-ray diffraction analyses have been completed for several complexes. Crystallographic data for $[Tb(\mathbf{4})_4{}^{3+}][(NO_3)_3(H_2O)(EtOH)^{3-}]$: $C_{74}H_{72}N_7O_{19}P_4Tb$, orthorhombic, space group *Pbca*, $a = 26.655(5)$ Å, $b = 25.738(5)$ Å, $c = 20.821(5)$ Å, $Z = 8$, $V = 14{,}284(5)$ Å^3; structure refined to $R_F = 6.24\%$ and $R_{wF} = 5.07\%$ on 7068 data with $F > 3\sigma(F)$. The four ligands **4** produce a square antiprismatic coordination polyhedron. Crystallographic data for $[Pr(\mathbf{4})_2(NO_3)_3]\cdot Et_2O\cdot{}^1/_2$ MeOH: $C_{40.5}H_{44}N_5O_{14.5}P_2Pr$, triclinic, space group $P\bar{1}$, $a = 11.02(5)$ Å, $b = 11.802(12)$ Å, $c = 18.560(4)$ Å, $\alpha = 96.70(2)°$, $\beta = 95.84(3)°$, $\gamma = 108.55(3)°$, $Z = 2$, $V = 2247.9(12)$ Å^3; structure refined to $R_F = 6.80\%$ and $R_{wF} = 5.65\%$ on 4561 data with $F > 2\sigma(F)$. The Pr(III) is bonded to two bidentate ligands and three nitrate ions. Crystallographic data for $[Yb(\mathbf{5})(NO_3)_3]\cdot MeOH$: $C_{32}H_{31}N_4O_{13}P_2Yb$, monoclinic, space group $P2_1/n$, $a = 11.677(2)$ Å, $b = 15.764(3)$ Å, $c = 20.242(3)$ Å, $\beta = 100.18(1)°$, $Z = 4$, $V = 3667.4(9)$ Å^3; structure refined to $R_F = 3.94\%$ and $R_{wF} = 4.64\%$ on 4680 data with $F > 3\sigma(F)$. The Yb(III) is bonded to **5** in a tridentate manner, along with three nitrate ions. Crystallographic data for $[Yb(\mathbf{5})_2(NO_3)^{2+}][(NO_3)_2(H_2O)_2(CH_3CN)_{2.5}{}^{2-}]$: $C_{67}H_{65.5}N_{7.5}O_{17}P_4Yb$, triclinic, space group $P\bar{1}$, $a = 14.328(3)$ Å, $b = 16.033(3)$ Å, $c = 17.001(3)$ Å, $\alpha = 99.27(3)°$, $\beta = 101.92(3)°$, $\gamma = 107.36(3)°$, $Z = 2$, $V = 3542(1)$ Å^3; structure refined to $R_F = 5.64\%$ and $R_{wF} = 7.32\%$ on 10 711 data with $F > 3\sigma(F)$. The Yb is bonded to **5** in a tridentate fashion, along with one nitrate ion. Crystallographic data for $[Th(\mathbf{5})_2(NO_3)_2{}^{2+}][(NO_3)_2(H_2O)_2{}^{2-}]$: $C_{62}H_{54}N_6O_{20}P_4Th$, monoclinic, space group $P2_1/n$, $a = 19.136(4)$ Å, $b = 18.365(4)$ Å, $c = 21.448(4)$ Å, $\beta = 109.48(3)°$, $Z = 4$, $V = 7106(3)$ Å^3; structure refined to $R_F = 8.52\%$ and $R_{wF} = 9.18\%$ on 3518 data with $F > 4\sigma(F)$. Two tridentate ligands **5** and two nitrate ions are bonded to Th(IV). This coordination chemistry is compared with that displayed by the bifunctional ligand, $2\text{-}[(C_6H_5)_2P(O)]C_5H_4NO$.

Introduction

Trivalent f-element ions are oxophilic, and they prefer to form coordination complexes with anionic or neutral ligands that have strong oxygen donor centers. As a result, monofunctional ligands containing a carbonyl, phosphoryl, or *N*-oxide group have been used not only to study fundamental f-element coordination chemistry but also to accomplish practical liquid–liquid extractions.[2] Metal ions that form coordination complexes with monofunctional ligands usually produce more stable complexes with related bifunctional chelating ligands.[3] In this vein, it is found that, in comparison to monofunctional phosphonate and amide ligands, the bifunctional (carbamoylmethyl)phosphonates (CMP) and (carbamoylmethyl)phosphine oxides (CMPO) that contain both amide and phosphonate donor centers are superior extractants for trivalent f-elements in highly acidic aqueous solutions.[2] The favorable practical extraction properties derive from a combination of factors including modestly better distribution ratios (*D*) for the extraction complexes, good organic solvent solubility for the complexes, and favorable back-extraction behavior into low-[acid] aqueous solutions.


$(RO)_2P(O)CH_2C(O)NR_2$

CMP


$R_2P(O)CH_2C(O)NR_2$

CMPO

The efficacy of CMP and CMPO as extractants has stimulated interest in the design of new extractants for selective f-element separations. In particular, we have been interested in the design, synthesis, and coordination chemistry of bifunctional and trifunctional ligands that contain both P═O and N—O donors.[4,5] Previous studies in our group on the coordination chemistry of bifunctional 2-(dialkoxyphosphino)pyridine *N,P*-dioxides and 2-(diphenylphosphino)pyridine *N,P*-dioxide (**1**) reveal that these ligands produce stable $UO_2(NO_3)_2\cdot L$ and $Ln(NO_3)_3\cdot 2L$ complexes.[4,5] In each case, the bifunctional ligands bond to the metal in a bidentate fashion. In the bis(ligand) lanthanum(III) complex, the two ligands form hydrophobic "caps" above and below an equatorial band provided by three inner-sphere, bidentate nitrate groups. Liquid–liquid extractions with chloroform solutions of $2\text{-}[(C_6H_5)_2P(O)]C_5H_4NO$ and $2\text{-}[(HxO)_2P(O)]C_5H_4NO$ in contact with acidic aqueous solutions of Eu^{3+}, Ce^{3+}, Yb^{3+}, and Am^{3+} demonstrate modestly effective metal ion partitioning into the

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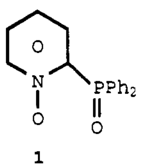

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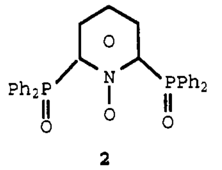

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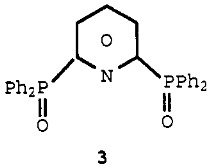

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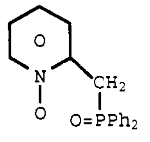

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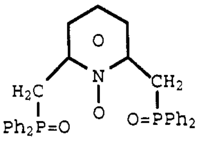

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organic phase from low-acid-concentration aqueous solutions and efficient back-extraction against highly acidic aqueous wash solutions.[6,7]

In continuing to further elucidate f-element coordination chemistry and to design and prepare ligands with practical binding and separation efficacy for f-element ions, we have sought to obtain additional *N,P*-oxide derivatives. In one design modification, the trifunctional ligand 2,6-bis(diphenylphosphino)pyridine *N,P,P′*-trioxide (**2**) was selected as a target. It was reasoned that the three neutral oxygen donor groups should be capable of binding to a trigonal face of 8–12-vertex lanthanide and actinide ion coordination polyhedra, and the resulting mono- and bis(ligand) complexes should display enhanced ligand binding strengths and greater organic solubility in comparison to the complexes formed by **1**. Unfortunately, all attempts to prepare the fully oxidized form failed; only 2,6-bis(diphenylphosphino)pyridine *P,P′*-dioxide (**3**) was obtained. As an alternative, the bifunctional and trifunctional diphenylmethylphosphino analogs **4** and **5** were then selected as target ligands. The syntheses and selected coordination chemistry of these ligands are presented in this paper.

Experimental Section

General Information. Thionyl chloride, 2,6-pyridinedimethanol, 2-(chloromethyl)pyridine hydrochloride, and KH were purchased from Aldrich Chemical Co. Lanthanide nitrates and thorium nitrate were purchased from Ventron. The ligand synthesis reactions were performed with rigorously dried solvents under a dry nitrogen atmosphere, unless otherwise specified. Infrared spectra were recorded on Nicolet 6000 and Matteson 2020 FT-IR spectrometers. Mass spectra were obtained from a Finnegan GC/MS, and NMR spectra were recorded on JEOL GSX-400 and Bruker FX-250 spectrometers. NMR standards were Me_4Si (^{13}C, ^1H) and H_3PO_4 (^{31}P). Elemental analysis data were obtained from the UNM microanalytical analysis facility and from Galbraith Laboratory. As found previously with analytical data for ligands **1** and **3**,[4,5] difficulties were encountered with the elemental analysis of the new pyridine *N*-oxide derivatives, especially for carbon content. In each case, the ligands appear to be pure, as judged by spectroscopic analysis.

Preparation of Ligands. In the syntheses of the precursors to **4** and **5**, solutions of $KPPh_2$ were prepared, and they were used immediately without isolation. Typically, excess KH was weighed under N_2 into a Schlenk flask containing a stir bar, and THF was added via cannulae. A solution of Ph_2PH in THF was slowly dripped into the slurry, and the solution became dark red. Following this addition, the mixture was stirred for 4 h, and the excess KH was allowed to settle overnight. The $KPPh_2$ supernatant solution was carefully decanted into a vessel appropriate for subsequent reactions.

2-((Diphenylphosphino)methyl)pyridine *P*-Oxide (6). A sample of 2-(chloromethyl)pyridine hydrochloride (17.9 g, 109 mmol), ice (20 g), and Na_2CO_3 (11.7 g, 110 mmol) were stirred under an ambient atmosphere. After gas evolution ceased (10 min), the aqueous phase was extracted with $CHCl_3$ (3 × 60 mL), the combined organic phases were dried ($MgSO_4$) and filtered, and $CHCl_3$ was removed on a rotary evaporator. The residue was clarified by addition of 4-Å molecular sieves and the liquid distilled at 60 °C (10^{-3} Torr).[8] 2-(Chloromethyl)pyridine was dissolved in THF (100 mL), and a THF (200 mL) solution of $KPPh_2$ (109 mmol) was slowly added (3h) at 23 °C. The red color rapidly disappeared, leaving a light brown suspension, which was stirred overnight. KCl was removed by centrifugation, the residue washed with CH_2Cl_2, and the combined CH_2Cl_2/THF filtrate evaporated in vacuo at 23 °C. The brown residue was dissolved in acetone (100 mL), and the solution was cooled in an ice bath. To this solution was added H_2O_2 (20 mL, 30%). The addition was accomplished dropwise at a rate resulting in gentle reflux of the solution. After addition, the solution was stirred (1 h), and solvent was removed by vacuum evaporation. The residue was redissolved in $CHCl_3$ (75 mL), the solution extracted with H_2O (6 × 50 mL), and the $CHCl_3$ fraction dried (4-Å molecular sieves). The organic solution was filtered and the filtrate vacuum-evaporated. The resulting solid was redissolved in CH_2Cl_2 (100 mL) and the solution added dropwise to stirred pentane (500 mL). The tan precipitate was collected by filtration: yield 22 g (73%); mp 135–136 °C; soluble in CH_2Cl_2 and $CHCl_3$. Anal. Calcd for $C_{18}H_{16}NOP$: C, 73.71; H, 5.50; N, 4.78. Found: C, 73.42; H, 5.49; N, 4.71.

