Inorganic Chemistry

Synthesis and Coordination Properties of 1-(Diphenylphosphine oxide)-1-(2′-pyridyl *N*-oxide)-3-(diphenylphosphine oxide)propane

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Received August 14, 2001

Introduction

The neutral bifunctional ligands (carbamoylmethyl)phosphonates (CMPs) and (carbamoylmethyl)phosphine oxides (CMPOs) coordinate effectively to trivalent and tetravalent f-block element cations even when in competition with high concentrations of mineral acids.[1–3] This property makes these ligands practical as analytical and process scale liquid−liquid extraction (LLE) reagents in nuclear materials separations.[1–4] This includes the development of the commercially useful TRUEX process.[1–5] Until recently, only CMP and CMPO ligands were known to display increased distribution ratios, $K_D = [M]_{org}/[M]_{aq}$, with increasing HCl or HNO$_3$ concentration above 1 M. Our group has been attempting to design and synthesize additional ligand classes with this performance capability. Using known and evolving fundamental coordination principles for f-block element cations, we have developed a new family of chelates that include phosphinopyridine *N,P*-dioxides (NOPOs), (phosphinomethyl)pyridine *N,P*-dioxides (MNOPOs), and bis(phosphinomethyl)-pyridine *N,P,P′*-trioxides (DMNOPOPOs).[6–14] On the basis
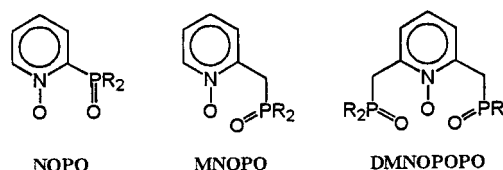
of coordination principles deduced for d-block metal ions,[15,16] it would be expected that NOPO ligands would produce more stable complexes with M(III) and M(IV) ions since this ligand would provide six-membered chelate ring structures. In fact, it appears that MNOPO complexes that display seven-membered chelate rings have superior stability compared to NOPO complexes.

The success of an LLE process depends on more than just the strength of the interaction between the metal ion and organic ligand. For example, it has also been observed that the extraction of Eu(III) and Am(III) in HNO$_3$ solutions is enhanced, at high acid concentrations, by addition of tributyl phosphate (TBP) to CMP or CMPO in an aliphatic diluent.[1,5,17,18] It has been suggested that the TBP acts not as a ligand but as an organic-phase modifier by enhancing the effective polarity of the organic-phase diluent. The parallel observations with NOPO and MNOPO have not yet been

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made since aliphatic-soluble derivatives have only recently been prepared[19] and extraction measurements have not yet been started. Nonetheless, successful use of TBP as a phase modifier in the CMPO/TRUEX LLE system suggests that it would be interesting to attempt to combine chelate ligation and phase modification properties in a single reagent.

In this paper, we report the formation and chelation behavior of an interesting new derivative in the MNOPO family, 1-(diphenylphosphine oxide)-1-(2′-pyridyl *N*-oxide)-3-(diphenylphosphine oxide)propane (**1**). Subsequent ques-

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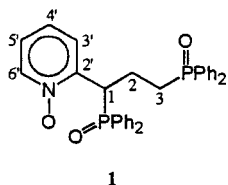
tions that should be addressed include the following: (a) Will this ligand form stable seven-membered chelate complexes with lanthanide(III) (Ln(III)) ions? (b) Can the pendant diphenylphosphine oxide arm serve as an intramolecular phase modifier in an LLE process? The first question is addressed in this paper, and the second will be the subject of future LLE studies.

Experimental Section

General Information. The organic reagents used in the syntheses were purchased from Aldrich Chemical Co. Organic solvents were purchased from VWR and either used as received or dried by standard procedures as required. The lanthanide nitrate salts were purchased from Ventron. Infrared spectra were recorded on a Mattson 2020 FTIR spectrometer (4 cm^{-1} resolution), and NMR spectra were obtained on Bruker FX-250 and JEOL GSX-400 NMR spectrometers with chemical shift standards: ^{1}H, ^{13}C (Me$_4$Si), ^{31}P (85% H$_3$PO$_4$). All downfield shifts from the reference were designated as $+\delta$. Mass spectra were obtained at the Midwest Center for Mass Spectrometry, University of Nebraska. Elemental analyses were acquired from Galbraith Laboratories.

