Inorganica Chimica Acta, 147 (1988) 265–274

Synthesis and Coordination Chemistry of Tripodal Dialkyl[1,2-bis(diethylcarbamoyl)ethyl]phosphonates with Lanthanide Nitrates

D. J. McCABE, E. N. DUESLER and R. T. PAINE*

Department of Chemistry, University of New Mexico, Albuquerque, N.M. 87131, U.S.A.

(Received January 5, 1988)

Abstract

Trifunctional dialkyl[1,2-bis(diethylcarbamoyl)ethyl]phosphonates, $(RO)_2P(O)CH[C(O)N(C_2H_5)_2][CH_2C(O)N(C_2H_5)_2]$ R = CH_3, C_2H_5, i-C_3H_7, n-C_6H_{13} were prepared from the respective sodium salts, $Na[(RO)_2P(O)CHC(O)N(C_2H_5)_2]$ and *N,N*-diethylchloroacetamide, and they were characterized by elemental analysis, mass, infrared and NMR spectroscopy. The molecular structure of $(i\text{-}C_3H_7O)_2P(O)CH[C(O)N(C_2H_5)_2][CH_2C(O)N(C_2H_5)_2]$ was determined by single crystal X-ray diffraction analysis and found to crystallize in the monoclinic space group $P2_1/c$ with $a = 15.589(6)$, $b = 9.783(4)$, $c = 16.283(7)$ Å, $\beta = 110.90(3)°$, $Z = 4$ and $V = 2320(2)$ Å^3. The structure was solved by direct methods and blocked least-squares refinement converged with $R_F = 5.7\%$ and $R_{wF} = 4.4\%$ on 2266 unique data with $F > 4\sigma(F)$. Important bond distances include P=O 1.459(3) Å, CHC=O 1.228(3) Å and $CHCH_2C$=O 1.223(3) Å. The coordination chemistry of the ligand with several lanthanides was examined, and the structure of the complex $Gd(NO_3)_3\{[(i\text{-}C_3H_7O)_2P(O)CH[C(O)N(C_2H_5)_2][CH_2C(O)N(C_2H_5)_2]\}_2\cdot H_2O$ was determined. The complex crystallized in the monoclinic space group $P2_1/n$ with $a = 13.524(5)$, $b = 22.033(4)$, $c = 19.604(4)$ Å, $\beta = 106.22(2)°$, $Z = 4$ and $V = 5609(3)$ Å^3. The structure was solved by heavy atom techniques and blocked least-squares refinement converged with $R_F = 5.9\%$ and $R_{wF} = 4.1\%$ on 5275 reflections with $F > 4\sigma(F)$. Both trifunctional ligands were found to bond to Gd(III) through only the phosphoryl oxygen atoms. The remainder of the Gd coordination sphere was composed of three bidentate nitrate oxygen atoms and an oxygen bonded water molecule. Several important bond distances include Gd–O(phosphoryl)$_{av}$ = 2.343(5) Å, Gd–O(nitrate)$_{av}$ = 2.475(7) Å, Gd–O(water) = 2.354(5) Å, P=O(phosphoryl)$_{av}$ = 1.467(6) Å, CHC=O$_{av}$ = 1.242(10) Å and $CHCH_2C$=O$_{av}$ = 1.209(11) Å.

Introduction

Bifunctional (carbamoylmethyl) phosphonates, $(RO)_2P(O)CH_2C(O)NR'_2$ (CMPs) are well known extractants for trivalent lanthanide and actinide ions [1, 2] and the structure–function characteristics of these and related bifunctional ligands have been under study in several laboratories [3–6]. On the basis of these studies, it appears that part of the unique extraction capability of CMPs for Ln(III) and An(III) ions, from highly acidic solutions, results from the structural combination of a phosphoryl group and a methylcarbamide group with the donor oxygen atoms in 1,3 positions. Horwitz and coworkers [3] have also suggested that the amide base site may function as an 'internal buffer' to improve the extraction process. In an effort to better understand these molecular structure–function characteristics of the CMP ligands, we have prepared several new families of polyfunctional mixed phosphoryl–carbonyl ligands, and the coordination and extraction chemistry of these ligands has been studied. We have briefly communicated the synthesis of dialkyl[1,2-bis(diethylcarbamoyl)ethyl]phosphonates [7], $(RO)_2P(O)CH[C(O)N(C_2H_5)_2]CH_2C(O)N(C_2H_5)_2]$ (**1**) R = CH_3, C_2H_5, i-C_3H_7, n-C_6H_{13}, and reported the formation and single crystal X-ray diffraction analysis of one complex [8], $Er(NO_3)_3\{[(i\text{-}C_3H_7O)_2P(O)CH[C(O)N(C_2H_5)_2][CH_2C(O)N(C_2H_5)_2]\}_2\cdot H_2O$ (**2**). We now report the full details of the synthesis and characterization of the ligands, the determination of the molecular structure of one ligand, $(i\text{-}C_3H_7O)_2P(O)CH[C(O)N(C_2H_5)_2][CH_2C(O)N(C_2H_5)_2]$ (**1c**), and more extensive coordination chemistry studies of **1c** including the crystal structure determination for $Gd(NO_3)_3\{[(i\text{-}C_3H_7O)_2P(O)CH[C(O)N(C_2H_5)_2][CH_2C(O)N(C_2H_5)_2]\}_2\cdot H_2O$ (**3**) which is isostructural with **2**.