2-((Diphenylphosphino)methyl)pyridine *N,P*-Dioxide (4). A sample of **6** (10 g, 34 mmol) in glacial acetic acid (50 mL) combined with H_2O_2 (6.0 mL, 41 mmol, 30%) was heated (60 °C, 24 h) under N_2. Unreacted acetic acid was removed at 60 °C, the oily residue dissolved in $CHCl_3$ (75 mL) was extracted with H_2O (4 × 50 mL), and the $CHCl_3$ solution dried (4-Å molecular sieves) and filtered, and the filtrate vacuum-evaporated, leaving a yellow solid. The solid was redissolved in $CHCl_3$ (50 mL), and the solution was added dropwise with stirring to pentane (500 mL). After 15 min, a white solid was obtained: yield 8.8 g (84%); mp 183–184 °C; soluble in $CHCl_3$ and CH_2Cl_2. Anal. Calcd for $C_{18}H_{16}NO_2P$: C, 69.90; H, 5.21; N, 4.53. Found: C, 69.04; H, 5.27; N, 4.80.

2,6-Bis((diphenylphosphino)methyl)pyridine *P,P*-Dioxide (7). A sample of 2,6-pyridinedimethanol (25 g, 180 mmol) was added with stirring to SO_2Cl_2. Upon completion of the exothermic reaction, the flask was fitted with a water-cooled condenser and purged with N_2, and the contents were refluxed (4 h). Excess SO_2Cl_2 was removed by vacuum evaporation at 25 °C and the residue combined with H_2O (200 mL). The solution was neutralized with saturated $NaHCO_3$ solution, and a white solid was collected by filtration and vacuum-dried. The solid was redissolved in ligroin (200 mL), and the resulting solution was decanted from a brown sludge. The ligroin solution was concentrated (100 mL), cooled (−20 °C), and white crystals of 2,6-bis(chloromethyl)pyridine[9,10] formed upon standing: yield 25.3 g (80%); mp 76–77 °C (lit: 76 °C).[10] The solid may also be purified by vacuum sublimation (100 °C).

A solution of $KPPh_2$ (114 mmol) in THF (50 mL) was dripped (3 h) into a solution of 2,6-bis(chloromethyl)pyridine (10 g, 57 mmol) in THF (100 mL), and the yellow suspension was stirred overnight. The solid was removed by centrifugation and rinsed with CH_2Cl_2, and the combined organic solution was filtered. The filtrate was evaporated to dryness. The residue was dissolved in 95% EtOH (200 mL), the solution was cooled to 0 °C, and H_2O_2 (18.5 mL, 30%) was added dropwise with stirring at a rate that resulted in gentle reflux of the reaction mixture. The solution was stirred (1 h, 25 °C) and the solvent removed by vacuum evaporation. The residue was redissolved in $CHCl_3$ (100 mL) and extracted with H_2O (3 × 100 mL). The $CHCl_3$ fraction was dried (4-Å molecular sieves) and vacuum-evaporated. The residue was redissolved in $CHCl_3$ (100 mL), and the solution was added dropwise to well-stirred pentane (500 mL). The resulting tan solid was collected and washed with a minimum of acetone: yield 23.2 g (80%); mp 188–194 °C; soluble in $CHCl_3$, CH_2Cl_2, EtOH, and *i*-PrOH, slightly soluble in THF, and insoluble in Et_2O and hexane. Anal. Calcd for $C_{31}H_{27}NO_2P_2$: C, 73.37; H, 5.36; N, 2.76. Found: C, 70.28; H, 5.38; N, 2.79.

2,6-Bis((diphenylphosphino)methyl)pyridine *N,P,P*-Trioxide (5). A sample of **7** (5.0 g, 9.8 mmol) was dissolved in glacial acetic acid (25 mL) in air, and H_2O_2 (1.6 mL, 30%) was added dropwise to the stirred solution. The mixture was flushed with N_2 and refluxed (60 °C, 2 d), and the product mixture was concentrated by vacuum evaporation. The residue was redissolved in $CHCl_3$ (50 mL), and the solution was washed with H_2O (4 × 50 mL). The last two washes had neutral pH. The $CHCl_3$ solution was dried (4-Å molecular sieves) and $CHCl_3$ removed by vacuum evaporation, leaving a yellow solid (4.8 g). The solid was washed with

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[8] Characterization data: ^1H NMR ($CDCl_3$) δ 8.44 (m), 7.57 (t, J_{HH} = 7.8 Hz), 7.32 (d, J_{HH} = 7.8 Hz), 7.10 (m), 4.54 (s). These data agree with data in the literature: Jeromin, G. E.; Orth, W.; Rapp, B; Weiss, W. *Chem. Ber.* **1987**, *120*, 649.

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Table I. Crystallographic Data

	[Tb(**4**)$_4{}^{3+}$][$(NO_3)_3$-$(H_2O)(EtOH)^{3-}$]	[Pr(**4**)$_2(NO_3)_3$]·Et_2O·$^1/_2$MeOH	[Yb(**5**)$(NO_3)_3$]·MeOH	[Yb(**5**)$_2(NO_3)^{2+}$][$(NO_3)_2$-$(H_2O)_2(CH_3CN)_{2.5}{}^{2-}$]	[Th(**5**)$_2(NO_3)_2{}^{2+}$][$(NO_3)_2$-$(H_2O)_2{}^{2-}$]
formula	$C_{74}H_{72}N_7O_{19}P_4Tb$	$C_{40.5}H_{44}N_5O_{14.5}P_2Pr$	$C_{32}H_{31}N_4O_{13}P_2Yb$	$C_{67}H_{65.5}N_{7.5}O_{17}P_4Yb$	$C_{62}H_{54}N_6O_{20}P_4Th$
fw	1646.2	1035.7	914.6	1540.7	1559.0
a, Å	26.655(5)	11.021(5)	11.677(2)	14.328(3)	19.136(4)
b, Å	25.738(5)	11.802(2)	15.764(3)	16.033(3)	18.365(4)
c, Å	20.821(5)	18.560(4)	20.242(3)	17.001(3)	21.448(4)
α, deg		96.70(2)	90.0	99.27(3)	90.0
β, deg		95.84(3)	100.18(1)	101.92(3)	109.48(3)
γ, deg		108.55(3)	90.0	107.36(3)	90.0
V, Å^3	14 284(5)	2247.9(12)	3667.4(9)	3542(1)	7106(3)
Z	8	2	4	2	4
d_{calcd}, g cm^{-3}	1.531	1.530	1.656	1.445	1.457
space group	$Pbca$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
T, °C	20	20	20	20	25
μ, cm^{-1} (Mo Kα)	1.164	1.217	2.693	1.473	2.328
transm min/max	0.7473/0.8416	0.8407/0.9251	0.8297/0.9731	0.8006/0.9294	0.8978/0.9976
cryst dimens, mm	0.14 × 0.25 × 0.69	0.09 × 0.12 × 0.37	0.21 × 0.28 × 0.46	0.35 × 0.58 × 0.69	0.08 × 0.35 × 0.35
no. of reflcns	7068 ($F > 3\sigma(F)$)	4561 ($F > 2\sigma(F)$)	4860 ($F > 3\sigma(F)$)	10 711 ($F > 3\sigma(F)$)	3518 ($F > 4\sigma(F)$)
R, %	6.24	6.80	3.94	5.64	8.52
R_w, %	5.07	5.65	4.64	7.32	9.18
GOF	1.16	1.13	0.94	1.58	1.81

acetone (4 × 15 mL), leaving a white solid: yield 3.6 g (70%); no melting point below 240 °C. Anal. Calcd for $C_{31}H_{27}NO_3P_2$: C, 71.12; H, 5.20; N, 2.68. Found: C, 66.91; H, 4.98; N, 2.56.

Spectroscopic Characterization of the Ligands. 2-$[(C_6H_5)_2P(O)CH_2]C_5H_4N$ (6). Mass spectrum (70 eV) *m/e*, (fragment) [relative intensity]: 294 (M^+) [1], 293 ($M - 1^+$) [8], 216 ($M - Ph^+$) [5], 201 ($Ph_2P(O)^+$) [30], 92 ($C_6H_6N^+$) [10], 77 ($C_6H_5{}^+$) [45]. Infrared spectrum (KBr, cm^{-1}): 3049 (br, w), 3004 (w), 2947 (w), 2904 (w), 1584 (m), 1568 (m), 1477 (m), 1439 (s), 1431 (s), 1404 (m), 1237 (m), 1184 (s, br), 1165 (w), 1148 (w), 1122 (sh), 1119 (m), 1101 (m), 1070 (w), 994 (m), 837 (m), 826 (w), 791 (m), 751 (m), 719 (s), 695 (s), 599 (m), 529 (s), 502 (s). NMR spectra (27 °C): $^{31}P\{^1H\}$ ($CDCl_3$) δ 30.2; ^1H ($CDCl_3$) δ 3.88 (d, J = 14.2, 2H), 7.02 (m, 1H), 7.5–7.3 (m, 8H), 7.75–7.6 (m, 4H), 8.31 (d, J = 5 Hz, 1H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 40.7 (d, J = 64 Hz), 121.6 (d, J = 2.4 Hz), 124.8 (d, J = 3.5 Hz), 128.3 (d, J = 11.8 Hz), 130.9 (d, J = 9.5 Hz), 132.2 (d, J = 100.6 Hz), 131.6 (d, J = 2.8 Hz), 136.2 (d, J = 2.3 Hz), 149.1 (d, J = 1.4 Hz), 152.4 (d, J = 7 Hz).

2-$[(C_6H_5)_2P(O)CH_2]C_5H_4NO$ (4). Mass spectrum (30 eV) *m/e*, (fragment) [relative intensity]: 310 (M^+) [1], 309 ($M - 1^+$) [4], 232 $[M - 1 - Ph]^+$ [100], 201 ($Ph_2P(O)^+$) [50]. Infrared spectrum (KBr, cm^{-1}): 3059 (w), 3018 (w), 2988 (w), 2873 (m), 1490 (m), 1437 (s), 1397 (m), 1263 (w), 1229 (s), 1186 (s), 1124 (m), 858 (s), 830 (m), 793 (m), 774 (m), 742 (m), 694 (m), 611 (m), 564 (m), 542 (m), 528 (m), 504 (m), 489 (s), 472 (m), 447 (w), 422 (w). NMR spectra (27 °C): $^{31}P\{^1H\}$ ($CDCl_3$) δ 31.7; ^1H ($CDCl_3$) δ 4.22 (d, J = 14 Hz, 2H), 7.05 (t, J = 7.6 Hz, 1H), 7.13 (t, J = 7 Hz, 1H), 7.5–7.3 (m, 6H), 7.90–7.78 (m, 5H), 8.10 (d, J = 6.2 Hz, 1H). $^{13}C\{^1H\}$ ($CDCl_3$) δ 30.7 (d, J = 66 Hz), 124.2 (d, J = 2.2 Hz), 125.5 (d, J = 2.1 Hz), 127.7 (d, J = 4 Hz), 128.6 (d, J = 12.2 Hz), 130.8 (d, J = 10 Hz), 131.9 (d, J = 102 Hz), 132.1 (d, J = 2.9 Hz), 139.2, 144.0 (d, J = 5.5 Hz).

2,6-$[(C_6H_5)_2P(O)CH_2]_2C_5H_3N$ (7). Mass spectrum (70 eV) *m/e*, (fragment) [relative intensity]: 508 (M^+) [13] 507 ($M - 1^+$) [30], 201 (Ph_2PO^+) [70]. Infrared spectrum (KBr, cm^{-1}): 3050 (m), 2948 (w), 2895 (m), 1967 (w), 1904 (w), 1824 (w), 1714 (w), 1588 (m), 1571 (m), 1485 (w), 1451 (s), 1435 (s), 1398 (m), 1272 (m), 1228 (w), 1195 (s), 1119 (s), 1105 (sh), 1065 (w), 1022 (w), 995 (w), 939 (w), 829 (m), 819 (sh), 753 (s), 739 (sh), 726 (s), 716 (s), 693 (s), 590 (m), 550 (w), 530 (s), 507 (w), 483 (m), 470 (m). NMR spectra (27 °C): $^{31}P\{^1H\}$ ($CDCl_3$) δ 34; ^1H ($CDCl_3$) δ 3.70 (d, J = 14 Hz), 7.03 (d, J = 7.7), 7.2–7.7 (m); $^{13}C\{^1H\}$ ($CDCl_3$) δ 152.0, 136.8, 133.2, 133.0, 132.7, 131.2, 131.1, 128.5, 128.3, 122.9, 41.0, 40.0.

