

Monodentate Coordination by a Tripodal Ligand System: Synthesis and Crystal and Molecular Structure of Bis[diisopropyl [1,2-bis(diethylcarbamoyl)ethyl]phosphonate]erbium(III) Nitrate Monohydrate

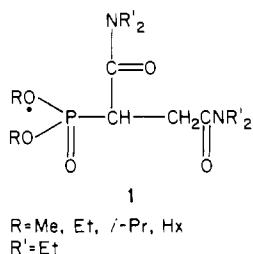
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Bis[diisopropyl [1,2-bis(diethylcarbamoyl)ethyl]phosphonate]erbium(III) nitrate monohydrate, $\text{Er}(\text{NO}_3)_3[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}[\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2][\text{CH}_2\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]]_2 \cdot \text{H}_2\text{O}$, has been prepared from the trifunctional phosphonate ligand and $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in ethanol. The complex has been characterized by infrared and NMR spectroscopy and single-crystal X-ray diffraction analysis. The complex was found to crystallize in the monoclinic space group $P2_1/n$ with $a = 13.438(2) \text{ \AA}$, $b = 22.022(4) \text{ \AA}$, $c = 19.596(5) \text{ \AA}$, $\beta = 106.21(2)^\circ$, $Z = 4$, $V = 5568(2) \text{ \AA}^3$, and $\rho_{\text{calcd}} = 1.38 \text{ g cm}^{-3}$. The structure was solved by heavy-atom techniques, and blocked least-squares refinement converged with $R_F = 5.32\%$ and $R_{wF} = 4.09\%$ on 5632 unique reflections with $F \geq 5\sigma(F)$. The structure contains an Er(III) ion bonded to the oxygen atom of a water molecule, oxygen atoms of three bidentate nitrate ions, and the phosphoryl oxygen atoms of two of the potentially tripodal ligand $(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}[\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2][\text{CH}_2\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]$. The overall erbium ion coordination number is 9. Two of the four carbonyl oxygen atoms are hydrogen bonded with the coordinated water molecule, while the remaining two carbonyl oxygen atoms remain uncoordinated. Several important bond distances include $\text{Er}-\text{O}(\text{phosphoryl})_{\text{av}} = 2.284(5) \text{ \AA}$, $\text{Er}-\text{O}(\text{nitrate})_{\text{av}} = 2.431(6) \text{ \AA}$, $\text{Er}-\text{O}(\text{water}) = 2.326(5) \text{ \AA}$, $\text{P}-\text{O}(\text{phosphoryl})_{\text{av}} = 1.472(5) \text{ \AA}$, and $\text{C}-\text{O}(\text{carbonyl})_{\text{av}} = 1.231(10) \text{ \AA}$. On the basis of the structural analysis it is tentatively concluded that the ligand arms are not optimally constructed to achieve tripodal coordination on Er(III), and it is anticipated that the liquid-liquid extraction coefficients may not be significantly larger than those found for bifunctional (carbamoylmethyl)phosphonates.

Introduction

Extensive examinations of the liquid-liquid extraction properties of bifunctional (carbamoylmethyl)phosphonates (CMP's), $(\text{RO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NR}_2$, have shown that these compounds act as unique extractants for trivalent lanthanide and actinide ions.¹⁻³ Chemical and structural studies in our laboratory⁴ of isolated coordination complexes formed by lanthanides, Th(IV), and UO_2^{2+} with CMP ligands suggest that improved extractants might be found in new families of properly constructed multifunctional ligands containing combinations of phosphoryl and carbonyl coordination sites. With a goal of developing new selective extractants in mind, we have set out to prepare ligand types with three to six carbonyl and phosphoryl coordination positions. On the basis of our initial synthetic efforts we have reported the synthesis of a family of dialkyl [1,2-bis(diethylcarbamoyl)ethyl]phosphonates (**1**), which can be considered to be trifunctional



relatives of the CMP ligands.⁵ The coordination chemistry of these ligands is now under study with primary objectives being to determine the denticity and coordination geometries favored by the ligands and to determine how the ligands might be further modified to enhance their extraction behavior. We report here the formation and molecular structure determination for the

coordination complex formed by **1c** (R = *i*-Pr) and a late lanthanide, Er(III).

Experimental Section

General Information. The trifunctional ligand $(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}[\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2][\text{CH}_2\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]$ (**1c**) was prepared as described in the literature.⁵ $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was obtained from Alfa Products (Ventron). Infrared spectra were recorded on a Nicolet Model 6000 Fourier transform spectrometer, and samples were prepared as KBr pellets or in benzene solution. NMR spectra were recorded on Varian FT-80 or Nicolet 360 MHz spectrometers operating at 32.2 or 141.8 MHz (^{31}P) and at 20.0 MHz (^{13}C). Spectral standards were 85% H_3PO_4 (^{31}P) and Me_4Si (^{13}C).

