

Synthesis and Coordination Chemistry of 2,6-Bis(diphenylphosphinomethyl)phenol *P,P'*-Dioxides

Robert T. Paine,* Yun-Chou Tan, and Xin-Min Gan

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

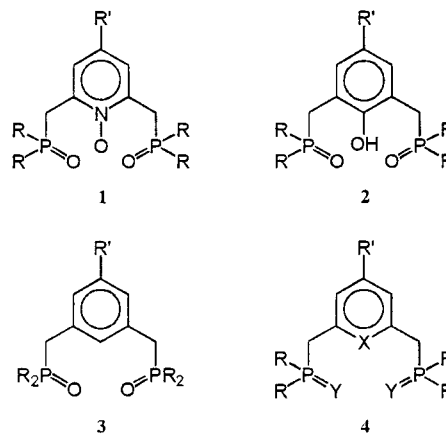
Received July 17, 2001

The 2,6-bis(diphenylphosphinomethyl)phenol-*P,P'*-dioxides, $[\text{Ph}_2\text{P}(\text{O})\text{CH}_2]_2\text{C}_6\text{H}_2(\text{R})\text{OH}$, with $\text{R} = \text{H}$ (**2a**), Br (**2b**), Me (**2c**), ^tBu (**2d**), were prepared via Arbusov reactions between Ph_2POEt and the phenol derivatives $(\text{ClCH}_2)_2\text{C}_6\text{H}_2(\text{R})\text{OH}$. The compounds have been characterized by spectroscopic methods, and their coordination chemistry with lanthanide nitrates, $\text{Ln}(\text{NO}_3)_3$, has been surveyed. The 1:1 complexes $[\text{Er}(\mathbf{2c})(\text{NO}_3)_3] \cdot \text{Me}_2\text{CO}$ and $[\text{Nd}(\mathbf{2d})(\text{NO}_3)_3 \cdot \text{Me}_2\text{CO}] \cdot \text{Me}_2\text{CO}$ have been structurally characterized by single-crystal X-ray diffraction methods, and the ligands found to act as neutral tridentate chelates. No evidence was found for the formation of 2:1 L:M complexes suggesting that these derivatives of **2** are weaker chelators than the related 2,6-bis(diphenylphosphinomethyl)pyridine *N,P,P'*-trioxide chelates.

Introduction

A family of 2,6-bis(diarylphosphinomethyl)pyridine *N,P,P'*-trioxides and 2,6-bis(dialkylphosphinomethyl)pyridine *N,P,P'*-trioxides $[\text{R}_2\text{P}(\text{O})\text{CH}_2]_2\text{C}_5\text{H}_3\text{NO}$ (**1**) ($\text{R}' = \text{H}$) have recently been found to form 1:1 and 2:1 neutral ligand:metal complexes with lanthanide and actinide trivalent and tetravalent cations.^{1–6} In each case, the ligands bind to the metal in a tridentate fashion. Further, when the ligands are present in 2:1 or greater amounts, they partially or completely displace chloride or nitrate ions from the inner coordination sphere of the metals. Companion liquid–liquid extraction studies reveal that several derivatives of **1** act as efficient reagents for scrubbing Ln(III), An(III), and An(IV) species from highly acidic (>3 M HNO_3 or HCl) aqueous solutions.^{7–10} The observed ligation behavior and extraction performance have stimulated us to extend these studies to related ligand architectures that might reveal additional details on the molecular-level electronic and steric features that influence the binding of **1** to strongly polarizing cations. In this regard, we recently reported the outcome of coordination chemistry between $\text{Ln}(\text{NO}_3)_3$ salts and the bifunctional ligand $[\text{Ph}_2\text{P}(\text{O})\text{CH}_2]_2\text{C}_6\text{H}_3\text{R}'$ (**3**) ($\text{R}' = \text{H}$).¹¹ This ligand forms 1:1

and 2:1 L:Ln complexes, and crystal structure determinations for 2:1 complexes show that the ligand acts as a bidentate chelator. Furthermore, the ligand backbone conformation is identical to that found for 2:1 complexes of **1** bonded to Ln(III) ions. The absence of the strong pyr N–O donor groups in the $\text{Ln}(\mathbf{3})_2^{3+}$ complexes, however, leaves open coordination space that is filled by two inner-sphere nitrate ions.