2,6-$[(C_6H_5)_2P(O)CH_2]_2C_5H_3NO$ (5). Mass spectrum (30 eV) *m/e*, (fragment) [relative intensity]: 523 (M^+) [4] 507 ($M - O^+$) [8], 201 (Ph_2PO^+) [100], 77 (Ph^+) [60]. Infrared spectrum (KBr, cm^{-1}): same as for **7** with additional bands at 1233 and 1150 cm^{-1}. NMR spectra (27 °C): $^{31}P\{^1H\}$ ($CDCl_3$) δ 31.3; ^1H ($CDCl_3$) δ 4.11 (d, J = 13.8 Hz, 4H), 6.94 (t, J = 8 Hz, 1H), 7.34–7.45 (m, 12H), 7.45 (d, J = 8 Hz, 2H), 7.70–7.80 (m, 8H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 31.45 (d, J = 67 Hz), 124.42, 125.79, 128.5 (d, J = 12 Hz), 130.7 (d, J = 9.9 Hz), 132 (d, J = 102 Hz), 132, 143 (d, J = 4.8 Hz).

Preparation of the Complexes. The 1:1 complexes were obtained from the combination of equimolar amounts (1 mmol) of metal nitrate (Pr, Tb, and Yb) in EtOH (25 mL) and **4** or **5** in 10 mL of EtOH/$CHCl_3$ (4:1). The mixtures were stirred (4 h) and evaporated to dryness, and the residues were collected. Complexes containing **4** were washed with diethyl ether (10 mL) and pentane (10 mL) and dried. The resulting crystalline solids were very hygroscopic. Complexes containing **5** were suspended in $CHCl_3$, the suspensions filtered, and the residues washed with ether. The 2:1 complexes of **4** and **5** with Pr, Gd, Tb, and Th were prepared in an identical fashion, except that 2-equiv amounts of ligand were employed. The 4:1 complexes of **4** with Pr, Tb, Yb, and Th were prepared from combinations of the metal nitrates with excess ligand (5:1) in EtOH. The solutions were evaporated, and the residues were washed with $CHCl_3$ (2 × 10 mL) and pentane (10 mL).

Characterization of the Complexes. The C, H, N elemental analysis data for the complexes show poor agreement with the anticipated compositions for *unsolvated* complexes of the general types $Ln(NO_3)_3$·L, $Ln(NO_3)_3$·2L, $Ln(NO_3)_3$·4L, $Th(NO_3)_4$·2L, and $Th(NO_3)_4$·4L. Subsequent single-crystal X-ray diffraction analyses reveal that the complexes are variably solvated. Attempts to fit the observed C, H, N data with potential solvate compositions are summarized in the supplementary material. The fits in some cases are not ideal; however, they are in general agreement with the proposed metal:ligand ratios. X-ray powder diffraction patterns for stoichiometrically related lanthanide complexes of **4** and **5** suggest that these complexes are isostructural. In addition, infrared spectra for related complexes are superimposable, and typical data are summarized below.

$M(NO_3)_3$·(**4**) (M = Pr, Tb, Yb) (KBr, cm^{-1}): 3400 (vs, br), 3081 (w, sh), 3059 (w), 3028 (w), 2971 (w), 1640 (m), 1438 (s, br), 1384 (s), 1321 (m), 1311 (sh), 1237 (m), 1158 (m), 1136 (w), 1120 (w), 1099 (w), 1037 (w), 875 (m), 819 (w), 796 (w), 754 (w), 724 (w), 715 (w), 694 (w), 614 (w), 576 (w), 546 (m), 500 (w), 466 (w).

$M(NO_3)_3$·(**4**) (M = Pr, Yb) (KBr, cm^{-1}): 3412 (w, br), 3123 (w), 3801 (w, sh), 3059 (w), 3028 (w), 2971 (w), 1491 (s), 1441 (m), 1383 (w), 1306 (s), 1231 (s), 1157 (s), 1138 (w, sh), 1125 (w, sh), 1099 (w, sh), 1030 (m), 997 (w), 874 (m), 816 (w), 799 (w), 748 (s), 723 (m), 692 (m), 615 (m), 579 (w), 544 (m), 525 (w), 507 (m), 488 (w, sh).

$M(NO_3)_3$·(**5**) (M = Pr, Tb, Yb) (KBr, cm^{-1}): 3061 (w), 2976 (w), 2924 (w), 1614 (w), 1591 (w), 1575 (w), 1486 (s, br), 1439 (m), 1385 (w), 1291 (w), 1278 (s), 1242 (m), 1215 (w), 1173 (w, sh), 1151 (m), 1123 (m), 1100 (w), 1073 (w), 1029 (m), 997 (m), 966 (w), 870 (s), 827 (m), 815 (m), 794 (w), 764 (w, sh), 746 (s), 724 (s), 699 (s), 692 (w, sh), 674 (w, sh), 640 (w, sh), 630 (m), 529 (w, sh), 529 (w, sh) 509 (s).

$M(NO_3)_3$·2(**5**) (M = Pr, Tb, Yb) (KBr, cm^{-1}): 3460 (m, br), 3078 (w), 3059 (w), 3025 (w), 2962 (w), 2822 (w), 1640 (w), 1489 (m), 1440 (s), 1384 (s), 1364 (sh), 1231 (s), 1158 (m), 1137 (w), 1124 (w), 1100 (w), 1072 (w), 998 (w), 874 (m), 822 (w), 779 (w), 751 (w), 723 (m), 694 (m), 614 (m), 574 (w), 545 (m), 526 (m), 507 (m), 487 (w).

$M(NO_3)_3$·4(**4**) (M = Pr, Tb, Yb) (KBr, cm^{-1}): 3056 (m), 2957 (m), 2908 (m), 1610 (w), 1589 (m), 1574 (m), 1486 (s), 1471 (s), 1437 (s), 1391 (m, sh), 1225 (s), 1212 (w, sh), 1168 (s), 1149 (w, sh), 1124 (s), 1102 (m, sh), 1071 (m, sh), 1027 (m), 997 (m), 970 (m), 860 (s), 829 (s), 755 (s), 726 (s), 694 (s), 633 (m), 562 (m), 506 (s).

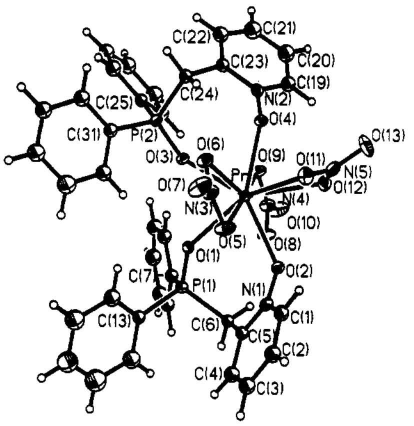
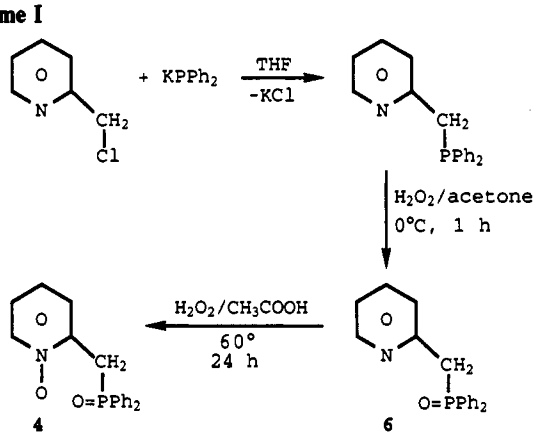


Figure 1. Molecular structure and atom-labeling scheme for $[Pr(\mathbf{4})_2(NO_3)_3]\cdot Et_2O\cdot {}^1/_2MeOH$ (25% ellipsoids; outer-sphere solvent molecules omitted).

Scheme I



$Th(NO_3)_4\cdot 2(\mathbf{5})$ (KBr, cm^{-1}): 3060 (m, br), 3057 (w), 2947 (w), 2920 (w), 2907 (w), 2857 (w), 1487 (m), 1439 (m), 1385 (s), 1337 (w), 1128 (s), 1090 (m), 1028 (m), 997 (w), 972 (w), 862 (m), 828 (m), 750 (m), 725 (m), 694 (m), 640 (w), 557 (w), 507 (m, br).

X-ray Diffraction Studies

Some crystals obtained as described above were unsuitable for crystallographic studies. Suitable crystals of $[Pr(\mathbf{4})_2(NO_3)_3]\cdot Et_2O\cdot {}^1/_2MeOH$ and $[Yb(\mathbf{5})(NO_3)_3]\cdot MeOH$ were obtained by dissolving the crude complexes in MeOH and allowing Et_2O to vapor-transfer slowly into the solution maintained in a closed vessel. Crystals of $[Yb(\mathbf{5})_2(NO_3)^{2+}][(NO_3)_2(H_2O)_2(CH_3CN)_{2.5}{}^{2-}]$ were obtained by dissolving the crude complex in CH_3CN and allowing Et_2O to vapor-transfer slowly into the solution. Crystals of $[Th(\mathbf{5})_2(NO_3)_2{}^{2+}][(NO_3)_2(H_2O)_2{}^{2-}]$ were obtained by slow vapor diffusion of pentane into a MeOH solution of the complex.

Single crystals of each complex lost solvent relatively quickly when handled in air; therefore, crystals were transferred as rapidly as possible from mother liquor to glass capillaries in a solvent-saturated glovebag. The loaded capillaries were sealed with a flame. Data for the thorium complex were collected by variable θ–2θ scans on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and using Mo Kα radiation. Data for the lanthanide complexes were collected by variable-speed ω scans on a Siemens R3m/V diffractometer similarly outfitted. Lattice and data collection parameters are summarized in Table I. All calculations were performed with SHELXTL PLUS (VMS version).[11] The structure of $[Yb(\mathbf{5})(NO_3)_3]\cdot MeOH$ was solved by using standard Patterson and difference Fourier methods, while the structure solutions for the remaining complexes were accomplished by using direct methods. Full-matrix least-squares refinements,[12] using appropriate neutral-atom scattering factors and anomalous scattering terms,[11] included anisotropic thermal parameters for all or most atoms heavier than hydrogen and corrections for secondary extinction. Data were corrected for absorption using an empirical method based on ψ scans. Some individual details of the refinement of each complex follow. $[Tb(\mathbf{4})_4{}^{3+}][(NO_3)_3(H_2O)(EtOH)^{3-}]$ was refined with all non-hydrogen atoms anisotropic and all hydrogen atoms included except those on the solvent molecules. The hydrogen atoms were placed in idealized positions with $U_{iso} = 1.25U_{eq}$ (riding model) of the parent atom. The crystals of $[Pr(\mathbf{4})_2(NO_3)_3]\cdot Et_2O\cdot {}^1/_2MeOH$ provided insufficient data to refine all non-hydrogen atoms anisotropically. Twenty-one atoms with $U_{iso} > 15$ Å^2 were refined anisotropically, and hydrogen atoms were added in idealized positions with $U_{iso} = 1.25U_{eq}$ of the parent atom. $[Yb(\mathbf{5})_2(NO_3)^{2+}][(NO_3)_2(H_2O)_2(CH_3CN)^{2-}]$ was refined with all non-hydrogen atoms anisotropic except for those atoms in a disordered nitrate ion and the acetonitrile N(5) atom. All hydrogen atoms, except those on water molecules (O(16) and O(17)), were added in idealized positions with $U_{iso} = 1.25U_{eq}$ of the parent atom. The occupancy factors on the nitrate oxygen atom positions O(15) and O(15′) refined to 0.592 and 0.408, respectively. $[Th(\mathbf{5})_2(NO_3)_2{}^{2+}][(NO_3)_2(H_2O)_2{}^{2-}]$ provided insufficient data for a full anisotropic refinement. The phenyl carbons were therefore treated isotropically, and the hydrogen distances were fixed in idealized positions. Atom coordinates are listed in Tables II–VI, and selected bond distances and angles are summarized in Table VII.