Preparation of 2. The complex was prepared by addition of 4.1 mmol of **1c** in 20 mL of ethanol to 2.0 mmol of $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ dissolved in 20 mL of ethanol. The resulting solution was allowed to evaporate, and the solid product was washed with two portions (10 mL) of hexane. The product was recrystallized from ethanol by slow evaporation, and lilac-colored crystals suitable for single-crystal X-ray analysis were obtained. Anal. Calcd for $\text{ErP}_2\text{O}_{20}\text{N}_7\text{C}_{36}\text{H}_{76}$: C, 37.40; H, 6.62. Found: C, 37.30; H, 6.71. Infrared spectrum (cm^{-1}): KBr pellet 1642 (ν_{CO} , s), 1611 (ν_{CO} , s), 1214 (ν_{PO} , s), 1198 (ν_{PO} , s), 1003 (ν_{POC} , s); benzene 1645 (s), 1615 (s, sh), 1215 (s), 1006 (s). NMR spectra (27 °C): $^{31}\text{P}\{^1\text{H}\}$ (D_2O solvent) δ 17.8; $^{13}\text{C}\{^1\text{H}\}$ δ 74.6 ($J_{\text{PC}} = 6.1 \text{ Hz}$, $(\text{CH}_3)_2\text{CHO}$), 44.1 (NCH_2), 43.4 (NCH_2), 43.3 (NCH_2), 43.1 (NCH_2), 30.0 ($\text{C}(\text{O})\text{CH}_2\text{CH}$), 25.9 m ($(\text{CH}_3)_2\text{CHO}$), 15.6 (NCH_2CH_3), 15.1 (NCH_2CH_3), 14.9 (NCH_2CH_3), 14.6 (NCH_2CH_3). The crystalline solid is soluble in ethanol, water, diethyl ether, tetrahydrofuran, and methylene chloride.

Crystallographic Measurements and Structure Solution. A suitable crystal (0.32 × 0.41 × 0.41 mm) approximately shaped as a hexagonal prism bounded by 100, 010, 011, and 001 faces was sealed in a glass capillary with a minute amount of mother liquor. The crystal was centered on a Syntex P3/F automated diffractometer, and determinations of crystal class, orientation matrix, and unit cell dimensions were performed in a standard manner.⁶ Data were collected at 20 °C in the Ω scan mode with use of $\text{Mo K}\alpha$ radiation, a scintillation counter, and pulse height analyzer. The data collection parameters are summarized in Table I. Examination of collected reflections indicated the space group to be $P2_1/n$ (variation No. 14, C_2^2).⁶ A small correction for absorption was made empirically on the basis of Ψ scans, and the agreement factors before and after the absorption correction were 2.23 and 1.79%.⁷ The estimated maximum and minimum transmissions were 0.235 and 0.204. Redundant and equivalent data were averaged and converted to unscattered $|F_o|$ values after corrections for Lorentz and polarization effects.

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- (2) Schulz, W. W.; McIsaac, L. D. "Transplutonium Elements"; Müller, W., Lindner, R., Eds.; North-Holland Publishing Co.: Amsterdam, 1976; p 433.
- (3) Schulz, W. W.; McIsaac, L. D. "Recent Developments in Separation Science"; Li, N. N. Ed.; CRC Press: Boca Raton, FL, 1982; Vol. VII, p 31.
- (4) (a) Bowen, S. M.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1982**, *21*, 261. (b) Bowen, S. M.; Duesler, E. N.; Paine, R. T. *Inorg. Chim. Acta* **1982**, *61*, 155. (c) Bowen, S. M.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1983**, *22*, 286. (d) Bowen, S. M.; Duesler, E. N.; Paine, R. T. *Inorg. Chim. Acta* **1984**, *84*, 221.
- (5) McCabe, D. J.; Bowen, S. M.; Paine, R. T., submitted for publication.

(6) Space group symmetry notation as given in: "International Tables for X-ray Crystallography"; D. Reidel Publishing Co.; Dordrecht, Holland, 1983; Vol. I, pp 73-346.

(7) The empirical absorption correction uses an ellipsoidal model fitted to azimuthal scans and then applied to the intensity data.