Ligand Synthesis. A sample of 2-[(diphenylphosphino)methyl)]-pyridine[10] (1.00 g, 3.41 mmol) and diphenylvinylphosphine oxide[20] (0.817 g, 3.58 mmol) were combined in dry tetrahydrofuran (THF, 30 mL) under dry nitrogen. The contents of the flask were cooled in an ice bath (15 min), and BuLi (0.5 mL, 0.92 M in hexane) solution was added dropwise from an airtight syringe. The mixture was stirred at ice temperature (3 h) and then overnight at room temperature. The solvent was removed with a rotary evaporator and the residue dissolved in ^{i}PrOH (15 mL). A white solid was recovered after addition of aqueous HCl solution (30 mL, 2 M). The subsequent workup can be accomplished in air. The mixture was chilled and filtered and the solid rinsed with pentane. The solid was then slurried with CHCl$_3$ (50 mL) and aqueous Na$_2$CO$_3$ solution (25 mL, 0.25 M) and transferred to a separatory funnel. After mixing, the aqueous phase was removed and the organic phase contacted with additional Na$_2$CO$_3$ solution (25 mL, 0.25 M). The

resulting combined chloroform phases were evaporated, leaving a white solid (**2**). Yield: 0.63 g (35%). Mp: 189−193 °C. Anal. Calcd for C$_{32}$H$_{29}$N$_4$O$_2$P$_2$: C, 73.70; H, 5.60; N, 2.69. Found: C, 73.21; H, 5.64; N, 2.55. IR (KBr, cm^{-1}): 1190 (ν_{PO}), 1175 (ν_{PO}). FAB-MS: *m/e* (fragment) 522 (M + 1$^+$), 201 (Ph$_2$P(O)$^+$). NMR (23 °C): ^{31}P{^{1}H} (CDCl$_3$) δ 32.7; ^{1}H (CDCl$_3$) δ 2.10−2.57 (m, H$_{2,3}$, 4H), 4.05 (m, H$_1$, 1H), 7.00 (m, H$_{5'}$, 1H), 7.17−7.56 (m, phenyl, 20H), 7.75−7.83 (m, 2H), 8.37 (m, H$_{6'}$, 1H); ^{13}C{^{1}H} δ 21.7 (C$_2$), 27.5 (dd, C$_3$, $^1J_{PC}$ = 71.0 Hz, $^3J_{PC}$ = 12.0 Hz), 49.5 (dd, C$_1$, $^1J_{PC}$ = 64.8 Hz, $^3J_{PC}$ = 11.9 Hz), 122.0 (C$_{5'}$), 124.3 (C$_{3'}$), 136.4 (C$_{4'}$), 149.0 (C$_{6'}$), 155.9 (C$_{2'}$), 127.9−133.8 (phenyl).