Results

Ligand Syntheses. Bifunctional 2-((diphenylphosphino)methyl)pyridine *N,P*-dioxide (**4**) is formed stepwise from the combination of $KPPh_2$ with 2-(chloromethyl)pyridine followed by exhaustive oxidation, as described in Scheme I. The first step produces a (phosphinomethyl)pyridine in high yield; however, this air-sensitive compound is not isolated and purified. Instead, the phosphine is immediately oxidized with hydrogen peroxide/acetone, and the resulting 2-((diphenylphosphino)methyl)pyridine *P*-oxide (**6**) is obtained in good yield as a tan solid. This compound is characterized by elemental analysis,[13] the appearance of a parent ion in the mass spectrum, an infrared band at 1184 cm^{-1} assigned to the phosphoryl stretching frequency,[14] a $^{31}P\{^1H\}$ resonance at δ 30.2,[15] and ^1H and $^{13}C\{^1H\}$ spectra consistent with the proposed structure.

As observed previously for phosphinopyridines,[4] N-oxidation of **6** requires forcing conditions provided here by heating **6** with H_2O_2/acetic acid at 60 °C. The desired bifunctional ligand **4** is isolated in good yield as a white crystalline solid that is characterized by elemental analysis[13] and the observation of a parent ion in the mass spectrum. An infrared spectrum displays strong stretching frequencies at 1229 and 1186 cm^{-1} that are tentatively assigned to ν_{NO}[16] and ν_{PO}, respectively. A $^{31}P\{^1H\}$ NMR spectrum shows a single resonance at δ 31.7, and the ^1H and $^{13}C\{^1H\}$ NMR spectra are closely comparable with the data for **6**.

The synthesis of the trifunctional ligand 2,6-bis((diphenylphosphino)methyl)pyridine *N,P,P′*-trioxide **5**, is also performed

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[11] Sheldrick, G. M. *Nicolet SHELXTL Operations Manual*; Nicolet XRD Corp.: Cupertino, CA, 1981. SHELXTL uses absorption, anomalous dispersion, and scattering factor data compiled in: *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1970; Vol. 4, pp 55–60, 99–101, 149–150. Anomalous-dispersion terms were included for all atoms with atomic numbers greater than 2.

[12] A general description of the least-squares algebra is found in: *Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970; p 187. The least-squares refinement minimizes $\sum w(|F_o| - |F_c|^2)$, where $w = 1/[\sigma(F)^2 + gF^2]$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_{wF} = [\sum(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$, and $GOF = [\sum w(|F_o| - |F_c|))^2/(NO - NV)]^{1/2}$ where NO = number of observations and NV = number of variables.

[13] The C, H, N analyses for **4**–**7** are typically low in carbon, and difficulty is encountered in achieving complete combustion. A similar observation was found during the characterizations of **1** and **3**.[4,5] Mass spectra for the compounds, however, provide confirmation of the assigned compositions.

[14] Phosphonates and phosphine oxides display a strong infrared P═O stretch in the region 1270–1150 cm^{-1}, and phenylphosphine oxide units typically appear at the low end of this range. The ν_{PO} for $[(C_6H_5)_2P(O)]C_5H_4N$ appears at 1185 cm^{-1}.

[15] The ^{31}P NMR shifts for organylphosphine oxides usually fall in a range δ 15–35, and the shifts for $[(C_6H_5)_2P(O)]C_5H_4N$ and $[(C_6H_5)_2P(O)]C_5H_4NO$ appear at δ 21.2 and 19.1, respectively.[4]

[16] The ν_{NO} for $[(C_6H_5)_2P(O)]C_5H_4NO$ was assigned to a band appearing at 1273 cm^{-1}. By comparison, ν_{NO} in pyridine *N*-oxide appears at 1250 cm^{-1}.[4]

Table II. Atomic Coordinates for $Pr\{2-[(C_6H_5)_2P(O)CH_2]C_5H_4NO\}_2(NO_3)_3 \cdot EtO_2 \cdot {}^1/_2MeOH$

	x	*y*	*z*
Pr	579(1)	1047(1)	-2349(1)
P(1)	296(3)	-1455(3)	-3835(1)
O(1)	381(6)	-894(6)	-3059(3)
O(2)	2131(6)	1512(6)	-3229(3)
N(1)	3008(7)	1034(7)	-3432(4)
C(1)	4227(10)	1521(10)	-3093(6)
C(2)	5173(11)	1121(10)	-3311(6)
C(3)	4864(11)	182(10)	-3899(6)
C(4)	3607(10)	-331(10)	-4240(6)
C(5)	2639(9)	107(9)	-4004(5)
C(6)	1264(8)	-398(8)	-4356(5)
C(7)	-1338(9)	-1958(9)	-4292(5)
C(8)	-1697(10)	-2433(9)	-5035(6)
C(9)	-2977(11)	-2842(10)	-5348(7)
C(10)	-3900(13)	-2835(11)	-4934(7)
C(11)	-3593(12)	-2402(11)	-4179(7)
C(12)	-2294(10)	-1952(10)	-3866(6)
C(13)	864(9)	-2706(9)	-3865(5)
C(14)	1175(12)	-3239(12)	-4494(7)
C(15)	1584(15)	-4247(15)	-4459(9)
C(16)	1734(13)	-4673(14)	-3830(8)
C(17)	1456(13)	-4150(13)	-3213(8)
C(18)	1044(11)	-3147(11)	-3232(6)
P(2)	-1854(3)	-953(2)	-1365(1)
O(3)	-1295(6)	-527(6)	-2032(3)
O(4)	-180(6)	2002(6)	-1343(3)
N(2)	-1329(8)	2021(7)	-1203(4)
C(19)	-1773(11)	2878(10)	-1442(6)
C(20)	-2915(12)	2969(12)	-1284(7)
C(21)	-3643(13)	2153(12)	-903(7)
C(22)	-3213(11)	1290(11)	-655(6)
C(23)	-2001(10)	1234(9)	-799(5)
C(24)	-1490(9)	265(8)	-603(5)
C(25)	-3600(9)	-1488(9)	-1547(5)
C(26)	-4345(11)	-2082(10)	-1054(6)
C(27)	-5665(11)	-2374(11)	-1165(6)
C(28)	-6240(13)	-2020(11)	-1740(7)
C(29)	-5529(13)	-1444(13)	-2235(8)
C(30)	-4190(11)	-1171(10)	-2134(6)
C(31)	-1254(9)	-2088(9)	-1066(5)
C(32)	-1497(10)	-2556(10)	-420(6)
C(33)	-1011(10)	-3458(10)	-248(6)
C(34)	-267(11)	-3853(11)	-681(6)
C(35)	13(12)	-3393(12)	-1307(7)
C(36)	-497(10)	-2515(10)	-1512(6)
N(3)	2501(10)	511(9)	-1256(5)
O(5)	2711(7)	608(8)	-1895(4)
O(6)	1371(7)	475(7)	-1123(3)
O(7)	3294(8)	446(9)	-774(4)
N(4)	-1427(9)	1306(8)	-3555(5)
O(8)	-405(7)	1144(7)	-3686(4)
O(9)	-1663(7)	1285(7)	-2903(4)
O(10)	-2156(8)	1473(9)	-4032(4)
N(5)	1801(9)	3705(10)	-1861(5)
O(11)	2307(7)	2986(7)	-1614(4)
O(12)	981(7)	3312(6)	-2442(4)
O(13)	2048(9)	4748(8)	-1533(5)
O(14)	3665(16)	5573(16)	2834(9)
C(37)	2174(31)	5775(31)	3469(18)
C(38)	2674(40)	5139(37)	3316(23)
C(39)	4202(30)	4717(31)	2659(18)
C(40)	5358(21)	4987(22)	2496(12)
O(15)	5619(21)	6228(20)	413(12)
C(41)	5000	5000	0

in a stepwise fashion. In this case, the 2,6-bis(chloromethyl)pyridine is not commercially available, and it was obtained from 2,6-pyridinedimethanol.[9,10] The air-sensitive intermediate 2,6-bis((diphenylphosphino)methyl)pyridine is not isolated. The overall synthesis is summarized in Scheme II. The second intermediate 2,6-bis((diphenylphosphino)methyl)pyridine *P,P'*-dioxide (**7**) is isolated in good yield as a tan solid.[13] The compound displays a parent ion in the mass spectrum, an infrared band at 1195 cm^{-1} assigned to ν_{PO}, and a single resonance in the ^{31}P NMR spectrum at δ 34. The trifunctional ligand **5** is obtained under forcing oxidative conditions in surprisingly good yield as a white solid. The compound is characterized by observation of a parent ion in the mass spectrum, infrared bands at 1233 and 1195 cm^{-1} assigned to ν_{NO} and ν_{PO}, respectively, and a single $^{31}P\{^1H\}$ NMR resonance appearing at δ 31.3.

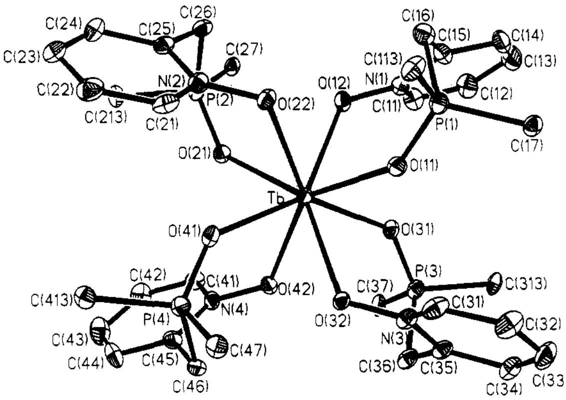

Figure 2. Molecular structure and atom-labeling scheme for $[Tb(\mathbf{4})_4{}^{3+}][(NO_3)_3(H_2O)(EtOH)^{3-}]$ (25% ellipsoids; NO_3^- ions and solvent molecules omitted).

The coordination chemistry of ligand **4** was studied with $Pr(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 6H_2O$, and $Yb(NO_3)_3 \cdot 5H_2O$ by utilizing ligand:metal stoichiometries of 1:1, 2:1, and 5:1. All attempts to obtain crystals of the 1:1 complexes of **4** suitable for X-ray structural analysis failed. The 2:1 mixtures, however, produce solvated crystalline solids,[17] and the molecular structure of one of these complexes, $[Pr(\mathbf{4})_2(NO_3)_3] \cdot Et_2O \cdot {}^1/_2$ MeOH, was determined. A view of the structure is shown in Figure 1. The structure determination confirms the 2:1 ligand:metal stoichiometry and reveals that the two ligands are bonded to the Pr(III) ion in a bidentate fashion. In this respect, the structure resembles that displayed by the complex $La(\{[(i\text{-}C_3H_7O)_2P(O)]C_5H_4NO\}_2)_2(NO_3)_3$.[5] The metals in both complexes are formally 10-coordinate, and the nitrate ions are bonded in an equatorial band about the central metal ion with the bidentate ligands positioned above and below the band. Further, no solvent molecules are present in the inner coordination sphere. The average Pr–O(P) and Pr–O(N) metal–ligand distances, 2.456 and 2.445 Å, are comparable to the La–O(P) and La–O(N) distances, 2.503(5) and 2.545(6) Å in $La(\mathbf{1})_2(NO_3)_3$ when the difference in ionic radii for La(III) and Pr(III) is considered. The average PrO═P and PrO—N distances, 1.500 and 1.327 Å, are similar to the respective LaO═P, 1.469(5) Å, and LaO—N, 1.318(8) Å, distances. The average Pr—O(nitrate) distance, 2.623 Å (range 2.690–2.587 Å), is also similar to the average La—O (nitrate) distance, 2.643(6) Å.