Table I. Experimental Data for the X-ray Diffraction Study of $\text{Er}(\text{NO}_3)_3[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}[\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2][\text{CH}_2\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]]_2 \cdot \text{H}_2\text{O}$

(A) Crystal Parameters at 20 (2) °C	
cryst syst: monoclinic	mol wt = 1156.24
space group: $P2_1/n$	$V = 5568 (2) \text{ \AA}^3$
$a = 13.438 (2) \text{ \AA}$	$\rho_{\text{calcd}} = 1.38 \text{ g cm}^{-3}$
$b = 22.022 (4) \text{ \AA}$	$\mu = 16.9 \text{ cm}^{-1}$
$c = 19.596 (5) \text{ \AA}$	$F(000) = 2396$
$\beta = 106.21 (2)^\circ$	
$Z = 4$	
(B) Data Collection	
diffractometer: Syntex P3/F	
radiation: Mo $K\alpha$ ($\lambda = 0.71069 \text{ \AA}$)	
monochromator: highly oriented graphite cryst	
reflens measd: $+h, -k, \pm l$	
2θ range: $1\text{--}55^\circ$	
scan type: Ω	
scan speed: $4\text{--}30^\circ \text{ min}^{-1}$	
scan range: $(\omega_0 - 0.65)\text{--}(\omega_0 + 0.7)^\circ$	
bkgd measurement: stationary cryst and counter; at the beginning and end of Ω scan, each for one-fourth of the total Ω scan time	
std reflens: 3 measd every 141 reflens [4,0,0; 0,8,0; 0,0,10]; no signif changes in intens obsd	
total reflens collected: 13 709	
unique reflens collected: 12 805	
obsd reflens used in refinement: 5632 with $F \geq 5\sigma(F)$	
weighting scheme: $1/[\sigma(F)^2 + gF^2]$, $g = 0.00030$	
no. of parameters: 595	

All calculations were performed with the R3/SHELXTL structure determination package.⁸ Least-squares refinements in this package use a blocked-cascade algorithm with full-matrix blocks of 103 parameters.⁹ The Er atom was located by Patterson methods, and subsequent difference Fourier maps revealed the remaining non-hydrogen atoms. Isotropic refinement on all non-hydrogen atoms gave $R_F = 9.0\%$. The thermal parameters of C(14), C(15), C(17), C(18), C(27), C(28), C(35), C(36), and O(13) were large ($U_{\text{iso}} > 0.14 \text{ \AA}^2$). These atoms were removed and a d map was examined for signs of possible multiply occupied sites. The difference maps, however, indicated only diffuse electron density with one apparent center. These atoms were put back in the previously determined positions, and all atoms were refined anisotropically. The agreement factor after several cycles of least-squares refinement was $R_F = 6.02\%$. The hydrogen atoms were included in fixed positions ($\text{C-H} = 0.96 \text{ \AA}$) and their isotropic thermal parameters U_{iso} fixed at 1.2 times the last U_{equiv} of the parent carbon atom. Final refinements converged at $R_F = 5.32\%$ and $R_{wF} = 4.09\%$. A final difference map showed no residual electron density greater than 0.6 e \AA^{-3} . The highest three peaks were close to the Er atom ($<1.15 \text{ \AA}$). The observed and calculated structure factor amplitudes (Table S-1), hydrogen atoms positions (Table S-2), anisotropic thermal parameters (Table S-3), and full listings of all bond angles (Table S-4) are available in the supplementary material. The non-hydrogen atom positional parameters are listed in Table II.

Results and Discussion

When combined in ethanol, $\text{Er}(\text{NO}_3)_3$ and the trifunctional ligand **1** form a complex, **2**, which was isolated as a lilac-colored solid by evaporation of the solvent. Elemental analyses are consistent with the composition $\text{Er}(\text{NO}_3)_3(\mathbf{1})_2 \cdot \text{H}_2\text{O}$. The infrared spectrum of **2** in benzene solution shows absorptions at 1645, 1615, and 1215 cm^{-1} . These frequencies can be compared with bands for the free ligand, **1**, in benzene solution, 1647 and 1258 cm^{-1} ,

Table II. Fractional Coordinates and Their Esd's for $\text{Er}(\text{NO}_3)_3[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}[\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2][\text{CH}_2\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]]_2 \cdot \text{H}_2\text{O}$