In the present contribution, we extend our study to include a second family of trifunctional ligands that is based upon 2,6-bis(phosphinomethyl)-substituted phenols, **2**. Given the relative donor capabilities of pyridine *N*-oxides compared to phenols, it was anticipated that **2** might provide an intermediate chelation performance between **1** and **3**. Syntheses for derivatives **2a–d** and coordination chemistry with $\text{Ln}(\text{NO}_3)_3$ salts are described. The results reveal unique features for these ligands, and it appears that the introduction of the phenol donor group does alter the binding capability of this general class of ligands.

Experimental Section

General Information. Organic reagents were purchased from Aldrich Chemical Co. Organic solvents were obtained from VWR and dried by standard procedures. The lanthanide nitrates were purchased from Ventron. All reactions were performed under dry nitrogen atmosphere unless noted otherwise. Infrared spectra were recorded on

* To whom correspondence should be addressed. Phone: (505) 277-1661. E-mail: rtpaine@unm.edu.

- Rapko, B. M.; Duesler, E. N.; Smith, P. H.; Paine, R. T.; Ryan, R. R. *Inorg. Chem.* **1993**, *32*, 2164.
- Engelhardt, U.; Rapko, B. M.; Duesler, E. N.; Frutos, D.; Paine, R. T. *Polyhedron* **1995**, *14*, 2361.
- Bond, E. M.; Gan, X.-M.; FitzPatrick, J. R.; Paine, R. T. *J. Alloys Compd.* **1998**, *271–273*, 172.
- Bond, E. M.; Duesler, E. N.; Paine, R. T.; Neu, M. P.; Matonic, J. H.; Scott, B. L. *Inorg. Chem.* **2000**, *39*, 4591.
- Bond, E. M.; Duesler, E. N.; Paine, R. T.; Nöth, H. *Polyhedron* **2000**, *19*, 2135.
- Gan, X.-M.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **2001**, *40*, 4420.
- Bond, E. M.; Engelhardt, U.; Deere, T. P.; Rapko, B. M.; Paine, R. T.; FitzPatrick, J. R. *Solvent Extr. Ion Exch.* **1997**, *15*, 381.
- Bond, E. M.; Engelhardt, U.; Deere, T. P.; Rapko, B. M.; Paine, R. T.; FitzPatrick, J. R. *Solvent Extr. Ion Exch.* **1998**, *16*, 967.
- Nash, K. L. Private communication.
- Abbreviations used in the text include Ln = lanthanide, An = actinide, Me = methyl, ^tBu = *tert*-butyl.
- Tan, Y. C.; Gan, X.-M.; Stanchfield, J. L.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **2001**, *40*, 2910.

a Mattson 2020 FTIR, and NMR spectra were obtained from Bruker FX-250 and JEOL GSX-400 spectrometers using Me₄Si (¹H, ¹³C) and 85% H₃PO₄ (³¹P) as shift standards. All downfield shifts from the reference were designated as +δ. Mass spectra were obtained at the Midwest Center for Mass Spectrometry, University of Nebraska. Elemental analyses were acquired from Galbraith Laboratories and the University of New Mexico.

Ligand Syntheses. 2,6-Bis(diphenylphosphinomethyl)phenol P,P'-Dioxide (2a). A sample of 2,6-bis(hydroxymethyl)phenol¹² (**5a**) (5.3 g, 0.034 mol) was suspended in concentrated HCl (60 mL) and the mixture stirred overnight at 23 °C. The resulting suspension was extracted with CH₂Cl₂ (3 × 50 mL). The combined CH₂Cl₂ phases were dried overnight with Na₂SO₄, and the liquid was decanted and vacuum evaporated, leaving a light brown solid, 2,6-bis(chloromethyl)phenol (**6a**): yield 4.2 g, 65%. A sample of **6a** (6.5 g, 0.034 mol) was dissolved in triglyme (25 mL), and this solution was added to a three-necked flask outfitted with a stir bar, a reflux condenser outfitted at the top with a valve connected to a vacuum line, an addition funnel, and a nitrogen inlet tube. The system was flushed with nitrogen, and then the vacuum and nitrogen inlet flow were adjusted to provide a 20 mTorr pressure in the system. The flask was then heated to 150 °C, and a solution of Ph₂POEt (16.45 g, 0.071 mol) in triglyme (5 mL) was added dropwise. The resulting mixture was heated at 150 °C (3 h, 20 mTorr) with continuous stirring. The mixture was then cooled to 80–100 °C and the solvent removed by vacuum evaporation, leaving a white solid. This was recrystallized from ethyl acetate, leaving **2a**: yield 13.6 g, 76.5%; mp 125–127 °C. ³¹P{¹H} NMR (CDCl₃): δ 38.2. HRMS (FAB): *m/z* calcd for C₃₂H₂₈O₃P₂, 522.1514; found, 522.1499. Anal. Calcd: C, 73.56; H, 5.40. Found: C, 70.48; H, 5.89.