The excess ligand:metal combinations with ligand **4** resulted in the formation of solvated ML_4 complexes.[17] The molecular structure of one of these complexes, $[Tb(\mathbf{4})_4{}^{3+}][(NO_3)_3(H_2O)(EtOH)^{3-}]$, was determined,[18] and a view of the molecule is shown in Figure 2. The three nitrate ions are displaced to the outer coordination sphere along with the solvent molecules. The eight inner-sphere oxygen atoms form a coordination polyhedron,

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(17) Many of the complexes of **4** and **5** lose water or organic solvent when placed in a dry environment or when vacuum-evaporated. The 1:1 complexes of **4** rapidly deliquesce, while crystals of the other complexes form powders upon exposure to ambient air. In an attempt to obtain reliable elemental analysis data for the complexes, samples were subjected to an oil pump vacuum overnight prior to analysis. Even with this precaution, analytical data were variable. Single-crystal X-ray analyses indicate that the complexes retain water and/or organic solvent, and it is expected that analytical samples contained nonstoichiometric quantities of solvent. Experimental C, H, N analytical data are presented in the supplementary material, along with calculated values for unsolvated and solvated compositions.

(18) A data set was also collected for the complex $[Pr(\mathbf{4})_4{}^{3+}][(NO_3)_3(Et_2O)^{3}]$ and it was refined isotropically. The inner-sphere geometry is identical to that displayed by the Tb complex.

Table III. Atomic Coordinates for Tb{2-[$(C_6H_5)_2P(O)CH_2]C_5H_4NO\}_4(NO_3)_3 \cdot H_2O \cdot EtOH$

	x	*y*	*z*		*x*	*y*	*z*
Tb	536(1)	727(1)	7560(1)	C(35)	1785(3)	–124(3)	8021(4)
P(1)	1347(1)	1002(1)	6194(1)	C(36)	1368(3)	–434(3)	8309(4)
O(11)	1212(2)	830(2)	6859(3)	C(37)	440(3)	–991(3)	8082(4)
N(1)	295(3)	229(3)	6077(3)	C(38)	546(4)	–1381(3)	8527(4)
O(12)	145(2)	542(2)	6548(3)	C(39)	156(5)	–1680(4)	8771(5)
C(11)	85(3)	–255(4)	6045(5)	C(310)	–328(5)	–1598(5)	8559(6)
C(12)	225(4)	–594(4)	5575(5)	C(311)	–431(4)	–1224(4)	8114(6)
C(13)	567(5)	–445(5)	5120(5)	C(312)	–54(4)	–918(4)	7884(5)
C(14)	768(4)	47(4)	5156(4)	C(313)	1245(3)	–1067(3)	7185(5)
C(15)	621(3)	397(4)	5624(4)	C(314)	1550(4)	–1463(3)	7430(6)
C(16)	810(3)	934(4)	5672(4)	C(315)	1768(5)	–1814(5)	7012(7)
C(17)	1842(3)	590(3)	5885(4)	C(316)	1683(5)	–1782(5)	6347(7)
C(18)	1855(4)	86(4)	6097(5)	C(317)	1374(5)	–1399(5)	6114(6)
C(19)	2229(4)	–242(4)	5875(6)	C(318)	1165(4)	–1031(4)	6542(5)
C(110)	2583(4)	–76(5)	5460(6)	P(4)	762(1)	1441(1)	9019(1)
C(111)	2565(4)	413(5)	5252(6)	O(41)	555(2)	1366(2)	8358(3)
C(112)	2199(4)	765(5)	5456(6)	N(4)	10(3)	364(3)	8982(3)
C(113)	1543(3)	1675(3)	6165(5)	O(42)	325(2)	246(2)	8507(3)
C(114)	1639(4)	1925(4)	5596(5)	C(41)	–459(3)	162(3)	8962(4)
C(115)	1813(4)	2427(5)	5608(6)	C(42)	–797(4)	272(4)	9440(5)
C(116)	1859(4)	2693(4)	6177(8)	C(43)	–651(4)	581(4)	9943(5)
C(117)	1753(4)	2447(5)	6755(7)	C(44)	–171(4)	772(4)	9965(4)
C(118)	1598(3)	1942(4)	6740(5)	C(45)	162(4)	661(3)	9482(4)
P(2)	–770(1)	1070(1)	7293(1)	C(46)	699(3)	849(3)	9480(4)
O(21)	–343(2)	854(2)	7678(3)	C(47)	1417(3)	1622(4)	9038(4)
N(2)	172(3)	1960(3)	7253(3)	C(48)	1551(4)	2068(4)	8716(5)
O(22)	429(2)	1555(2)	7025(3)	C(49)	2044(4)	2230(5)	8683(6)
C(21)	420(3)	2332(3)	7586(4)	C(410)	2407(4)	1919(5)	8964(7)
C(22)	169(4)	2748(4)	7843(5)	C(411)	2273(4)	1488(5)	9299(7)
C(23)	–342(4)	2790(4)	7753(5)	C(412)	1780(4)	1328(4)	9333(5)
C(24)	–584(3)	2425(3)	7381(4)	C(413)	419(3)	1947(3)	9411(4)
C(25)	–329(3)	2005(3)	7134(2)	C(414)	–62(4)	2054(4)	9218(5)
C(26)	–567(3)	1578(3)	6758(4)	C(415)	–339(5)	2452(5)	9508(6)
C(27)	–1097(3)	588(3)	6832(4)	C(416)	–133(6)	2743(5)	9970(7)
C(28)	–1381(3)	737(4)	6298(4)	C(417)	356(5)	2637(4)	10175(6)
C(29)	–1662(4)	349(5)	5991(5)	C(418)	624(4)	2235(4)	9898(5)
C(210)	–1647(4)	–156(5)	6193(6)	N(5)	1571(4)	807(4)	1303(5)
C(211)	–1363(4)	–299(4)	6714(6)	O(51)	1416(3)	444(4)	1630(5)
C(212)	–1080(4)	77(4)	7036(5)	O(52)	1414(4)	875(4)	773(4)
C(213)	–1236(3)	1366(3)	7803(4)	O(53)	1890(4)	1080(4)	1538(6)
C(214)	–1659(3)	1604(3)	7554(6)	N(6)	1059(5)	1458(4)	3887(6)
C(215)	–2007(4)	1813(4)	7973(6)	O(61)	1170(3)	1674(3)	3375(5)
C(216)	–1949(5)	1778(5)	8612(7)	O(62)	637(5)	1326(5)	3994(7)
C(217)	–1534(5)	1545(5)	8878(6)	O(63)	1394(5)	1348(5)	4256(5)
C(218)	–1180(4)	1333(4)	8454(5)	N(7)	3622(5)	2300(6)	9429(7)
P(3)	927(1)	–624(1)	7706(1)	O(71)	3696(4)	1835(4)	9542(5)
O(31)	727(2)	–166(2)	7338(3)	O(72)	3490(4)	2588(5)	9858(5)
N(3)	1725(3)	395(3)	7960(3)	O(73)	3636(4)	2453(5)	8885(6)
O(32)	1297(2)	609(2)	8168(3)	O(81)	2085(3)	1501(4)	2759(4)
C(31)	2084(3)	702(4)	7725(4)	O(82)	3313(5)	1417(5)	4314(6)
C(32)	2516(3)	490(4)	7478(6)	C(81)	2855(12)	1495(10)	4104(14)
C(33)	2582(3)	–37(4)	7513(6)	C(82)	2376(13)	1365(12)	3884(16)
C(34)	2230(4)	–342(4)	7792(5)				

which is shown in Figure 3. The average Tb—O(P) distance, 2.363 Å (range 2.399–2.335 Å), and average Tb—O(N) distance, 2.406 Å (range 2.420–2.395 Å), are comparable to the distances in [$Pr(\mathbf{4})_2(NO_3)_3$]·Et_2O·$^1/_2$MeOH when corrected for expected ionic radii differences. The average P═O distance, 1.498 Å (range 1.503–1.495 (Å)), and the average N—O distance, 1.334 Å (range 1.337–1.332 Å), in the Tb(**4**)$_4$ complex are identical to the respective average distances in the [$Pr(\mathbf{4})_2(NO_3)_3$] complex: P—O, 1.500 Å, N—O, 1.327 Å.

With the trifunctional ligand **5**, ligand:lanthanide stoichiometries of 1:1 and 2:1 and a ligand:Th(IV) stoichiometry of 2:1 were examined.[17] The molecular structure of the 1:1 complex [$Yb(\mathbf{5})(NO_3)_3$]·MeOH was determined, and a view of the structure is shown in Figure 4. In this case, the nine-coordinate inner-sphere environment for Yb is provided by the oxygen atoms of one tridentate ligand and three bidentate nitrate groups. The average Yb—O(P) distance, 2.243 ± 0.009 Å, and the Yb—O(N) distance, 2.260(4) Å, are similar and comparable to the corresponding distances in [$Pr(\mathbf{4})_2(NO_3)_3$], taking into account the differences in Pr(III) and Yb(III) ionic radii. The average P═O distance, 1.504 Å, and the N—O distance, 1.333(7) Å, are also similar to the parameters in the [$Pr(\mathbf{4})_2(NO_3)_3$] complex. The average Yb—O (nitrate) distance is 2.435 Å.

The molecular structure determination (Figure 5) for the bis(ligand) complex [$Yb(\mathbf{5})_2(NO_3)^{2+}$][$(NO_3)_2(H_2O)_2(CH_3CN)_{2.5}{}^{2-}$] reveals that the two *N,P,P'*-trioxide donor ligands are bound to Yb(III) in a tridentate fashion, and only one bidentate nitrate ion contributes to the formation of the inner-sphere polyhedron (Figure 6). The average Yb—O(N) distance is 2.375 ± 0.004 Å, and this distance is significantly longer than the corresponding distance in [$Yb(\mathbf{5})(NO_3)_3$]·MeOH. The average Yb—O(P) distance, 2.245 ± 0.024 Å, on the other hand, is indistinguishable from the average distance in the 1:1 complex. It is interesting to note that each ligand has a long (2.269, 2.259 Å) and a short (2.222, 2.232 Å) Yb—O(P) distance, and the long Yb—O(P) bonds are approximately trans to the Yb—O(N) bonds. The average P═O distance, 1.493 Å, and average N—O distance, 1.348 Å, are comparable with the distances found in the 1:1 complex. The average Yb—O (nitrate) distance is 2.426 Å.