atom	x/a	y/b	z/c
Er(1)	0.21936 (3)	0.12097 (2)	0.83983 (2)
P(1)	-0.06893 (14)	0.11791 (11)	0.76312 (10)
O(1)	0.0434 (3)	0.1184 (2)	0.7968 (2)
O(2)	-0.1291 (4)	0.0785 (3)	0.8035 (3)
O(3)	-0.1198 (4)	0.1813 (2)	0.7540 (3)
O(4)	0.0219 (4)	0.1262 (3)	0.6215 (3)
O(5)	-0.2032 (4)	0.0009 (3)	0.5789 (3)
N(1)	-0.1345 (5)	0.1690 (3)	0.5817 (3)
N(2)	-0.0632 (4)	-0.0588 (3)	0.5923 (3)
C(1)	-0.1051 (5)	0.0887 (3)	0.6742 (4)
C(2)	-0.0684 (6)	0.1298 (4)	0.6239 (4)
C(3)	-0.0579 (6)	0.0251 (3)	0.6739 (4)
C(4)	-0.1133 (6)	-0.0121 (3)	0.6104 (4)
C(5)	-0.0954 (7)	0.2086 (4)	0.5343 (5)
C(6)	-0.0385 (8)	0.2594 (5)	0.5735 (6)
C(7)	-0.2441 (6)	0.1776 (4)	0.5793 (5)
C(8)	-0.3159 (6)	0.1491 (5)	0.5148 (5)
C(9)	0.0469 (6)	-0.0727 (4)	0.6240 (4)
C(10)	0.1153 (7)	-0.0434 (4)	0.5854 (5)
C(11)	-0.1178 (7)	-0.0966 (4)	0.5321 (5)
C(12)	-0.1498 (9)	-0.1548 (4)	0.5553 (7)
C(13)	-0.0906 (7)	0.0438 (4)	0.8681 (4)
C(14)	-0.1553 (11)	-0.0106 (6)	0.8627 (7)
C(15)	-0.0901 (10)	0.0783 (5)	0.9284 (5)
C(16)	-0.0993 (7)	0.2292 (4)	0.8089 (6)
C(17)	-0.1972 (9)	0.2323 (5)	0.8318 (7)
C(18)	-0.0863 (11)	0.2838 (4)	0.7775 (8)
P(2)	0.47817 (15)	0.07192 (9)	0.82154 (11)
O(6)	0.3768 (3)	0.0861 (2)	0.8332 (2)
O(7)	0.4925 (4)	0.0036 (2)	0.8067 (3)
O(8)	0.5728 (3)	0.0912 (2)	0.8841 (2)
O(9)	0.3481 (3)	0.0966 (2)	0.6595 (2)
O(10)	0.5849 (5)	0.1869 (3)	0.6684 (4)
N(3)	0.4847 (4)	0.0507 (3)	0.6381 (3)
N(4)	0.4934 (6)	0.2694 (3)	0.6808 (4)
C(19)	0.5060 (5)	0.1101 (3)	0.7485 (4)
C(20)	0.4416 (5)	0.0852 (3)	0.6774 (4)
C(21)	0.4865 (6)	0.1780 (3)	0.7510 (4)
C(22)	0.5244 (7)	0.2127 (4)	0.6961 (5)
C(23)	0.5956 (5)	0.0374 (4)	0.6501 (4)
C(24)	0.6269 (7)	-0.0237 (4)	0.6840 (5)
C(25)	0.4169 (6)	0.0299 (4)	0.5697 (4)
C(26)	0.4096 (7)	0.0783 (5)	0.5139 (5)
C(27)	0.5427 (9)	0.3054 (5)	0.6350 (6)
C(28)	0.4888 (11)	0.2940 (7)	0.5667 (8)
C(29)	0.4210 (8)	0.2995 (4)	0.7124 (6)
C(30)	0.3089 (9)	0.2916 (5)	0.6700 (6)
C(31)	0.4251 (7)	-0.0464 (4)	0.8113 (5)
C(32)	0.3648 (8)	-0.0602 (5)	0.7373 (6)
C(33)	0.4908 (9)	-0.0984 (4)	0.8441 (6)
C(34)	0.5736 (6)	0.0983 (4)	0.9575 (4)
C(35)	0.6328 (9)	0.1528 (6)	0.9808 (7)
C(36)	0.6315 (1)	0.0476 (7)	0.9968 (6)
N(5)	0.1652 (6)	-0.0036 (3)	0.8411 (5)

and in a melted, thin-film sample, 1645 and 1259 cm^{-1} . The bands in the region $1647\text{--}1615 \text{ cm}^{-1}$ are tentatively assigned as carbonyl stretching modes while the bands in the region $1259\text{--}1215 \text{ cm}^{-1}$ are assigned to the phosphoryl stretching modes.¹⁰ These data indicate coordination shifts of $\Delta\nu_{\text{CO}} = 0\text{--}2$ and $32\text{--}30 \text{ cm}^{-1}$ and $\Delta\nu_{\text{PO}} = 44\text{--}43 \text{ cm}^{-1}$.