A sample of **2** (2.048 g, 3.93 mmol) dissolved in glacial acetic acid (10 mL) was combined with hydrogen peroxide (2 mL, 30%, 17.6 mmol), and the solution was stirred in a closed flask (23 °C). After 2 days an additional portion (2 mL) of H$_2$O$_2$ was added and stirred (1 day). The resulting mixture was evaporated, the solid treated with water (10 mL), and the resulting mixture evaporated. The resulting yellow residue was treated with CHCl$_3$ (30 mL) and extracted with saturated aqueous Na$_2$CO$_3$ (2 × 25 mL). The separated aqueous phase was then extracted with fresh CHCl$_3$ (10 mL), and the CHCl$_3$ phases were combined and treated with distilled water (25 mL). The separated water phase was extracted with CHCl$_3$, and all of the CHCl$_3$ phases were combined. This cycling is required since the CHCl$_3$ solution of **1** has a small solubility in water. The CHCl$_3$ phase was evaporated to dryness and recrystallized from CHCl$_3$/pentane as a white solid (**1**). Yield: 1.89 g (89.5%). Mp: 214−216 °C. Anal. Calcd for C$_{32}$H$_{29}$NO$_3$P$_2$: C, 71.50; H, 5.44; N, 2.61. Found: C, 70.42 H, 5.67 N, 2.47. IR (KBr, cm^{-1}): 1231 (ν_{NO}), 1198 (ν_{PO}), 1181 (ν_{PO}). FAB-MS: *m/e* (fragment): 538 (M + 1$^+$). HRMS calcd for ^{12}C$_{32}$H$_{30}$^{14}N^{16}O$_3$^{31}P$_2$ 538.1701, found 538.1713. NMR (23 °C): ^{31}P{^{1}H} (CDCl$_3$) δ 36.7, 36.8; ^{1}H (CD$_3$OD) δ 2.04−2.43 (m, H$_{2,3}$, 4H), 5.32 (m, H$_1$, 1H), 7.19−7.81 (aromatic, 24H), 8.08 (d, J = 6.4 Hz, H$_{6'}$, 1H); ^{13}C-{^{1}H} (CDCl$_3$) δ 22.8 (C$_2$), 28.0 (dd, C$_3$, $^1J_{PC}$ = 71.0 Hz, $^3J_{PC}$ = 11.9 Hz), 39.1 (dd, C$_1$, $^1J_{PC}$ = 66.7 Hz, $^3J_{PC}$ = 13.8 Hz), 126.6 (C$_{5'}$), 127.9 (C$_{3'}$), 140.7 (C$_{6'}$), 148.4 (C$_{2'}$), 129.6−133.9 (C$_{4'}$, phenyl). Compound **1** is soluble in CHCl$_3$ and slightly soluble in water, 0.1 M HNO$_3$, and benzene.

Preparation of the Complexes. Solutions of lanthanide salts (0.5 mmol in 10 mL of EtOH) and **1** (0.5 mmol in 5 mL of CHCl$_3$) were combined and stirred (2 h). Precipitates formed immediately. These were recovered by filtration and washed with pentane. The solid samples were vacuum-dried prior to analysis. The infrared spectrum for each complex was recorded (KBr, cm^{-1}): Pr(**1**)(NO$_3$)$_3$, 1150 (ν_{NO}), 1125 (ν_{PO}), 1096 (ν_{PO}); Tb(**1**)(NO$_3$)$_3$, 1153 (ν_{NO}), 1125 (ν_{PO}) 1098 (ν_{PO}); Yb(**1**)(NO$_3$)$_3$, 1157 (ν_{NO}), 1125 (ν_{PO}), 1098 (ν_{PO}). The CHN analysis was completed only for the Pr(**1**)(NO$_3$)$_3$ complex. Anal. Calcd for Pr(**1**)(NO$_3$)$_3$·H$_2$O, C$_{32}$H$_{31}$N$_4$O$_{13}$P$_2$Pr: C, 43.55; H, 3.54; N, 6.35. Found: C, 43.32; H, 3.84; N, 6.01.

X-ray Diffraction Study. A small (0.10 × 0.08 × 0.06 mm) colorless prism-shaped crystal of Pr(**1**)(NO$_3$)$_3$ obtained by slow evaporation of a methanol solution of the complex was mounted in a glass capillary tube which was then sealed and placed in a cold stream (193 K) on a Siemens P4 X-ray diffractometer with a CCD area detector. Data collection was performed with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Selected crystal and refinement data are summarized in Table 1. Data were recorded in the hemisphere mode with a measurement rate of 10 s per frame. A small absorption correction was applied using SADABS. Data reduction and refinement were accomplished with SHELXL 97.[21] The structure was solved by direct methods, and full-matrix least-

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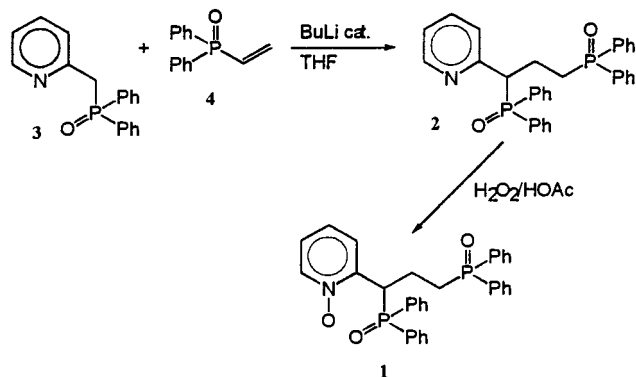(21) Sheldrick, G. M. *SHELXL 97*; Bruker Instruments: Madison, WI, 1999.