The molecular structure for [$Th(\mathbf{5})_2(NO_3)_2{}^{2+}$][$(NO_3)_2(H_2O)_2{}^{2-}$,

Table IV. Atomic Coordinates for $Yb\{2,6\text{-}[(C_6H_5)_2P(O)CH_2]_2C_5H_3NO\}(NO_3)_3 \cdot MeOH$

	x	*y*	*z*
Yb	1361(1)	839(1)	2119(1)
O(1)	1190(4)	−485(3)	1684(2)
N(1)	423(5)	−1109(3)	1691(3)
C(1)	617(6)	−1691(4)	2200(3)
C(2)	−112(7)	−2377(5)	2176(4)
C(3)	−1024(7)	−2483(5)	1652(4)
C(4)	−1229(7)	−1856(5)	1156(4)
C(5)	−487(6)	−1163(4)	1184(3)
C(6)	1558(6)	−1494(4)	2784(4)
C(7)	−670(6)	−474(4)	678(3)
C(8)	−339(6)	−1168(5)	3466(3)
C(9)	−1393(7)	−866(6)	3121(4)
C(10)	−2427(8)	−1272(7)	3168(5)
C(11)	−2426(9)	−1954(7)	3567(6)
C(12)	−1389(10)	−2266(7)	3917(5)
C(13)	−332(8)	−1884(5)	3876(5)
C(14)	1974(7)	−596(5)	4083(3)
C(15)	1687(12)	−9(9)	4514(6)
C(16)	2381(14)	118(11)	5130(7)
C(17)	3356(13)	−321(11)	5308(6)
C(18)	3588(17)	−907(14)	4892(10)
C(19)	2929(12)	−1027(11)	4259(7)
C(20)	−2648(6)	217(4)	1219(3)
C(21)	−2897(7)	575(5)	1802(4)
C(22)	−3962(9)	394(6)	1991(5)
C(23)	−4751(8)	−131(6)	1607(6)
C(24)	−4495(7)	−497(6)	1040(5)
C(25)	−3438(7)	−325(5)	843(4)
C(26)	−1552(6)	1210(4)	293(3)
C(27)	−2381(7)	1036(5)	−268(4)
C(28)	−2584(8)	1613(7)	−787(5)
C(29)	−2026(10)	2368(7)	−742(5)
C(30)	−1198(10)	2537(7)	−188(6)
C(31)	−936(8)	1960(5)	330(4)
P(1)	985(2)	−714(1)	3304(1)
O(2)	726(4)	113(3)	2942(2)
P(2)	−1281(1)	483(1)	984(1)
O(3)	−478(4)	869(3)	1574(2)
N(2)	3510(6)	724(5)	2998(3)
O(4)	3141(4)	126(3)	2602(3)
O(5)	2838(4)	1361(3)	2985(3)
O(6)	4459(5)	703(4)	3354(3)
N(3)	2597(6)	1307(4)	1026(3)
O(7)	3093(5)	1438(4)	1620(3)
O(8)	1621(5)	942(3)	963(3)
O(9)	3017(6)	1521(4)	540(3)
N(4)	620(5)	2492(4)	2365(4)
O(10)	1105(4)	2322(3)	1863(3)
O(11)	473(5)	1883(3)	2735(3)
O(12)	313(6)	3209(4)	2468(4)
O(13)	6241(18)	6536(14)	1410(11)
C(32)	5627(30)	7000(22)	797(20)
O(14)	6050(25)	7273(21)	1232(16)
C(33)	5682(47)	6490(31)	882(29)

shown in Figure 7, confirms that this complex contains two tridentate ligands and two bidentate nitrate ions bonded to Th(IV). The remaining two nitrate ions and water molecules appear in the outer coordination sphere. The average Th—O(N) distance, 2.395 Å, and average Th—O(P) distance, 2.380 Å, are normal, and the similarity in bond distances indicates that the ligands are symmetrically bonded to Th. The average ThO—N distance, 1.297 Å, is significantly shorter than the N—O distances in the lanthanide complexes, while the average ThO═P distance, 1.496 Å, is comparable to the P═O distances in the lanthanide complexes.

Discussion

In 1964, Michalski[19] briefly reported formation of **6** in a Michaelis–Becker reaction between 2-(chloromethyl)pyridine and $NaOPPh_2$, and Katritzky[20] subsequently presented the UV and ^1H NMR spectra for the compound. In 1968, Uhlig[21] described a synthesis of the phosphane precursor to **6**, 2-((diphenylphosphino)methyl)pyridine, from the reaction of 2-(chloromethyl)pyridine and $KPPh_2$. Although they noted that ether solutions of the phosphane were oxidized in air, the product of the oxidation was not isolated and characterized. By using samples of **6** prepared as described by Michaelis, Uhlig[22] found that the ligand, in combination with Ni(II) and Co(II), produced stable $M(L)_2X_2$ complexes. It was suggested that coordination was through six-membered chelate rings.

We have now extended the study of the metathetical reaction of $KPPh_2$ with chloromethylated pyridines, and the 2-((diphenylphosphino)methyl)pyridine **6** and 2,6-bis((diphenylphosphino)methyl)pyridine **7** have been obtained in good yields and fully characterized by spectroscopic methods. Although these ligands would be expected to display effective coordination properties, particularly toward transition metal ions, that chemistry has not yet been further developed. Instead, the oxidation chemistry of **6** and **7** has been studied. Reaction of **6** and **7** with peracetic acid at 60 °C results in N-oxidation with very little arene ring degradation. The *N*,*P*-dioxide **4** and *N*,*P*,*P*-trioxide **5** are obtained in high yields, and these new ligands have also been fully characterized. Higher reaction temperatures do lead to facile arene oxidation and decomposition.

It is immediately apparent from the coordination chemistry surveyed that **4** and **5**, in combination with Ln(III) and Th(IV) ions, display a wider range of metal:ligand stoichiometries than typically found with **1** or neutral (carbamoylmethyl)phosphonate bifunctional and trifunctional ligands. Further, by introduction of an "elbow" methylene group between the pyridine *N*-oxide and the phosphoryl group, the ligands are apparently sterically more flexible than **1**, and they are able to adopt a wider range of inner-sphere coordination geometries on the metals. Finally, the ligands are sufficiently basic that, under some conditions, they displace nitrate ion from the metal inner coordination sphere. Such inner-sphere anion displacement is found with some anionic chelating ligands; however, it is uncommon for *neutral* donor ligands.[23-26] Some additional features of each structure type are discussed below.

In combination with trivalent Ln(III) ions, ligand **4** forms solvated $Ln(\mathbf{4})_n(NO_3)_3$ complexes with $n = 2$ and 4. The complexes are obtained as crystalline solids variably solvated by water and/or organic donor solvents used in the preparations and recrystallizations of the complexes. Single-crystal X-ray structure analyses reveal that the solvent molecules are present only in the outer coordination sphere. After vacuum evaporation, the crystalline complexes become microcrystalline powders, and powder X-ray diffraction analyses indicate that complexes with the same metal:ligand stoichiometry are isostructural. The infrared spectra for the complexes are superimposable; however, unambiguous assignments of ν_{PO} and ν_{NO} and determination of coordination shifts from the free-ligand bands are not possible due to the complexity of the spectra in the region 1250–1000 cm^{-1}.

The crystallographic structure determinations for both 2:1 and 4:1 complexes of **4** unambiguously show that the ligand is bonded

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Table V. Atomic Coordinates for Yb{2,6-[$(C_6H_5)_2P(O)CH_2]_2C_5H_3NO\}_2(NO_3)_3\cdot 2H_2O\cdot 2.5CH_3CN$

	x	*y*	*z*		*x*	*y*	*z*
Yb	1110(1)	2687(1)	3046(1)	C(41)	3756(9)	230(11)	4639(8)
N(1)	77(4)	1170(4)	4118(3)	C(42)	4311(10)	920(14)	5305(8)
O(1)	642(3)	1402(3)	3596(3)	C(43)	4414(12)	1752(14)	5243(8)
C(1)	–942(5)	737(5)	3794(4)	C(44)	3937(7)	1944(8)	4515(6)
C(2)	–1529(6)	443(5)	4322(5)	C(45)	3702(5)	1722(5)	2318(5)
C(3)	–1086(6)	608(6)	5159(5)	C(46)	4254(6)	1155(6)	2161(5)
C(4)	–56(6)	1050(5)	5468(5)	C(47)	4857(7)	1292(8)	1648(6)
C(5)	535(5)	1333(5)	4936(4)	C(48)	4922(8)	1967(8)	1276(7)
C(6)	–1387(5)	623(5)	2903(4)	C(49)	4396(10)	2544(9)	1403(8)
P(1)	–1545(1)	1659(1)	2694(1)	C(50)	3793(7)	2428(6)	1920(6)
O(2)	–550(3)	2401(3)	2826(3)	C(38)	5(5)	1916(5)	463(4)
C(8)	–2322(5)	1374(5)	1645(4)	P(4)	705(2)	3090(1)	979(1)
C(9)	–3005(6)	534(6)	1255(5)	O(6)	1045(4)	3230(3)	1897(3)
C(10)	–3578(7)	359(8)	443(6)	C(51)	–150(6)	3674(5)	690(5)
C(11)	–3434(7)	1032(8)	37(5)	C(52)	–593(7)	3607(7)	–135(6)
C(12)	–2795(9)	1844(9)	418(7)	C(53)	–1288(8)	4027(7)	–338(7)
C(13)	–2195(6)	2040(7)	1225(6)	C(54)	–1524(9)	4527(7)	269(8)
C(14)	–2214(5)	2031(6)	3377(5)	C(55)	–1080(9)	4597(7)	1079(8)
C(15)	–3148(6)	1497(7)	3399(5)	C(56)	–396(7)	4172(6)	1313(6)
C(16)	–3656(7)	1812(9)	3921(6)	C(57)	1785(6)	3479(5)	591(5)
C(17)	–3218(9)	2686(10)	4427(7)	C(58)	1757(7)	3219(6)	–238(5)
C(18)	–2287(10)	3218(10)	4371(8)	C(59)	2616(8)	3562(7)	–498(6)
C(19)	–1768(8)	2904(8)	3857(6)	C(60)	3497(8)	4176(8)	59(8)
C(7)	1636(5)	1841(5)	5249(5)	C(61)	3520(8)	4420(8)	874(7)
P(2)	1908(1)	3023(1)	5287(1)	C(62)	2670(7)	4090(6)	1144(6)
O(3)	1643(4)	3184(3)	4444(3)	N(3)	1921(5)	4580(4)	3585(4)
C(20)	1180(6)	3426(5)	5899(5)	O(7)	991(4)	4169(3)	3424(3)
C(21)	676(8)	3970(7)	5580(6)	O(8)	2470(4)	4132(3)	3408(3)
C(22)	128(9)	4331(9)	6032(7)	O(9)	2319(6)	5383(4)	3929(5)
C(23)	32(8)	4098(8)	6766(8)	N(4)	315(8)	8459(7)	2187(6)
C(24)	526(9)	3559(7)	7073(6)	O(10)	813(7)	8669(6)	2911(4)
C(25)	1111(7)	3227(6)	6644(6)	O(11)	578(7)	8129(7)	1635(5)
C(26)	3230(6)	3592(6)	5818(5)	O(12)	–494(9)	8605(9)	2011(7)
C(27)	3692(7)	3391(8)	6500(6)	N(5)	5323(11)	9048(10)	2490(9)
C(28)	4678(8)	3807(10)	6914(7)	O(13)	6254(9)	9170(7)	2785(7)
C(29)	5227(9)	4493(11)	6655(8)	O(14)	4768(19)	8306(17)	2576(14)
C(30)	4796(10)	4739(12)	5987(8)	O(15)	5083(14)	9346(13)	1923(13)
C(31)	3786(9)	4285(9)	5543(7)	O(15′)	4839(21)	9414(19)	2723(17)
N(2)	858(4)	1123(4)	1298(3)	O(16)	7900(7)	8356(6)	2772(5)
O(4)	467(3)	1409(3)	1906(3)	O(17)	2758(7)	8898(6)	1815(6)
C(32)	1447(5)	613(5)	1444(4)	N(6)	6249(18)	4672(16)	1448(15)
C(33)	1772(6)	254(5)	809(5)	C(63)	6579(16)	4530(14)	2013(14)
C(34)	1556(6)	438(5)	51(5)	C(64)	6909(15)	4216(13)	2707(12)
C(35)	986(6)	994(5)	–74(5)	N(7)	4693(24)	6957(21)	787(18)
C(36)	631(5)	1334(5)	551(4)	C(65)	5471(21)	7547(19)	893(16)
C(37)	1755(5)	499(5)	2313(5)	C(66)	6267(19)	8164(17)	891(15)
P(3)	2809(1)	1502(1)	2918(1)	N(8)	2914	6287	2205
O(5)	2486(3)	2292(3)	3103(3)	N(8′)	2368	5918	2397
C(39)	3366(6)	1241(7)	3845(5)	C(67)	2665(14)	6778(14)	2684(12)
C(40)	3292(7)	377(8)	3902(6)	C(68)	2660(15)	7506(13)	3335(12)

to the Ln(III) ions in a bidentate manner, forming nonplanar seven-membered chelate rings. In the complex $[Pr(\mathbf{4})_2(NO_3)_3]\cdot Et_2O\cdot {}^1/_2MeOH$, the neutral ligand is a sufficiently strong base to completely displace inner-sphere water present in $Pr(NO_3)_3\cdot 6H_2O$; however, the three nitrate ions remain in the Pr(III) inner coordination sphere. This coordination condition is also found in complexes of ligands **1**, CMP, and CMPO with early (La–Eu) lanthanide ions.[4,5,23,24] On the other hand, CMP and CMPO complexes with smaller, later lanthanides retain a molecule of water in the inner coordination sphere, and the ligand amide C—O group hydrogen-bonds with coordinated water instead of binding to the metal. The inner-sphere geometry of $[Pr(\mathbf{4})_2(NO_3)_3]$ is irregular, and it does not fit into the conventional CN = 10 coordination polyhedra types. It is also interesting that the two ligands are arranged toward one side of the inner sphere so that there appear to be a hydrophobic (organic) side and a hydrophilic (inorganic) side in the molecule. This feature may be responsible for the ready solubility of these complexes in organic solvents.