4-Bromo-2,6-bis(diphenylphosphinomethyl)phenol P,P'-Dioxide (2b). The precursor 4-bromo-2,6-bis(chloromethyl)phenol (**6b**) was prepared as described for **6a** from **5b**¹³ (3.0 g, 0.013 mol) and HCl (15 mL), and it was isolated as an off-white solid following recrystallization from ethyl acetate/cyclohexane: yield 2.7 g, 77%. A sample of **6b** (4.0 g, 0.015 mol) was treated with Ph₂POEt (7.16 g, 0.031 mol) as described in the synthesis of **2a**, and **2b** was isolated as a white solid: yield 7.42 g, 82.2%; mp 200–201 °C. ³¹P{¹H} NMR (CDCl₃): δ 38.0. HRMS (FAB): *m/z* calcd for C₃₂H₂₇BrO₃P₂, 600.0619; found, 600.0592. Anal. Calcd: C, 63.91; H, 4.53. Found: C, 63.39; H, 4.59.

4-Methyl-2,6-bis(diphenylphosphinomethyl)phenol P,P'-Dioxide (2c). The precursor 4-methyl-2,6-bis(chloromethyl)phenol (**6c**) was prepared as described for **6a** from **5c**¹⁴ (29.8 g, 0.177 mol) and HCl (100 mL), and it was isolated as a tan solid: yield 26.3 g, 72.5%. A sample of **6c** (6.0 g, 0.029 mol) was treated with Ph₂POEt (13.86 g, 0.060 mol) as described for the synthesis of **2a**, and **2c** was obtained as a white solid, which was recrystallized from ethyl acetate: yield 14.7 g, 94.5%; mp 176–178 °C. ³¹P{¹H} NMR (CDCl₃): δ 38.11. HRMS (FAB): *m/z* calcd for C₃₃H₃₀O₃P₂, 536.1670; found, 536.1674. Anal. Calcd: C, 73.87; H, 5.64. Found: C, 72.88; H, 5.68.

4-tert-Butyl-2,6-bis(diphenylphosphinomethyl)phenol P,P'-Dioxide (2d). The precursor 4-tert-butyl-2,6-bis(chloromethyl)phenol (**6d**) was prepared as described for **6a** from **5d**¹⁴ (34.0 g, 0.162 mol) and HCl (120 mL), and it was isolated as a light yellow solid: yield 26.5 g, 66.2%. A sample of **6d** (6.0 g, 0.024 mol) was treated with Ph₂POEt (11.75 g, 0.051 mol) as described for **2a**, and **2d** was obtained as a white solid: yield 13.6 g, 97.9%; mp 196–198 °C. ³¹P{¹H} NMR (CDCl₃): δ 38.00. HRMS (FAB): *m/z* calcd for C₃₆H₃₆O₃P₂, 578.2140; found, 578.2118. Anal. Calcd: C, 74.13; H, 6.27. Found: C, 72.71; H, 6.30.

Synthesis of the Complexes. A sample of Nd(NO₃)₃·6H₂O (87.7 mg, 0.2 mmol) was combined with **2d** (0.116 g, 0.2 mmol) in ethyl acetate (10 mL) and stirred at 23 °C (20 min). A purple solid formed, which was collected by filtration, washed with ethyl acetate, and then redissolved in acetone (7 mL). Ethyl acetate (10 mL) was added, the

Table 1. Crystallographic Data

	[Er(2c)(NO ₃) ₃]·Me ₂ CO	[Nd(2d)(NO ₃) ₃ ·Me ₂ CO]·Me ₂ CO
empirical formula	C ₃₆ H ₃₆ ErN ₃ O ₁₃ P ₂	C ₄₂ H ₄₈ N ₃ NdO ₁₄ P ₂
fw	947.88	1025.01
<i>a</i> (Å)	28.844(3)	18.417(3)
<i>b</i> (Å)	28.844(3)	16.661(2)
<i>c</i> (Å)	10.575(1)	15.994(2)
α (deg)	90	90
β (deg)	90	103.81(1)
γ (deg)	90	90
<i>V</i> , Å ³	8798(2)	4765(1)
cryst syst	tetragonal	monoclinic
space group	I 4̄	P2 ₁ /c
<i>Z</i>	8	4
<i>D</i> _{calcd} (g/cm ³)	1.431	1.429
μ (mm ⁻¹)	2.04	1.221
R1 ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0473	0.0403
wR2 ^b	0.0983	0.0725