Table 1. Crystallographic Data for Pr(**1**)(NO$_3$)$_3$·0.75H$_2$O

empirical formula	C$_{32}$H$_{30.5}$N$_4$O$_{12.75}$P$_2$Pr	V, Å^3	7468.8(11)
fw	877.95	space group	Pbca
a, Å	20.991(2)	Z	8
b, Å	16.397(1)	D_{calcd}, g/cm^3	1.562
c, Å	21.700(2)	μ, mm^{-1}	1.457
α, deg	90	R1,^{a} wR2^b	0.0489, 0.1125
β, deg	90	($I > 2\sigma(I)$)	
γ, deg	90		

^{a} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

Scheme 1

squares refinements were employed.[22] The refinements were well behaved except for that of the outer-sphere water molecule. The occupancy of the O(13) position was varied, and it converged to 0.73. Hence, it was set at 0.75 in the final model to achieve an integral number (6) of waters in the unit cell. The H atoms on O(13) were not located, and they were placed in idealized positions. All other H atoms were included (riding model) with $U_{iso} = 1.25U_{eq}$ of the parent atom.

Results and Discussion

The target ligand **1** was obtained in about 30% overall yield from the unoptimized reaction sequence outlined in Scheme 1. The first step in the synthesis produces the precursor 1-(diphenylphosphine oxide)-1-(2′-pyridyl)-3-(diphenylphosphine oxide)propane (**2**) in about 35% yield from the Michael addition of the reactive methylene group in 2-[(diphenylphosphino)methyl]pyridine (**3**) to the activated vinyl group in diphenylvinylphosphine oxide (**4**). The reaction is catalyzed with the strong base BuLi in THF solution. The formation of **2** is indicated by its ^{31}P{^{1}H} NMR resonance at δ 32.7. No other reaction products are formed, and reaction mixtures monitored by ^{31}P{^{1}H} NMR spectroscopy show only the resonance for **2** along with resonances for the starting materials **3** (^{31}P{^{1}H} δ 30) and **4** (^{31}P{^{1}H} δ 24). The precursor is a white solid that was characterized by CHN analysis, FAB-MS, and IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The IR spectrum shows two absorptions at 1190 and 1175 cm^{-1} that are tentatively assigned on the basis of literature precedence[9,10,23] to ν_{PO} for the two Ph$_2$P-(O) fragments. FAB-MS shows an intense ion for the M + 1$^+$ species (m/e 522) that is characteristic of MNPOPO ligands.[9,10,23] The ^{31}P{^{1}H} NMR spectrum unexpectedly

(22) The least-squares refinement minimizes $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F)^2 + gF^2$.
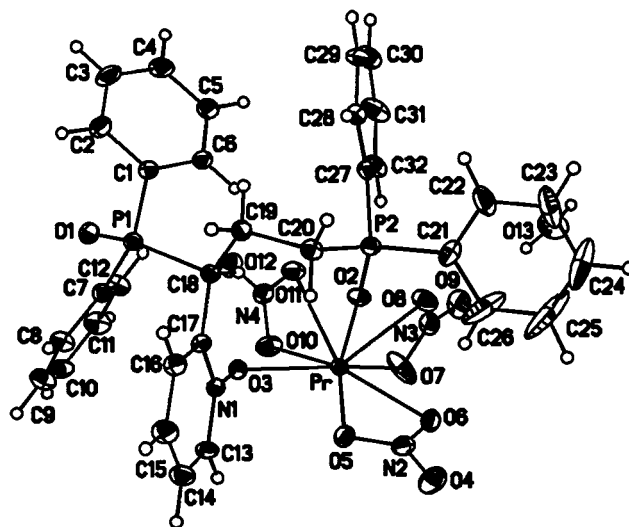(23) Gan, X.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.*, in press.