It is instructive to compare the results given above with infrared data for the related bifunctional CMP ligand $(i\text{-PrO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NET}_2$ (**3**) and its Er(III) complex **4**,^{4b} $\text{Er}(\text{NO}_3)_3[(i\text{-PrO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NET}_2]_2 \cdot \text{H}_2\text{O}$: **3**, $\nu_{\text{CO}} = 1648 \text{ cm}^{-1}$, $\nu_{\text{PO}} = 1253 \text{ cm}^{-1}$; **4**, $\nu_{\text{CO}} = 1621 \text{ cm}^{-1}$, $\nu_{\text{PO}} = 1207 \text{ cm}^{-1}$; $\Delta\nu_{\text{CO}} = -27 \text{ cm}^{-1}$, $\Delta\nu_{\text{PO}} = -46 \text{ cm}^{-1}$. The coordination shifts from **3** to **4** suggested the presence of a strong Er-O(phosphoryl) interaction and a weaker carbonyl oxygen atom interaction. Subsequent single-

(8) Sheldrick, G. M. "Nicolet SHELXTL Operations Manual"; Nicolet XRD Corp.: Cupertino, CA, 1981. SHELXTL uses absorption, anomalous dispersion, and scattering data compiled in: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 55-60, 99-101, 149-150. Anomalous dispersion terms were included for all atoms with atomic numbers greater than 2. Corrections for extinction were not found to be necessary, and none were made.

(9) A general description of the least-squares algebra is found in: Ahmed, F. R.; Hall, S. R.; Huber, C. P., Eds. "Crystallographic Computing"; Munksgaard Publishing Co.: Copenhagen, 1970; p 187. The least-squares refinement minimizes $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F)^2 + gF^2]$ and $g = 0.0003$, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_{wF} = [\sum (|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$, and $\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$ where NO = number of observations and NV = number of variables.

(10) The infrared spectrum of **2** obtained from a KBr pellet shows bands at 1642, 1611, 1214, and 1198 cm^{-1} . The origin of the "splitting" of the phosphoryl absorption is not known at this time.

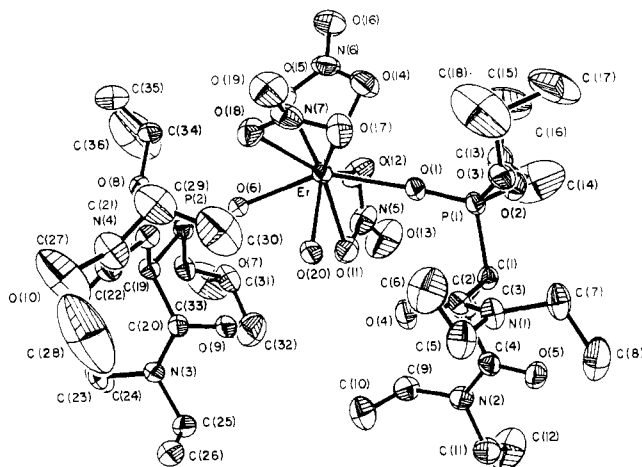


Figure 1. Molecular geometry and atom-labeling scheme for $\text{Er}(\text{NO}_3)_3[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}[\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2][\text{CH}_2\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]]_2\cdot\text{H}_2\text{O}$ (25% probability ellipsoids).

crystal X-ray diffraction analysis revealed that the bifunctional CMP ligands in **4** are directly bonded to Er(III) through the phosphoryl oxygen atoms while the carbonyl oxygen atoms are hydrogen bonded to a water molecule that is oxygen atom bonded to the Er ion. In the light of these results the infrared spectrum of **2** suggests that the phosphoryl group is directly bonded to the Er(III) and that there are two nonequivalent carbonyl group environments. One carbonyl group may be completely uninvolved in a coordination interaction with Er(III) ($\nu_{\text{CO}} = 1645 \text{ cm}^{-1}$, $\Delta\nu_{\text{CO}} = 0\text{--}2 \text{ cm}^{-1}$) while the second carbonyl group may be directly bonded to the Er(III) ion or hydrogen bonded to a coordinated water molecule ($\nu_{\text{CO}} = 1615 \text{ cm}^{-1}$, $\Delta\nu_{\text{CO}} = 32\text{--}30 \text{ cm}^{-1}$).

Attempts to detect two nonequivalent carbonyl groups for **2** by ^{13}C NMR spectroscopy have not yet been successful; however, the ^{13}C resonances for the remaining carbon atoms in the coordinated ligand have been observed and assigned. It should be noted that the carbamide alkyl group carbon atoms each show a distinct resonance which must result from restricted rotation about the $(\text{O})\text{C}\text{--}\text{N}(\text{Et})_2$ bonds. The ^{31}P NMR spectrum shows a single, broadened resonance, 17.8 ppm, upfield of the singlet observed for the free ligand, 22.7 ppm.