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

mixture filtered, and the filtrate placed in a loosely capped vial. After several days, purple single crystals of the complex [Nd(**2d**)(NO₃)₃·Me₂CO]·Me₂CO formed. Infrared spectrum (KBr, cm⁻¹): 3371 (br), 3061 (m), 2958 (s), 2710 (m), 1691 (s), 1481 (s), 1386 (s), 1284 (s), 1190 (s), 1145 (s), 1124 (s), 1093 (s), 1028 (s), 925 (w), 848 (w), 727 (s), 694 (s). The complex [Er(**2c**)(NO₃)₃]·Me₂CO was prepared by combination of Er(NO₃)₃·5H₂O (88.7 mg, 0.2 mmol) and **2c** (0.107 g, 0.2 mmol) in ethyl acetate (6 mL). The mixture was stirred (40 min), and a pink solid precipitated. Acetone (9 mL) was added to dissolve the solid, the mixture was filtered, and the filtrate was placed in a loosely capped vial. Slow solvent evaporation produced X-ray quality crystals of [Er(**2c**)(NO₃)₃]·Me₂CO. Infrared spectrum (KBr, cm⁻¹): 3404 (br), 3059 (m), 2978 (m), 2926 (m), 1593 (w), 1485 (s), 1440 (s), 1384 (m), 1294 (s), 1213 (m), 1151 (s), 1128 (s), 1095 (m), 1030 (m), 815 (w), 746 (s), 729 (s), 694 (s), 623 (w).

X-ray Diffraction Studies. The single crystals for the two complexes were obtained from the preparative workups described above. Data were collected by variable speed ω scans on a Siemens R3m/V diffractometer equipped with a graphite monochromator using Mo Kα radiation (λ = 0.71073 Å). Crystal data parameters are summarized in Table 1. Calculations were performed with SHELXTL (VMS version),¹⁵ and the structures were solved by direct methods. Full-matrix least-squares refinements were completed using appropriate neutral atom scattering factors and anomalous dispersion terms including anisotropic thermal parameters on the heavy atoms. Data were corrected for adsorption by using semiempirical ψ scans. The refinement for [Er(**2c**)(NO₃)₃]·Me₂CO revealed that the outer sphere acetone molecule is disordered; O(13) and C(35) occupy single sites, but C(34) and C(36) are displaced over two sites with occupancy factors of 0.53 and 0.47. Hydrogen atoms were included in the final cycles of least-squares refinements in idealized positions (riding model) with isotropic *U*'s set to 1.25*U*_{iso} of the parent atom. The refinement for [Nd(**2d**)(NO₃)₃·Me₂CO]·Me₂CO revealed disorder in the ^tBu group: C(9A), C(9B), C(9C) and C(9D), C(9E), C(9F) with occupancies set to 0.52/0.48. The inner-sphere acetone oxygen atom was also disordered over two sites: O(1s)/O(2s) with occupancies 0.69/0.31. In the final refinements, the ^tBu methyl groups were constrained to have a tetrahedral geometry. The position of the phenol OH hydrogen atom was allowed to vary while the remaining H-atom positions were fixed in idealized positions (riding model). Selected bond distances for both molecules are presented in Table 2.

Results and Discussion

Trivalent and tetravalent f-element ions form coordination complexes with neutral oxo-donor ligands, and unlike d-element

(12) Compound **5a** was obtained by reduction of **5b** with H₂ (55 psi) and Raney Ni.

(13) Moshfegh, A. A.; Mazandarani, B.; Nahid, A.; Hakimelaki, G. H. *Helv. Chim. Acta* **1982**, *65*, 1229.