Figure 1. Thermal ellipsoid plot (30%) for Pr(**1**)(NO$_3$)$_3$·0.75H$_2$O.

shows only one resonance, δ 32.7. This requires that the inequivalent Ph$_2$P(O) groups must be accidentally magnetically equivalent. The ^{1}H and ^{13}C{^{1}H} NMR spectra have been assigned, and they are consistent with the proposed structure.

The second step of the ligand synthesis involves the oxidation of the pyridine fragment with a hydrogen peroxide/glacial acetic acid mixture at 23 °C for 2 days. The reaction is accelerated by use of higher reaction temperatures, but some decomposition also takes place. Compound **1** is isolated as a white solid that provides adequate CHN analytical data. The compound displays three strong absorptions in the IR spectrum, 1231, 1198, and 1181 cm^{-1}, that are tentatively assigned to ν_{NO},ν_{PO}, and ν_{PO} stretching frequencies, respectively. The high-resolution FAB-MS shows an M + 1$^+$ parent ion at 538.1713 (calcd 538.1701). In this case, the ^{31}P{^{1}H} NMR spectrum displays two closely spaced (δ 36.7, 36.8), equal-intensity resonances. The ^{1}H and ^{13}C{^{1}H} NMR spectra are closely comparable to the spectra for **2**.

As indicated in the Introduction, the primary interest in compound **1** revolves around its potential tridentate ligation properties and/or its potential to act as a phase modifier in two-phase extractions. As a result, the coordination chemistry of **1** with Pr(NO$_3$)$_3$, Tb(NO$_3$)$_3$, and Yb(NO$_3$)$_3$ was explored. When combined in a 1:1 L:M ratio, solid complexes are isolated as crystalline solids. The infrared spectra of the complexes are identical and show bands at 1157−1150 cm^{-1} that can be assigned to ν_{NO} and 1125 and 1096 cm^{-1} that are assigned to ν_{PO}. Each band is shifted to a lower frequency compared to the corresponding absorption in the free ligand: $\Delta\nu_{NO} = 74$−81 cm^{-1}, $\Delta\nu_{PO} = 73$−85 cm^{-1}. These data suggest that all three functional groups of **1** are involved in the lanthanide coordination; however, they provide no evidence related to ligand denticity. Therefore, the molecular structure of one of the complexes, Pr(**1**)(NO$_3$)$_3$, was determined by single-crystal X-ray diffraction techniques.

The compound crystallizes in the orthorhombic space group *Pbca*. A view of the molecule is shown in Figure 1, and selected bond lengths are listed in Table 2. The parent MNOPO ligand (R = Ph) has been shown to coordinate with
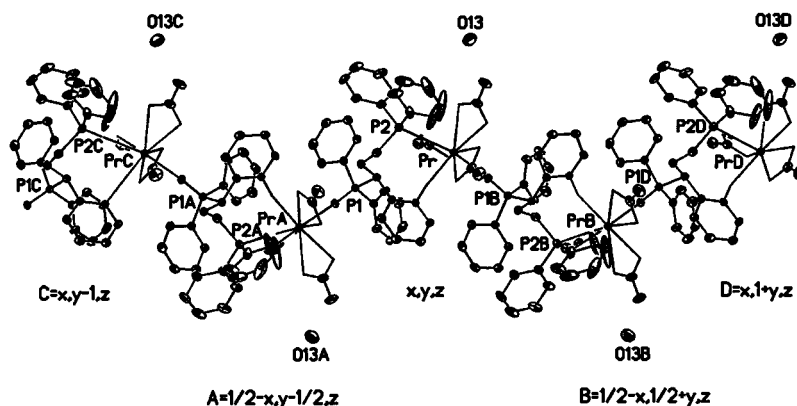
Figure 2. Structure of chains formed along the *b* axis for Pr(**1**)(NO$_3$)$_3$·0.75H$_2$O.