The present single-crystal X-ray diffraction structure determination verifies the composition and establishes the molecular structure of **2** in the solid state. The structure contains discrete monomeric units with four molecules per unit cell. A view of the molecule is shown in Figure 1, and a list of bond distances is given in Table III. It is immediately apparent that the structure of **2** is related to the structure of **4**.^{4b} The erbium atom in **2** has a nine-coordinate tricapped-trigonal-bipyramid coordination polyhedron derived from bonding interactions with three bidentate nitrate ions, one water molecule, and two phosphoryl oxygen atoms from two *monodentate* trifunctional ligands, **1**. The Er–O (phosphoryl) distances, 2.279 (4) and 2.289 (5) Å, compare favorably with the related distances in **4**, 2.290 (6) and 2.259 (6) Å. Examination of the positions of the four carbonyl functional groups reveals that the “short-leg” carbonyls, C(2)–O(4) and C(20)–O(9), point in the direction of the metal atom while the “long-leg” carbonyl groups, C(4)–O(5) and C(22)–O(10), point away from the metal atom. Nonetheless, as found in **4**, even the short-leg carbonyl groups have Er...O separations greater than 4.0 Å. Consequently, none of the carbonyl oxygen atoms are directly bonded to the Er atom. The Er–O(water) distance, Er–O(20), is 2.326 (5) Å, which is slightly longer than the related distance in **4**, 2.302 (7) Å, and similar to the distances in $\text{Er}_2(\text{C}_2\text{O}_2\text{H}_3)_6\cdot 4\text{H}_2\text{O}$,¹¹ 2.30–2.31 Å. The water hydrogen atoms were not precisely located in **2**; however, the O...O separations O(4)...O(20) = 2.689 Å and O(9)...O(20) = 2.653 Å and angles

Table III. Bond Distances (Å) for $\text{Er}(\text{NO}_3)_3[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}[\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2][\text{CH}_2\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]]_2\cdot\text{H}_2\text{O}$

Er(1)–O(1)	2.279 (4)	Er(1)–O(6)	2.289 (5)
Er(1)–N(5)	2.839 (8)	Er(1)–O(11)	2.473 (6)
Er(1)–O(12)	2.433 (6)	Er(1)–N(6)	2.839 (9)
Er(1)–O(14)	2.403 (7)	Er(1)–O(15)	2.421 (5)
Er(1)–N(7)	2.860 (7)	Er(1)–O(17)	2.427 (6)
Er(1)–O(18)	2.429 (5)	Er(1)–O(20)	2.326 (5)
P(1)–O(1)	1.469 (4)	P(1)–O(2)	1.546 (6)
P(1)–O(3)	1.544 (6)	P(1)–C(1)	1.792 (7)
O(2)–C(13)	1.444 (9)	O(3)–C(16)	1.475 (11)
O(4)–C(2)	1.231 (9)	O(5)–C(4)	1.228 (8)
N(1)–C(2)	1.344 (9)	N(1)–C(5)	1.474 (12)
N(1)–C(7)	1.472 (10)	N(2)–C(4)	1.331 (10)
N(2)–C(9)	1.468 (9)	N(2)–C(11)	1.463 (10)
C(1)–C(2)	1.518 (11)	C(1)–C(3)	1.538 (9)
C(3)–C(4)	1.503 (10)	C(5)–C(6)	1.449 (13)
C(7)–C(8)	1.497 (12)	C(9)–C(10)	1.491 (14)
C(11)–C(12)	1.465 (14)	C(13)–C(14)	1.467 (16)
C(13)–C(15)	1.402 (14)	C(16)–C(17)	1.506 (18)
C(16)–C(18)	1.384 (15)	P(2)–O(6)	1.476 (5)
P(2)–O(7)	1.555 (5)	P(2)–O(8)	1.559 (4)
P(2)–C(19)	1.786 (8)	O(7)–C(31)	1.444 (10)
O(8)–C(34)	1.444 (9)	O(9)–C(20)	1.232 (8)
O(10)–C(22)	1.234 (13)	N(3)–C(20)	1.325 (11)
N(3)–C(23)	1.471 (10)	N(3)–C(25)	1.468 (9)
N(4)–C(22)	1.324 (12)	N(4)–C(27)	1.484 (16)
N(4)–C(29)	1.451 (15)	C(19)–C(20)	1.523 (9)
C(19)–C(21)	1.521 (9)	C(21)–C(22)	1.519 (13)
C(23)–C(24)	1.508 (11)	C(25)–C(26)	1.510 (13)
C(27)–C(28)	1.355 (17)	C(29)–C(30)	1.514 (14)
C(31)–C(32)	1.482 (14)	C(31)–C(33)	1.479 (13)
C(34)–C(35)	1.443 (16)	C(34)–C(36)	1.453 (17)
N(5)–O(11)	1.245 (12)	N(5)–O(12)	1.225 (10)
N(5)–O(13)	1.217 (10)	N(6)–O(14)	1.255 (10)
N(6)–O(15)	1.266 (12)	N(6)–O(16)	1.205 (12)
N(7)–O(17)	1.244 (10)	N(7)–O(18)	1.281 (9)
N(7)–O(19)	1.205 (9)		

Er–O(20)–O(4) = 120.7°, Er–O(20)–O(9) = 123.1°, and O(4)–O(20)–O(9) = 106.7° are consistent with water hydrogen-bonding interactions with the two short-leg carbonyl oxygen atoms, O(4) and O(9). This type of interaction has already been demonstrated in the structure of **4**, and the intermediate magnitude of the $\Delta\nu_{\text{CO}}$ shift (35–32 cm^{-1}) for one carbonyl infrared band of **2** is consistent with the hydrogen-bonding assignment. The Er–O(nitrate) bond distances range from 2.473 (6) to 2.403 (7) Å (average 2.431 Å). These distances are normal and similar to those found in **4**.