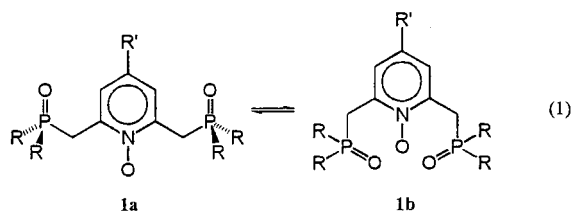
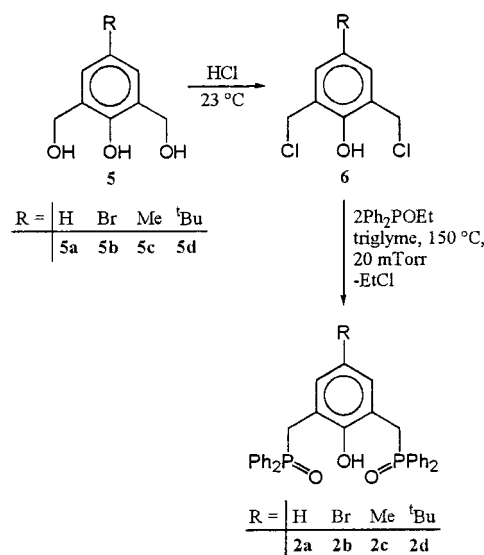
(14) Hampton, P. D.; Bencze, Z.; Tong, W.; Daitch, C. E. *J. Org. Chem.* **1994**, *59*, 4838.

(15) Sheldrick, G. M. *Nicolet SHELXTL Operations Manual*; Nicolet XRD Corp.: Cupertino, CA, 1981. The least-squares refinement minimizes $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F)^2 + gF^2]$.

Table 2. Selected Bond Distances (Å)

	[Er(2c)(NO ₃) ₃]·Me ₂ CO	[Nd(2d)(NO ₃) ₃]·Me ₂ CO		
M—O(P)	Er—O(2)	2.266(5)	Nd—O(2)	2.359(4)
	Er—O(3)	2.266(5)	Nd—O(3)	2.370(5)
M—O(C)	Er—O(1)	2.386(6)	Nd—O(1)	2.635(5)
M—O(N) _{nitrate}	Er—O(4)	2.421(6)	Nd—O(1A)	2.615(5)
	Er—O(5)	2.457(6)	Nd—O(1B)	2.575(5)
	Er—O(7)	2.424(5)	Nd—O(2A)	2.615(5)
	Er—O(8)	2.427(6)	Nd—O(2B)	2.695(5)
	Er—O(10)	2.419(7)	Nd—O(3A)	2.525(6)
	Er—O(11)	2.447(8)	Nd—O(3B)	2.517(6)
M—O _{solvent}			Nd—O(1S)	2.472(9)
P—O	P(1)—O(2)	1.501(6)	P(1)—O(2)	1.498(5)
	P(2)—O(3)	1.500(6)	P(2)—O(3)	1.493(5)
C—O	C(1)—O(1)	1.438(10)	C(1)—O(1)	1.387(7)
O—H	O(1)—H(1)	0.868(5)	O(1)—H(1)	0.73(6)

ions the resulting complexes often have coordination numbers greater than six, typically eight to ten. Many of the resulting coordination polyhedra¹⁶ are considered to be composed of edge-fused triangles with edge distances that approximate the nonbonded, van der Waals separation of two oxygen atoms, O···O ~ 2.8 Å. Therefore, one approach to the development of f-element specific chelating ligands involves the construction of organic backbones containing pendant oxo donor groups that can bind with minimal strain on the trigonal faces of 8–10 vertex polyhedra. With that concept in mind, we have previously reported that examples of **1** readily undergo configurational reorientation from the free ligand state (**1a**) to a tridentate chelate-poised configuration (**1b**), as shown in eq 1, when a highly polarizing metal ion is present. Even though the chelate ring size formed by **1** and Ln³⁺ ions is seven, the complex stabilities are large enough to produce excellent extraction reagents. Surprisingly, this is true even when the f-element ion is present in strongly acidic aqueous solutions where H⁺, H₃O⁺, or HX would be expected to competitively bind with the ligand.

**Scheme 1**

(hydroxymethyl)phenols **5a–d** were obtained as described in the literature,^{12–14} and these were converted to the corresponding bis(chloromethyl)phenols, **6a–d**, by treatment with concentrated HCl. These solids were dissolved in triglyme, and the solutions were heated to 150 °C and allowed to react by dropwise addition of Ph₂POEt. The resulting Arbusov reactions produced EtCl, which was removed from the reactor to a cold trap under reduced pressure, and the desired products **2a–d** remained in the triglyme, which was removed by vacuum evaporation at 80–100 °C. Compounds **2b–d** are indefinitely stable as solids or in organic solutions. Compound **2a** appears to be somewhat more fragile, decomposing very slowly in the solid state and more rapidly (days) in organic solutions. The slow decomposition of **2a** has made it difficult to obtain analytically pure samples, as indicated by the CH analysis data.