Table 2. Selected Bond Lengths (Å) for Pr(**1**)(NO$_3$)$_3$·0.75H$_2$O

Pr−O(1)	2.400(4)	P(1)−O(1)	1.501(4)
Pr−O(2)	2.370(4)	P(2)−O(2)	1.506(4)
Pr−O(3)	2.400(4)	N(1)−O(3)	1.329(6)
Pr−O(5)	2.582(4)	N(2)−O(4)	1.219(7)
Pr−O(6)	2.554(4)	N(2)−O(5)	1.263(7)
Pr−O(7)	2.559(5)	N(2)−O(6)	1.278(7)
Pr−O(8)	2.580(5)	N(3)−O(9)	1.234(7)
Pr−O(10)	2.536(5)	N(3)−O(7)	1.238(8)
Pr−O(11)	2.540(4)	N(3)−O(8)	1.247(8)
Pr···N(2)	2.998(5)	N(4)−O(12)	1.224(7)
Pr···N(3)	2.999(5)	N(4)−O(10)	1.257(7)
Pr···N(4)	2.957(5)	N(4)−O(11)	1.270(7)

Ln(III) ions in a bidentate mode through the pyr N−O group and the P=O group terminating the *exo* −CH$_2$(Ph)$_2$P=O arm.[9] In fact, with sufficient MNOPO available, 4:1 L/M complexes form in which the bidentate ligand oxygen atoms generate the entire inner coordination sphere (CN = 8) and the nitrate ions are displaced to the outer sphere. The new MNOPO derivative **1** presents, to an approaching Ln(III) ion, three potential donor sites: the pyr N−O, the short-arm −CH(Ph)$_2$P=O, and the long-arm −C(H)(C$_2$H$_4$)(Ph)$_2$P=O oxygen atoms. On the basis of earlier studies, we expected that the resting free ligand would have a structure with the three O-donor dipoles rotated away from each other. In the presence of a strong field generated by a highly charged Ln-(III) cation, we also expected that the short-arm phosphoryl group would reorient, forming, together with the pyr N−O, a seven-membered bidentate chelate interaction. It was not clear if the long arm could also reorient its secondary structure in a manner that would produce a tridentate interaction. Therefore, it was not surprising to find that the structure adopted in the 1:1 **1**/Pr(III) complex crystal structure contains three bidentate nitrate anions and one bidentate chelating ligand, **1**, in the inner coordination sphere. It was unexpected, however, to find that the long-arm −C(H)-(C$_2$H$_4$)(Ph)$_2$P=O and the pyr N−O donor groups are used, producing a nine-atom chelate ring. The short-arm −C(H)-(Ph)$_2$P=O is not silent. This group, in each Pr(**1**)(NO$_3$)$_3$ unit, coordinates with the Pr(III) ion in a neighboring Pr(**1**)(NO$_3$)$_3$ unit. The result is a chain structure extending along the *b* axis as shown in Figure 2, with each Pr(III) having a coordination number of nine. The inner coordination sphere as shown in Figure 3 approximates a distorted capped square antiprism. Although IR spectral data are not unambiguous since the ν_{NO} and ν_{PO} assignments are only tentative, the IR
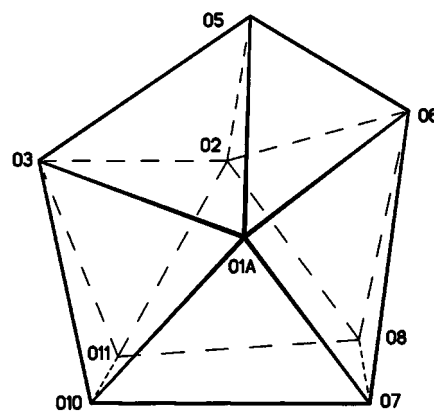

Figure 3. Coordination polyhedron for Pr(**1**)(NO$_3$)$_3$·0.75H$_2$O.

of the complex in CHCl$_3$ was obtained to assess possible chelate structure changes in solution. The ν_{NO} and two ν_{PO} bands are found at the same frequencies as reported for the complex in KBr. This suggests that the bridged chain structure persists in CHCl$_3$ solution.

The chain structure described here is reminiscent of the chain structure adopted by the trifunctional octahydroacridine *N,P,P′*-trioxide ligand **5** with Ln(III) ions.[24] Here one Ph$_2$P=
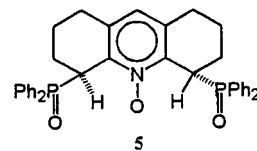
O group reorients its P=O dipole so that a bidentate pyr N−O/Ph$_2$P=O seven-membered chelate interaction with Ln-(III) occurs. The second Ph$_2$P=O group in the *threo* isomer obtained cannot approach the same Ln(III) ion. Instead, this Ph$_2$P=O group bridges to a second Ln(**5**)(NO$_3$)$_3$ complex unit, and a chain structure results.