An interesting consequence of the strong basicity of **4** is revealed when excess ligand is provided to Ln(III) ions. Complexes containing four bidentate ligands are isolated, and the molecular structure of $[Tb(\mathbf{4})_4{}^{3+}][(NO_3)_3(H_2O)(EtOH)^{3-}]$ shows that *all* of the water molecules and the nitrate ions are displaced from the inner coordination sphere. The bidentate ligands form a four-bladed propeller arrangement about the central Tb(III), and the resulting coordination polyhedron (Figure 3) is a square antiprism. A similar Ln(III) ion coordination condition has been observed with several other bidentate ligands;[25,26] however, in most cases the ligands are *anionic*. The neutral CMP and CMPO ligands have *not* been observed to form this type of complex, although tetramethylmalonamide is reported to form $LnL_4{}^{3+}$ complexes in the presence of the noncoordinating anion $PF_6{}^-$.[26,27]

In earlier studies, we found that trifunctional carbamoylbis(phosphonates) and bis(carbamoyl)phosphonates, despite their backbone flexibility, are usually unable to adopt a tridentate chelation geometry with a Ln(III) ion.[28–31] Instead, these ligands typically form bidentate chelates with two of the donor centers,

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Table VI. Atomic Coordinates for Th$\{2,6\text{-}[(C_6H_5)_2P(O)CH_2]_2C_5H_3NO\}_2(NO_3)_4\cdot2H_2O$

	x	*y*	*z*		*x*	*y*	*z*
Th(1)	4817(1)	2171(1)	2057(1)	C(16)	3172(19)	533(21)	2555(16)
P(1)	4375(5)	237(5)	2173(5)	C(17)	2461(24)	362(25)	2571(20)
P(2)	6118(4)	2464(4)	1105(5)	C(18)	2123(21)	−280(21)	2365(17)
P(3)	5446(5)	4073(5)	2485(5)	C(19)	2463(20)	−813(22)	2123(16)
P(4)	2821(5)	2067(5)	960(6)	C(20)	3173(19)	−624(20)	2051(16)
N(1)	5015(13)	953(14)	943(12)	C(21)	5083(15)	−371(17)	2657(15)
N(2)	3914(12)	3571(14)	1099(12)	C(22)	5174(19)	−1072(19)	2431(18)
N(7)	6229(18)	1343(19)	2823(22)	C(23)	5743(18)	−1533(21)	2852(17)
N(8)	4064(17)	2786(23)	2963(20)	C(24)	6133(19)	−1282(20)	3417(18)
O(1)	4566(11)	996(10)	2418(9)	C(25)	6092(20)	−624(21)	3662(19)
O(2)	5817(9)	2493(9)	1670(9)	C(26)	5524(20)	−160(20)	3264(18)
O(3)	5337(11)	3282(10)	2595(9)	C(27)	7407(15)	2046(15)	2038(15)
O(4)	3497(11)	1943(10)	1539(11)	C(28)	8146(19)	1817(18)	2269(19)
O(5)	4616(10)	1461(11)	1079(10)	C(29)	8494(18)	1725(17)	1862(17)
O(6)	4407(11)	3062(10)	1191(11)	C(30)	8207(17)	1778(16)	1215(16)
O(7)	5912(17)	1144(15)	2249(16)	C(31)	7446(16)	1991(15)	963(16)
O(7a)	6765(14)	1040(14)	3206(13)	C(32)	7054(15)	2151(18)	1372(15)
O(7b)	5947(12)	1864(12)	3031(12)	C(33)	6148(16)	3352(16)	761(14)
O(8)	3901(13)	3051(14)	2412(13)	C(34)	6723(18)	3788(18)	1086(16)
O(8a)	3837(17)	3022(15)	3387(15)	C(35)	6762(19)	4497(19)	891(16)
O(8b)	4512(15)	2253(14)	3103(12)	C(36)	6198(21)	4728(24)	331(19)
N(11)	3800(24)	7858(36)	1089(30)	C(38)	5589(21)	3579(21)	244(17)
O(11)	3702(22)	7380(24)	646(20)	C(39)	5106(16)	4621(16)	3008(17)
O(12)	3944(23)	7622(29)	1625(17)	C(40)	4923(16)	5358(18)	2870(17)
O(13)	3744(18)	8443(16)	756(15)	C(41)	4706(18)	5751(21)	3314(17)
N(23)	5966(30)	7585(30)	943(26)	C(42)	4671(22)	5407(25)	3865(22)
O(21)	6061(23)	6952(20)	899(19)	C(43)	4882(22)	4707(25)	4029(22)
O(22)	6115(19)	8023(21)	564(16)	C(44)	5095(18)	4306(22)	3587(18)
O(23)	5632(24)	7820(23)	1251(18)	C(45)	6407(16)	4236(17)	2630(14)
O(1w)	5011(17)	6329(15)	1617(12)	c(46)	6906(18)	3687(20)	2867(15)
O(2w)	1459(41)	6326(49)	567(17)	C(47)	7638(20)	3790(20)	2943(15)
C(1)	4250(16)	114(17)	1300(14)	C(48)	7862(19)	4439(19)	2798(16)
C(2)	5575(16)	1891(14)	434(14)	C(49)	7364(21)	5036(22)	2589(17)
C(3)	4987(13)	4347(14)	1632(12)	C(50)	6641(17)	4924(17)	2520(14)
C(4)	2973(18)	2768(17)	437(15)	C(51)	2078(20)	2356(20)	1233(20)
C(5)	4893(16)	226(18)	1077(14)	C(52)	2197(25)	2340(22)	1861(22)
C(6)	5316(16)	−298(18)	931(14)	C(53)	1621(32)	2502(29)	2148(33)
C(7)	5875(18)	−179(19)	702(15)	C(54)	1054(28)	2739(26)	1663(25)
C(8)	5973(16)	561(16)	540(14)	C(55)	832(30)	2761(26)	1032(26)
C(9)	5526(18)	1115(17)	659(15)	C(56)	1415(26)	2523(24)	733(27)
C(10)	3208(20)	3478(20)	761(16)	C(57)	2506(15)	1274(15)	459(15)
C(11)	2710(20)	4024(20)	645(17)	C(58)	2568(16)	1175(17)	−155(16)
C(12)	2925(20)	4697(21)	931(16)	C(59)	2363(19)	541(21)	−507(20)
C(13)	3667(17)	4849(18)	1265(14)	C(60)	2042(20)	4(22)	−221(19)
C(14)	4173(17)	4265(17)	1367(15)	C(61)	1985(18)	87(20)	380(17)
C(15)	3509(16)	30(17)	2268(15)	C(62)	2207(16)	749(17)	740(16)

Table VII. Selected Bond Distances (Å)

Dist	$[Pr(\mathbf{4})_2(NO_3)_3]\cdot Et_2OH\cdot{}^1/_2MeOH$	$[Tb(\mathbf{4})_4][(NO_3)_3\text{-}(H_2O)(EtOH)^{3-}]$	$[Yb(\mathbf{5})(NO_3)_3]\cdot MeOH$	$[Yb(\mathbf{5})_2(NO_3)^{2+}]\text{-}[(NO_3)_2(H_2O)_2(CH_3CN)_{2.5}{}^{2-}]$	$[Th(\mathbf{5})_2(NO_3)_2{}^{2+}]\text{-}[(NO_3)_2(H_2O)_2{}^{2-}]$
M—O(P)	2.439(6) 2.474(6)	2.335(5) 2.379(5) 2.399(5) 2.338(5)	2.252(5) 2.235(4)	2.222(5) 2.269(5) 2.232(6) 2.259(6)	2.394(1) 2.398(1) 2.386(1) 2.431(1)
M—O(N)	2.465(7) 2.426(7)	2.398(6) 2.420(6) 2.411(6) 2.395(6)	2.260(4)	2.372(5) 2.379(4)	2.391(1) 2.400(1)
P=O	1.495(6) 1.506(7)	1.496(6) 1.499(6) 1.503(6) 1.495(6)	1.500(5) 1.509(4)	1.506(5) 1.488(6) 1.484(6) 1.494(5)	1.491(1) 1.509(1) 1.500(1) 1.484(1)
N—O	1.329(12) 1.325(11)	1.332(9) 1.335(9) 1.337(9) 1.332(9)	1.333(7)	1.343(8) 1.353(8)	1.297(1) 1.296(1)

and the third base site remains uncoordinated, or it serves to bridge to another metal center. In addition, all of the nitrate ions remain in the inner coordination sphere of the metal ion. Finally, survey extraction measurements indicate that these ligands produce only small distribution values (*D*).

In the present study, we observe that the trifunctional ligand, **5**, adopts a *tridentate* binding mode in both 1:1 and 2:1 complexes. In the 1:1 complex, $[Yb(\mathbf{5})(NO_3)_3](MeOH)$, **5** displaces all the water from the inner coordination sphere, and the resulting coordination polyhedron (CN = 9) can be described either as an irregular, monocapped, square antiprism (capping atom = O(11)) or as a tricapped prism. In either case, it is clear that the tridentate ligand defines a triangular face, for which the nonbonded PO(2)···O(3)P distance is 3.11 Å. Unlike the NO(1)···O(2)P and NO(1)···O(3)P nonbonding distances (average 2.863 ± 0.008 Å), the PO(2)···O(3)P distance is significantly larger than the

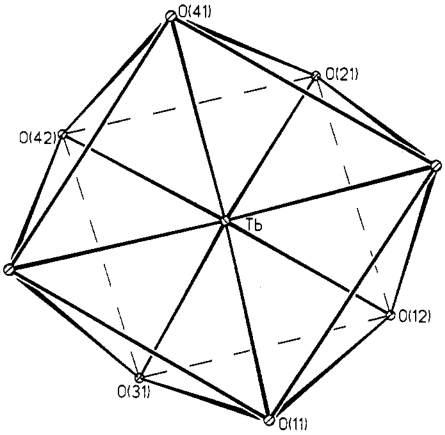


Figure 3. Coordination polyhedron for $[\mathrm{Tb}(\mathbf{4})_4{}^{3+}][(\mathrm{NO_3})_3(\mathrm{H_2O})(\mathrm{EtOH})^{3-}]$.