The high-resolution FAB mass spectra of **2a–d** show in each case a strong parent ion M⁺ (relative intensity 42–47). The ion of highest intensity is the (M + H)⁺ ion. Logical fragment ions including M – CH₂P(O)Ph₂⁺ and M – (CH₂P(O)Ph₂)₂⁺ also are prominent in each spectrum. The infrared spectra of **2a–d** contain a strong, “split” adsorption that is tentatively assigned to the phosphoryl stretching mode, ν_{PO}: **2a** 1188, 1159 cm⁻¹; **2b** 1184, 1163 cm⁻¹; **2c** 1184, 1163 cm⁻¹; **2d** 1186, 1157 cm⁻¹. The ³¹P NMR spectra of **2a–d** show a single resonance in the narrow range δ 38.3–38.0 indicating that 4-position substitution on the phenolic ring has little effect on the ³¹P shift of the phosphoryl group. The ¹³C{¹H} NMR spectra contain a diagnostic doublet δ 33.1–32.7, ¹J_{PC} = 68.0–67.4 Hz, which is assigned to the methylene carbons connecting the phenol ring with the Ph₂P(O) donor groups. The ¹H NMR spectra show a doublet δ 3.72–3.67, ²J_{PH} = 14–13 Hz, for the same groups. These resonances are comparable to data for the related compounds **1**² and **3**.¹¹ The remaining ¹H and ¹³C NMR data are provided in Supporting Information.

In order to characterize the chelation properties of **2** with trivalent lanthanides, combinations of several Ln(NO₃)₃·nH₂O salts¹⁸ and **2a–d** were examined in 1:1 and 2:1 ligand:metal ratios. At this time, 2:1 complexes have not been isolated. Instead, only 1:1 complexes are isolated as crystalline solids. Furthermore, NMR spectroscopic data provide no evidence for

From a ligand design perspective, we are interested in how the chelation ability of the general class of ligands **4** changes by variation of R, R', Y, the number of CH₂ groups in the exo arms, and X. In the last instance, it is clear that replacement of X = N–O with X = C–H results in a change from tridentate chelation to bidentate.¹¹ It is expected that this occurs with concomitant weaker binding to Ln(III) ions.¹⁷ It is interesting, however, that the ligand backbone atom positions of **3** in 1:1 and 2:1 complexes closely match the atom positions in the related 1:1 and 2:1 complexes of **1**, suggesting that the metal coordinated ligand geometries are largely strain-free. In the current study, we were interested in determining the coordination characteristics of related phenolic derivatives, **2**, which also offer the potential to serve as tridentate chelators in a fashion related to **1**.

Four bis(diphenylphosphinomethyl)phenol *P,P'*-dioxides, **2a–d**, have been prepared as outlined in Scheme 1. The parent bis-

(16) Kepert, D. L. *Inorganic Stereochemistry*; Springer-Verlag: Berlin, 1982.

(17) Titration calorimetric studies will be undertaken in the near future in order to test this hypothesis.

(18) The coordination chemistry with Ln(NO₃)₃·xH₂O was examined for Ln = Pr, Nd, Eu, Er, Yb. Only the Nd and Er complexes were fully characterized.

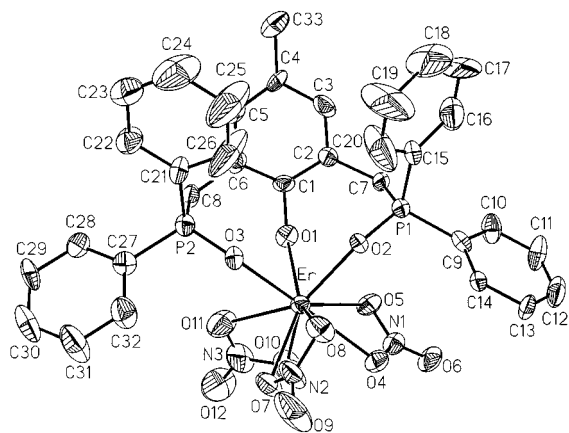


Figure 1. Molecular structure and atom-labeling scheme for $[\text{Er}(\mathbf{2c})(\text{NO}_3)_3] \cdot \text{Me}_2\text{CO}$ (30% thermal ellipsoids).