Experimental

General Information

Dialkyl(*N,N*-diethylcarbamoyl)methylphosphonates, $(RO)_2P(O)CH_2C(O)NEt_2$, R = Me, Et, i-Pr,

---

*Author to whom correspondence should be addressed.

0020-1693/88/$3.50

n-Hx, were prepared as described in the literature [9]. *N,N*-diethylchloroacetamide was obtained from Fairfield Chemical Co., and it was distilled prior to its use in reactions. Sodium hydride and solvents were obtained from Aldrich Chemical Co. The solvents were dried with appropriate reagents and distilled under nitrogen. $Gd(NO_3)_3 \cdot 6H_2O$ was obtained from Alpha (Ventron). Infrared spectra were obtained on a Nicolet FT-IR Model 6000, and NMR spectra were recorded on Varian FT-80 or GE NT-360 spectrometers. Samples were contained in 5 mm tubes, and spectra were referenced against 85% H_3PO_4 (^{31}P) or Me_4Si (^{1}H, ^{13}C). Elemental analyses were obtained from Galbraith Laboratories or from R. Ju of the UNM Analytical Services Laboratory.

Preparation of the Ligands, 1

All of the ligands were prepared in the same general fashion, and the synthesis of the diisopropyl phosphonate **1c** is specifically described here. A 250 ml Schlenk vessel was purged with dry nitrogen and then charged with a stir bar, NaH (2.9 g, 0.12 mol) and 100 ml dry THF[†]. Under a positive flow of nitrogen, this flask was jointed to a 100 ml Schlenk vessel containing 27.9 g (0.1 mol) $(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2$. The NaH/THF slurry was cooled to 0 °C, stirred vigorously, and the phosphonate was added over 1 h to the slurry. Hydrogen was swept from the reaction vessel with a slow nitrogen stream. After the addition was complete, the mixture was stirred at 25 °C for 8 h and the resulting pale yellow solution was filtered to remove excess NaH. The filtrate was collected in a 250 ml Schlenk vessel containing a stir bar, and the filtrate was cooled to 0 °C. To this solution was added *N,N*-diethylchloroacetamide (15.0 g, 0.1 mol) over 1 h, and the resulting mixture was warmed to 25 °C and stirred for an additional 8 h. The resulting mixture was centrifuged and decanted to remove NaCl, and THF was removed from the mixture by vacuum evaporation. Specific purification and characterization data follow.

$(MeO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]$ (1a)

Vacuum distilled, boiling point (b.p.) 131–155 °C (25 mTorr). Yield: 90%. Solubility: benzene, hexane, CH_3CN, $CHCl_3$, CH_2Cl_2, C_2H_5OH, acetone and H_2O. *Anal.* Calc. for $PO_5N_2C_{14}H_{29}$: C, 49.99; H, 8.69; N, 8.33. Found: C, 50.21; H, 8.91; N, 8.22%. Mass spectrum [*m*/*e* (ion) relative intensity]: 336 (M^+) 8, 264 ($M - NEt_2^+$) 27, 236 ($M - C(O)NEt_2^+$) 39. Infrared spectrum (neat, cm^{-1})[‡]: 2975(m), 2937(m), 1643(s), 1452(m), 1261(m), 1053(s), 1032(s). NMR spectra (27 °C): $^{31}P\{^{1}H\}$ (neat) δ 26.7; $^{13}C\{^{1}H\}$ (C_6D_6) δ 169.0 (J_{PC} = 17.2 Hz, CH*C*(O)), 166.9 (J_{PC} = 4.3 Hz, CH$_2$*C*(O), 53.3 (J_{PC} = 6.2 Hz, *C*H$_3$O), 52.4 (J_{PC} = 6.7 Hz, *C*H$_3$O), 42.8 (N*C*H$_2$), 41.8 (N*C*H$_2$), 40.9 (N*C*H$_2$), 40.4 (N*C*H$_2$), 38.3 (J_{PC} = 131.6 Hz, P(O)*C*H), 31.8 (J_{PC} = 2.5 Hz, CH*C*H$_2$-C(O)), 14.1 (NCH$_2$*C*H$_3$), 13.7 (NCH$_2$*C*H$_3$), 13.1 (NCH$_2$*C*H$_3$), 12.8 (NCH$_2$*C*H$_3$); ^{1}H (C_6D_6) δ 3.78 (d, J_{HH} = 10.6 Hz, *CH*$_3$OP), 3.58 (m, J_{HH} = 6.7 Hz, N*CH*$_2$), 3.36 m, J_{HH} = 6.1 Hz, N*CH*$_2$), 3.19 (m, J_{HH} = 6.6 Hz, N*CH*$_2$), 3.06 (m, J_{HH} = 5.8 Hz, N*CH*$_2$), 2.75 (d of d, J_{HH} = 9.1 Hz, J_{HP} = 13.7 Hz, CH–*CH*$_2$-C(O)), 1.38 (t, J_{HH} = 7.1 Hz, NCH$_2$*CH*$_3$), 1.14 (t, J_{HH} = 7.0 Hz, NCH$_2$*CH*$_3$), 1.03 (t, J_{HH} = 7.0 Hz, NCH$_2$*CH*$_3$), 1.01 (t, J_{HH} = 7.0 Hz, NCH$_2$*CH*$_3$).