Bond distances along the ligand backbone also can be compared with related distances found in **4**.^{4b} In particular, the C–O (carbonyl) distances, C(2)–O(4) = 1.231 (9) Å, C(4)–O(5) = 1.228 (8) Å, C(20)–O(9) = 1.232 (8) Å, and C(22)–O(10) = 1.234 (13) Å, are essentially identical, and they compare with the distances in **4**, 1.239 (11) and 1.240 (11) Å. The P–O (phosphoryl) distances in **2**, P(1)–O(1) = 1.469 (4) Å and P(2)–O(6) = 1.476 (5) Å, also are similar to those in **4**, 1.479 (6) and 1.452 (7) Å.

On the basis of the structural studies of **2** and **4**^{4b} it is appropriate to briefly speculate on the relative abilities of the bifunctional (**3**) and trifunctional (**1**) ligands to extract Ln(III) and An(III) ions from acidic aqueous solutions. It is already well-known that the bifunctional ligands are excellent Ln and An ion extractants.^{2,12} The composition, $\text{Ln}(\text{NO}_3)_3(\text{L})_2\cdot\text{H}_2\text{O}$, and structural similarities in the solid state between **2** and **4** initially suggest that the ligands might have similar liquid–liquid extraction power. Supporting this conclusion, infrared spectra for the complexes in benzene solution display similar coordination shifts, $\Delta\nu_{\text{PO}}$ and $\Delta\nu_{\text{CO}}$. One might also conclude that the proposed “buffering effect”¹² of the carbamide group in **3** might be greater in **1**, and this in turn might result in improved extraction power for **1**. On the other hand, the observation that the “long-arm” carbamide group does not

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coordinate with Er(III) may indicate that this ligand is not optimally constructed and, in fact, the ligand may not be as good of an extractant as the bifunctional CMP ligands. Characterization of that extraction chemistry is in progress in collaboration with co-workers at Los Alamos National Laboratories. In addition, efforts are under way to isolate and structurally characterize complexes of **1** containing early lanthanides, as well as two metal centers. The structure of **2** and the propensity for high coordination numbers for Ln(III) ions also suggest that ligands containing additional methylene groups, $(\text{CH}_2)_x$ ($x = 2, 3$), in the long-leg carbamide group may prove to have useful multidentate coordination properties.

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Supplementary Material Available: Listings of structure factors, hydrogen atom positional parameters, and thermal parameters and a full listing of bond angles (36 pages). Ordering information is given on any current masthead page.

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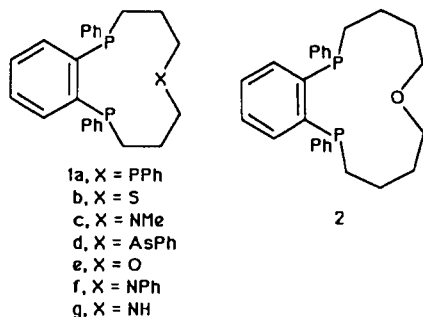
Structural Characterization of Tridentate 11-Membered Phosphino Macrocyclic Complexes of Transition Metals. Examples of Octahedral, Square-Pyramidal, and Tetrahedral Geometries¹