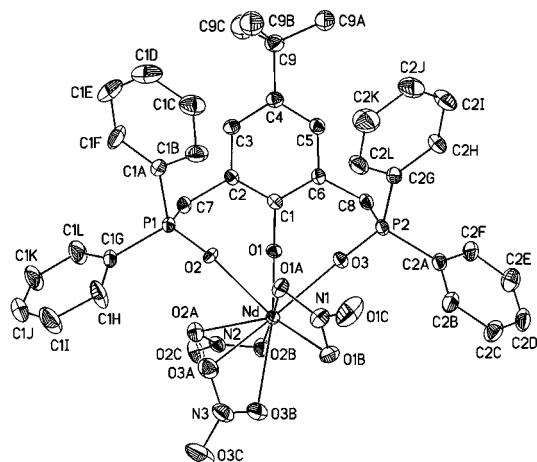


Figure 2. Molecular structure and atom-labeling scheme for $[\text{Nd}(\mathbf{2d})(\text{NO}_3)_3] \cdot \text{Me}_2\text{CO}$ (30% thermal ellipsoids).

the formation of 2:1 complexes. Two of the complexes, $[\text{Er}(\mathbf{2c})(\text{NO}_3)_3] \cdot \text{Me}_2\text{CO}$ and $[\text{Nd}(\mathbf{2d})(\text{NO}_3)_3] \cdot \text{Me}_2\text{CO}$, have been structurally characterized by single-crystal X-ray diffraction methods. Views of the molecules are shown in Figures 1 and 2, and selected bond distances are summarized in Table 2. Both complexes show the central lanthanide ion bonded to a neutral, tridentate bis(phosphinomethyl)phenol P,P' -dioxide ligand and to three bidentate nitrate ions. For the smaller Er(III) ion ($r = 1.00 \text{ \AA}$, coordination number (CN) = VIII),¹⁹ **2c** and the nitrate ions provide nine oxygen atoms that form a nine-vertex inner-sphere coordination polyhedron. The larger Nd(III) ion ($r = 1.12 \text{ \AA}$, CN = VIII)¹⁹ accommodates one **2d** ligand, three bidentate nitrate ions, and an O-bonded acetone molecule in the inner sphere. This results in a ten-vertex coordination polyhedron. The two Er–O(P) distances, 2.266(5) \AA , are shorter than the Nd–O(P) distances, 2.359(4) and 2.370(5) \AA . This is expected given the ionic radius differences between the central ions.

The refinements for the two X-ray data sets resolve the phenol O–H atom positions confirming that **2c** and **2d** act as neutral chelate ligands. The presence of three inner-sphere nitrate ions

in each complex provides the charge balance for the Ln(III) ions. This noted, it is interesting that the difference in M–O(C)_{phenol} distances in the two complexes, Nd–O(C) 2.635(5) \AA and Er–O(C) 2.386(6) \AA , $\Delta = 0.249 \text{ \AA}$, is much greater than the difference in lanthanide ionic radii, 0.12 \AA , suggesting that **2d** may not be as tightly bound to Nd(III) through the phenol functional group. A similar trend is reflected in a shorter C(1)–O(1) distance, 1.387(7) \AA , in the Nd complex compared to 1.438(10) \AA in the Er complex. This probably results from the competitive inner-sphere interaction with the acetone oxygen atom: Nd–O(acetone), 2.472(9) \AA . The acetone also impacts the size of the tridentate ligand “footprint” in the two complexes which can be assessed by comparison of nonbonded O \cdots O separations: Nd(**2d**), O(1) \cdots O(2) 2.932 \AA , O(1) \cdots O(3) 2.873 \AA , O(2) \cdots O(3) 3.421 \AA ; Er(**2c**), O(1) \cdots O(2) 2.934 \AA , O(1) \cdots O(3) 2.913 \AA , O(2) \cdots O(3) 3.142 \AA . These data indicate that inclusion of the acetone oxygen atom in the inner sphere of $[\text{Nd}(\mathbf{2d})(\text{NO}_3)_3] \cdot \text{Me}_2\text{CO}$ results in an expansion of the **2d** ligand footprint.