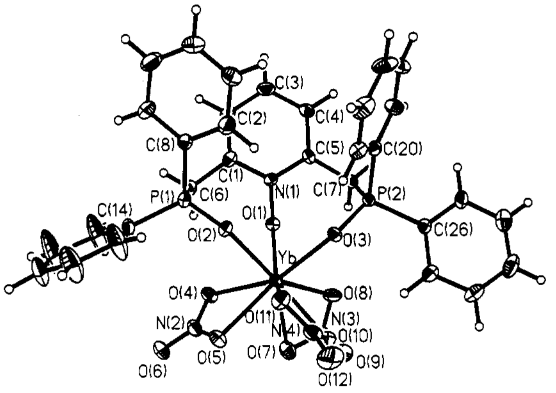
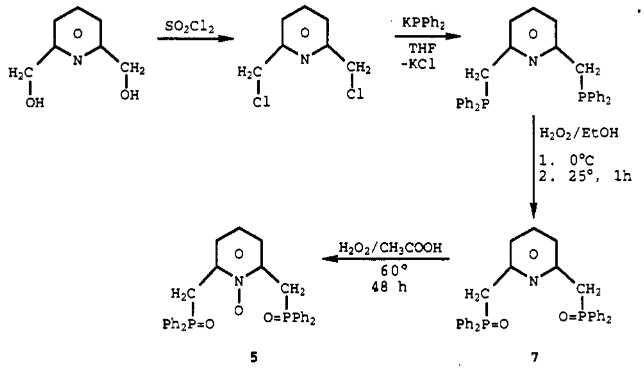


Figure 4. Molecular structure and atom-labeling scheme for $[\mathrm{Yb}(\mathbf{5})(\mathrm{NO_3})_3]\cdot\mathrm{MeOH}$ (25% ellipsoids; solvent molecule omitted).

Scheme II



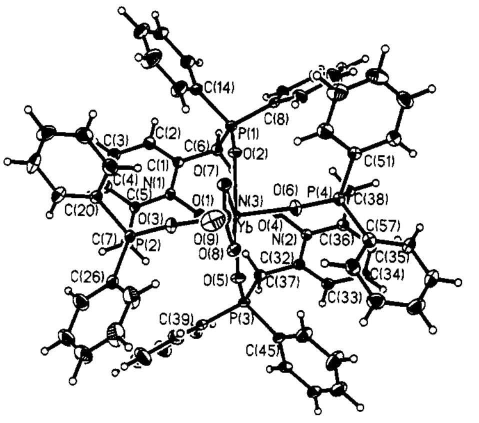


Figure 5. Molecular structure and atom-labeling scheme for $[\mathrm{Yb}(\mathbf{5})_2(\mathrm{NO_3})^{2+}][(\mathrm{NO_3})_2(\mathrm{H_2O})_2(\mathrm{CH_3CN})_{2.5}{}^{2-}]$ (25% ellipsoids; solvent molecules and two outer-sphere nitrate ions omitted).

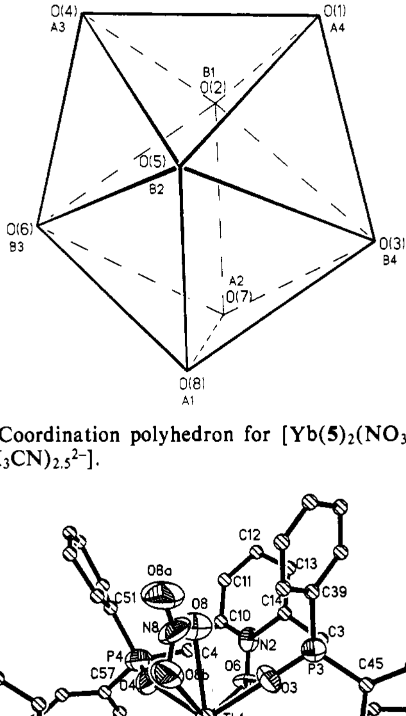


Figure 6. Coordination polyhedron for $[\mathrm{Yb}(\mathbf{5})_2(\mathrm{NO_3})^{2+}][(\mathrm{NO_3})_2(\mathrm{H_2O})_2(\mathrm{CH_3CN})_{2.5}{}^{2-}]$.

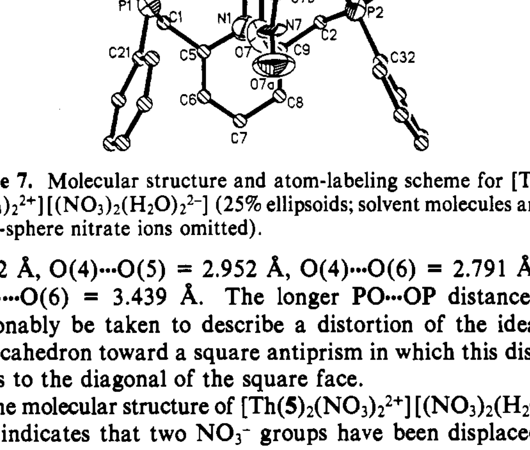


Figure 7. Molecular structure and atom-labeling scheme for $[\mathrm{Th}(\mathbf{5})_2(\mathrm{NO_3})_2{}^{2+}][(\mathrm{NO_3})_2(\mathrm{H_2O})_2{}^{2-}]$ (25% ellipsoids; solvent molecules and two outer-sphere nitrate ions omitted).

van der Waals contact distance, ~2.8Å. Molecular modeling (vide infra) suggests that PO···OP distances of less than ~3.1 Å may not be energetically accessible for the ligand in this overall conformation.

In the 2:1 complex, $[\mathrm{Yb}(\mathbf{5})_2(\mathrm{NO_3})^{2+}][(\mathrm{NO_3})_2(\mathrm{H_2O})_2(\mathrm{CH_3CN})_{2.5}{}^{2-}]$, the ligands succeed at displacing two nitrate ions and all solvent molecules from the inner coordination sphere. As illustrated in Figure 6, the coordination polyhedron can be idealized to a dodecahedron with triangular faces in which the ligand donor atoms occupy B(1)–B(4)–A(4) and B(2)–B(3)–A(3) positions, while the A(1)–A(2) positions are occupied by the oxygen atoms of the inner-sphere, bidentate nitrate group.[32] The intraligand O···O distances are more irregular than the similarly defined coordination triangle in $[\mathrm{Yb}(\mathbf{5})(\mathrm{NO_3})_3]\cdot\mathrm{MeOH}$: O(1)···O(2) = 2.929 Å, O(1)···O(3) = 2.770 Å, O(2)···O(3) = 3.462 Å, O(4)···O(5) = 2.952 Å, O(4)···O(6) = 2.791 Å, and O(5)···O(6) = 3.439 Å. The longer PO···OP distances can reasonably be taken to describe a distortion of the idealized dodecahedron toward a square antiprism in which this distance maps to the diagonal of the square face.

The molecular structure of $[\mathrm{Th}(\mathbf{5})_2(\mathrm{NO_3})_2{}^{2+}][(\mathrm{NO_3})_2(\mathrm{H_2O})_2{}^{2-}]$ also indicates that two NO_3^- groups have been displaced and inner-sphere water molecules have been completely removed. The inner coordination polyhedron (Figure 8) can best be viewed as a bicapped, square antiprism for which the vertices of the squares are occupied by the O atoms from **5** and an oxygen atom from each nitrate group. The coordinated NO_3^- groups have a distinctly asymmetric bite that allows one oxygen atom on each bonded

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[32] The letter scheme for the vertices of a dodecahedron is that enumerated in the literature: Kepert, D. L. *Inorganic Stereochemistry*; Springer Verlag: Berlin, 1982.

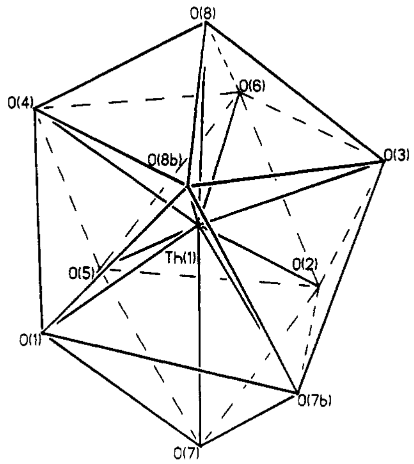

Figure 8. Coordination polyhedron for $[Th(5)_2(NO_3)_2^{2+}][(NO_3)_2(H_2O)_2^{2-}]$.

nitrate group to occupy a capping position. The intraligand distances between the three oxygen atoms that occupy three of the four vertices of the squares forming the antiprism core are O(2)···O(5) = 2.922 Å, O(1)···O(5) = 3.028 Å, O(1)···O(2) = 4.292 Å, O(3)···O(6) = 2.971 Å, O(4)···O(6) = 2.946 Å, and O(3)···O(4) = 4.273 Å. In this view, the PO···OP distances form the diagonal of the square faces and are indeed related to the edges by approximately the square root of 2.

It is interesting to note that the general conformation of ligand **5** is the same for the three structures reported here. In all cases, there exists an approximate mirror plane perpendicular to the pyridine ring that relates the two $-CH_2P(O)Ph_2$ coordination arms, and the conformational relationship about all heavy-atom bonds in the ligand are similar. However, the intraligand nonbonded PO···OP distances vary considerably: $[Yb(5)(NO_3)_3](MeOH)$, 3.113 Å; $[Yb(5)_2(NO_3)^{2+}][(NO_3)_2(H_2O)_2(CH_3CN)_{2.5}^{2-}]$, 3.462 and 3.439 Å; $[Th(5)_2(NO_3)_2^{2+}][(NO_3)(H_2O)_2^{2-}]$, 4.292 and 4.273 Å. Clearly, **5** is capable of binding to triangular faces of common f-element ion coordination polyhedra, and it apparently can accommodate a relatively wide range of edge lengths.

In order to estimate the differences in ligand steric energies over the range of PO···OP nonbonded distances found in the observed structures containing **5** and to approximate the shape of the potential function, we have completed a set of molecular mechanics calculations on **5** by using the CAChe system (version 2.8). The standard full potential function and Newton–Ralfson minimization were used in all cases, with the N–O and P–O distances constrained to values typical of those determined from the crystal structures.

Two sets of starting ligand coordination arm conformations, fixed by the dihedral angle[33] about each of the P–C vectors, were used to define the starting structures. The values chosen for the dihedral angles were 60° and –60° for one set of starting structures and 40° and –40° for the second set of starting structures. These most closely correspond to the values observed in the crystal structure determinations. For each dihedral angle, the nonbonded PO···OP distances were then initially set at values between 3 and 5 Å, and the entire molecule was allowed to relax to minimum-energy configurations. For each dihedral angle condition, a local minimum was found. The calculations indicate that the potential function, in regions near the observed ligand conformations, is relatively flat and contains multiple local minima which differ in energy by less than ~2 kcal/mol but which exhibit significant structural differences. It appears that PO···OP distances up to ~4.7Å are energetically feasible, but those shorter than ~3.1 Å can be achieved only at the expense of significant intraligand strain energy. The small difference in energy across the observed span of OP···OP distances leads us to suggest that the differences in the observed structures can be rationalized on the basis of inner-sphere coordination requirements (some of which are mentioned above) or other packing considerations.

The unique complexing ability of ligands **4** and **5** suggests that they may be unusually effective solvent extraction agents. Indeed, initial studies confirm this proposal,[34] and extensive examination of the liquid–liquid extraction behavior is in progress. In addition, syntheses for additional polyfunctional phosphinopyridine *N,P*-oxides are under study.

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Supplementary Material Available: Tables SI–SVI, listing analytical data, X-ray data collection parameters, thermal parameters, hydrogen atom coordinates, and bond distances and angles (69 pages). Ordering information is given on any current masthead page.

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(33) The dihedral angle on each methylphosphonate arm is defined by the bond vectors $O \leftarrow P \rightarrow C(H)_2$ and $P \leftarrow C(H)_2 \rightarrow C$ (ring).

(34) Smith, B. F. Unpublished results.