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Three structures of 11-membered phosphino macrocyclic complexes of transition metals have been determined: tri(carbonyl- κ C)[*meso-cis*-6-methyl-2,10-diphenyl-6-aza- κ N-2,10-diphospha- κ^2 P-bicyclo[9.4.0]pentadeca-11(1),12,14-triene]molybdenum(0) (**3a**, $\text{C}_{28}\text{H}_{29}\text{MoNO}_3\text{P}_2 \cdot 0.5\text{C}_6\text{H}_5\text{CH}_3$), tri(carbonyl- κ C)[*meso-cis*-2,6,10-triphenyl-2,6,10-triphospha- κ^3 P-bicyclo[9.4.0]pentadeca-11(1),12,14-triene]tungsten(0) (**3b**, $\text{C}_{33}\text{H}_{31}\text{O}_3\text{P}_3\text{W}$), and dichloro[*meso-cis*-2,10-diphenyl-6-aza- κ N-2,10-diphospha- κ^2 P-bicyclo[9.4.0]pentadeca-11(1),12,14-triene]nickel(II) (**4**, $\text{C}_{24}\text{H}_{27}\text{Cl}_2\text{NiN}_2\text{P}_2$). Structures **3a,b** are *fac* octahedral, and **4** is square pyramidal with the NH moiety in the apical position. These structures are compared with each other and with another described previously, chloro[*meso-cis*-2,10-diphenyl-2,10-diphospha- κ^2 P-6-thia- κ S-bicyclo[9.4.0]penta-11(1),12,14-triene]copper(I) (**5**), which is approximately tetrahedral. Unusually long metal-nitrogen bond lengths are observed for **3a** (Mo-N = 2.428 (3) Å) and for **4** (Ni-N = 2.428 (3) Å). The conformations of the trimethylene strands joining the heteroatoms in the coordinated macrocyclic rings are analyzed, and explanations are proposed for the observation of chair-chair conformations for the two 6-membered rings $\text{WPCH}_2\text{CH}_2\text{CH}_2\text{P}$ in **3b** and the two 6-membered rings $\text{CuPCH}_2\text{CH}_2\text{CH}_2\text{S}$ in **5** but chair-boat conformations for the two 6-membered rings $\text{MoPCH}_2\text{CH}_2\text{CH}_2\text{N}$ in **3a** and the two 6-membered rings $\text{NiPCH}_2\text{CH}_2\text{CH}_2\text{N}$ in **4**. X-ray data were collected on a Syntex P2₁ autodiffractometer and refined by the full-matrix least-squares method. For **3a** from toluene (as $3a \cdot 1/2\text{C}_7\text{H}_8$), $a = 10.083$ (1) Å, $b = 17.509$ (3) Å, $c = 9.082$ (1) Å, $\alpha = 96.36$ (1)°, $\beta = 112.70$ (1)°, $\gamma = 77.89$ (1)°, triclinic, $P\bar{1}$, $Z = 2$, and $R_1 = 0.0314$, $R_2 = 0.0322$ for 5647 reflections with $|F_o| > 4\sigma_{|F_o|}$. For **3b**, $a = 12.366$ (1) Å, $b = 15.436$ (2) Å, $c = 16.867$ (2) Å, $\beta = 103.914$ (8)°, monoclinic, $P2_1/c$, $Z = 4$, and $R_1 = 0.0365$, $R_2 = 0.0364$ for 4761 reflections with $|F_o| > 4\sigma_{|F_o|}$. For **4**, $a = 9.240$ (1) Å, $b = 15.474$ (3) Å, $c = 9.035$ (2) Å, $\alpha = 96.90$ (2)°, $\beta = 67.38$ (2)°, $\gamma = 111.69$ (1)°, triclinic, $P\bar{1}$, $Z = 2$, and $R_1 = 0.0348$, $R_2 = 0.0349$ for 4136 reflections having $|F_o| > 4\sigma_{|F_o|}$.

For some time now we have been involved in the synthesis of tertiary-phosphino-containing macrocycles and the study of their coordination behavior toward transition metals.² We have shown that the 11-membered cycles **1** can function in a tridentate or a bidentate fashion depending on several factors. The thermal reaction of **1** with group 6 metal hexacarbonyls produced tridentate facial complexes in good yields when X was relatively soft, i.e., **1a-c**³ and **1d**,⁴ but only bidentate complexes were formed when



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X was hard (**1f,g**).³ Additionally, the configuration of PPh^3 and AsPh^4 was important; only the *meso-cis* ligands gave tridentate complexes unless temperatures were reached that allowed pyramidal inversion of phosphorus. With Co(II), we found that **1e** could behave in a tridentate fashion, but the 13-membered analogue (**2**) would not.¹

We have been interested in how ligands **1** "wrap" themselves around the metal center, a question that can only be approached conveniently by X-ray crystallography. Although ligands such as **1** readily form complexes with many transition metals, our problem has been that crystals of X-ray quality from these complexations have been relatively rare. Nonetheless, we have been able to obtain examples of complexes of **1** that include tetrahedral, square-pyramidal, and octahedral types, and we describe their structural details herein.

Results and Discussion

Octahedral Complexes. The thermal reaction of **1c** with $\text{Mo}(\text{CO})_6$ in boiling toluene to give **3a** in 60% yield (eq 1) has been described.³ Similarly, a mixture of *meso-cis*- and *meso-trans*-**1a**^{2b} upon being heated with $\text{W}(\text{CO})_6$ in boiling mesitylene for 16 h gave **3b** in 41% yield. The reaction was monitored as a function of time by IR spectroscopy, which showed that about 10 h was required for all of the $\text{W}(\text{CO})_6$ to react. At this time all of the

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