It is possible to compare these findings with structural data for related 1:1 complexes containing ligands of type **1**: Nd(**1a**)(NO₃)₃ and Er(**1a**)(NO₃)₃ (**1a** = **1** with R = Ph, Bz and R' = H).²⁰ These complexes are isostructural, with CN = 9, and there is no additional solvent molecule in the inner sphere of the Nd(III). The inner-sphere M–O bond lengths are Nd–O(P) 2.390(3) \AA , 2.378(3) \AA , Nd–O(N) 2.382(3) \AA and Er–O(P) 2.280(7) \AA , 2.281(6) \AA , Er–O(N) 2.278(7) \AA . Once more, the shorter M–O(P) distances in the Er complex compared to the Nd complex are consistent with the ionic radius difference between Er(III) and Nd(III). Further, the Nd–O(N) distance is significantly shorter than the Nd–O(C)_{phenol} distance which parallels the anticipated weaker Lewis basicity of a phenol oxygen atom relative to a pyridine *N*-oxide oxygen atom. The ligand “footprint” for **1a** in these two complexes also do not show the distortion found in the $[\text{Nd}(\mathbf{2d})(\text{NO}_3)_3] \cdot \text{Me}_2\text{CO}$ complex: Nd(**1a**)O(1) \cdots O(2) 2.991 \AA , O(1) \cdots O(3) 3.040 \AA , O(2) \cdots O(3) 3.389 \AA ; Er(**1a**)O(1) \cdots O(2) 2.900 \AA , O(1) \cdots O(3) 2.961 \AA , O(2) \cdots O(3) 3.239 \AA .

It is also worth noting that the phenol group hydrogen atoms in both structures are involved in hydrogen-bonding schemes. In the structure containing the Nd (**2d**) unit, a pair of molecules hydrogen bond about a center of symmetry with the phenolic H atom in one molecule interacting with the terminal oxygen atom, O(2C'), of a Nd(III) coordinated nitrate ion in a second molecule. The resulting nonbonded O(1) \cdots O(2C') distance is 2.698 \AA , and the O(1)H \cdots O(2C') angle is 151.2°. In the structure containing the Er (**2c**) unit, the phenol O–H group hydrogen bonds to the outer sphere acetone C=O group, resulting in a nonbonded separation O(1) \cdots O(13), 2.601 \AA , and O(1)–H \cdots O(13) angle, 178.1°. In addition, there appears to be a weak hydrogen bond between the methylene hydrogen atoms on C(7) and the terminal nitrate oxygen atom O(9) resulting in a nonbonded separation C(7) \cdots O(9), 3.153 \AA and O(9) \cdots H–C(7) angle, 164.0°. For comparison, the sum of O and C van der Waal distances is 3.25 \AA . These interactions result in formation of chains along the *z* axis. The suggested H-bonding of the methylene hydrogens is consistent with the observed acidity of this center.²¹

Conclusion

Although the picture is still evolving, the ligands **1**, **2**, and **3** appear to display both similarities and interesting differences

(19) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1970**, *B26*, 1076. The effective ionic radii selected from Table 1(a) in this reference are the “IR” values or effective ionic radii based on $r(\text{VI}\text{O}^{2-}) = 1.40 \text{ \AA}$. The values for CN = 8 are quoted here since a value for Er(III) CN = 9 is not provided in the reference. One also could consider the CR or crystal radii based upon $r(\text{VI}\text{F}^-) = 1.19 \text{ \AA}$: Er(III), $r = 1.14 \text{ \AA}$, CN = 8; Nd(III), $r = 1.26 \text{ \AA}$, CN = 8. In either case, Er(III) is smaller.

(20) Gan, X.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.*, accepted for publication.

(21) Wen, Y.; Gan, X.; Bond, E. M.; Paine, R. T. To be published.

in chelation properties toward Ln(III) ions. For example, the fact that all three ligands chelate with identical ligand backbone geometries suggests that all coordinate in a relatively strain free condition. However, at this point it is not clear why **2** does not produce 2:1 complexes that can be isolated as found for **1** and **3**. It is also apparent that variations in R and X on **4** lead to subtle differences in the ligand footprints adapted by **1–3** on Ln(III) ions. It will be very informative to determine if these variations are reflected in thermodynamic binding constants. Solution microcalorimetric analyses will be undertaken in the near future to probe for these features. We will also soon report

on the nature of complexation studies with related ligands **4** with Y = S.

Acknowledgment. Financial support for this study came from the U.S. Department of Energy, Office of Basic Energy Sciences, Grant No. DE-FG03-94ER14446.

Supporting Information Available: ¹H and ¹³C NMR data for the ligands and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0107633