The long-arm Ph$_2$P(O)−Pr bond length in the Pr(**1**)(NO$_3$)$_3$ unit is 2.370(4) Å, and this is shorter than the bridging short-arm Ph$_2$P(O)−Pr bond length, 2.400(4) Å, and the pyr N(O)−Pr bond length, 2.400(4) Å. These distances can be compared with bond lengths in Nd(**5**)(NO$_3$)$_3$: Ph$_2$P(O)−Nd = 2.324(13) Å, bridging Ph$_2$P(O)−Nd = 2.330(8) Å, and

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pyr N(O)−Nd = 2.424(10) Å. The difference in ionic radii,[25] Pr(III) (CN = 8) 1.14 Å, Nd(III) (CN = 8) 1.12 Å, is partially responsible for the M−O bond length variations in these complexes; however, it does not explain all the variations. Clearly, both P(O)−Pr bond lengths are longer than comparable P(O)−Nd bond lengths, which suggests that the phosphoryl/metal interactions are not as strong in Pr(**1**)-(NO$_3$)$_3$. In contrast, the N(O)−Pr bond length is slightly shorter. That said, the P(O)−Pr and N(O)−Pr bond lengths in Pr(**1**)(NO$_3$)$_3$ are both shorter than the average separations in the 2:1 complex (MNOPO)$_2$Pr(NO$_3$)$_3$ (R = Ph) (CN = 10): P(O)−Pr = 2.456(6) Å and N(O)−Pr = 2.445(7) Å.[9] This may reflect both an increased Pr(III) coordination number and potentially greater ligand packing repulsions in the latter complex.[26,27]

Some points related to the secondary structure of Pr(**1**)-(NO$_3$)$_3$ are worth mention. First, six water molecules appear

in the unit cell. The occupancy of the O(13) atom position was varied from 0.5 to 0.75 and found to converge best with a model having 0.75 occupancy. H-atoms on the water molecules were not resolved; therefore, they were placed in idealized positions to link the closest nonbonded O···O contacts: O(4)···O(13)···O(9).[28] The result is a two-dimensional corrugated net in the $x−y[a−b]$ plane that is not connected in the $z[c]$ direction. It is also apparent that there are numerous nonbonded interactions involving the phenyl groups; however, these C−H···O interactions will be much weaker, and they should play a diminished role in the crystal chemistry.

The ligand chelate structure is certainly unexpected; however, given the features found in the secondary structure, especially nonbonded phenyl group interactions, it may be that **1** simply cannot orient properly to produce a seven-membered chelate ring using pyr N−O and short-arm −C(H)(Ph)$_2$P=O donor groups. Studies of the extraction behavior of **1** and its derivatives are planned, and the impact of the structural preference of **1** on extraction performance will be tested.

Supporting Information Available: Crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0109041

(25) Ionic radii were taken from Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925.

(26) Encouraged by an alert reviewer's comment, we also note that the unexpected adoption of a nine-membered chelate ring by **1** is unique in comparison to a prior report from our group on modified CMP-like ligands.[27] In the earlier study, it was reported that the trifunctional ligand (i-PrO)$_2$P(O)CH[C(O)NEt$_2$] [CH$_2$CH$_2$C(O)NEt$_2$], which potentially could form six- and/or eight-membered chelate rings, selects the smaller six-membered condition when bonding to Er(III). The longer armed amide group serves as a bridging ligand to a second Er(III) ion. We refrain, at this stage, from lengthy speculative comparisons of the different coordination conditions adopted by these very different ligand families.

(27) Paine, R. T.; Conary, G. S.; Russell, A. A.; McCabe, D. J.; Duesler, E. N.; Karthikiyan, S.; Schaeffer, R. *Solvent Extr. Ion Exch.* **1989**, *7*, 767.

(28) O(9) is in the *x, y, z* unit, and O(4) is in the *x* − 0.5, *y*, 0.5 − *z* (*a*-glide-related) unit.