$(EtO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]$ (1b)

Vacuum distilled, b.p. 128–130 °C (25 mTorr). Yield 93%. Solubility: benzene, hexane, acetone, $CHCl_3$, CH_2Cl_2, C_2H_5OH, water. *Anal.* Calc. for $PO_5N_2C_{16}H_{33}$: C, 52.73; H, 9.13; N, 7.69. Found: C, 52.59; H, 9.35; N, 7.63%. Mass spectrum [*m*/*e* (ion) rel. inten.]: 364 (M^+) 4, 319 ($M - EtO^+$) 2, 292 ($M - NEt_2^+$), 13, 264 ($M - C(O)NEt_2^+$) 18. Infrared spectrum (cm^{-1}, neat): 2979(m), 2936(m), 1642(s), 1433(m), 1260(m), 1051(s), 1024(s). NMR spectra (27 °C): $^{31}P\{^{1}H\}$ (neat) δ 22.7; $^{13}C\{^{1}H\}$ (C_6D_6) δ 169.0 (J_{PC} = 17.3 Hz, CH*C*(O)), 166.8 (J_{PC} = 4.2 Hz, CH$_2$*C*(O)), 62.7 (J_{PC} = 6.0 Hz, O*C*H$_2$), 61.8 (J_{PC} = 6.4 Hz, O*C*H$_2$), 42.8 (N*C*H$_2$), 41.8 (N*C*H$_2$), 40.9 (N*C*H$_2$), 40.4 (N*C*H$_2$), 38.8 (J_{PC} = 131.6 Hz, P(O)*C*H), 31.9 (J_{PC} = 2.3 Hz, CH*C*H$_2$-C(O)), 16.5 (J_{PC} = 5.7 Hz, OCH$_2$*C*H$_3$), 14.1 (NCH$_2$-*C*H$_3$), 13.9 (NCH$_2$*C*H$_3$), 13.8 (NCH$_2$*C*H$_3$), 13.1 (NCH$_2$*C*H$_3$); ^{1}H (C_6D_6) δ 3.95 (m, POC*H*$_2$), 3.36 (q, J_{HH} = 5.8 Hz, NC*H*$_2$), 3.14 (q, J_{HH} = 6.4 Hz, NC*H*$_2$), 3.00 (q, J_{HH} = 5.2 Hz, NC*H*$_2$), 2.88 (q, J_{HH} = 5.5 Hz, NC*H*$_2$), 2.54 (d of d, J_{HH} = 9.9 Hz, J_{PH} = 11.7 Hz, CHC*H*$_2$C(O)), 1.15 (t, J_{HH} = 7.1 Hz, NCH$_2$C*H*$_3$), 1.06 (d of t, J_{HH} = 7.1 Hz, J_{PH} = 11.0 Hz, C*H*$_3$CH$_2$OP), 0.91 (t, J_{HH} = 6.9 Hz, NCH$_2$C*H*$_3$), 0.81 (t, J_{HH} = 7.0 Hz, NCH$_2$C*H*$_3$).

$(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]$ (1c)

Vacuum distilled, b.p. (125–150 °C) (25 mTorr); melting point (m.p.) 42–43 °C. Yield: 86%. Solubility: EtOH, MeOH, THF, benzene, hexane, CH_3CN, acetone, Et_2O, methylcyclohexane, H_2O. *Anal.* Calc. for $PO_5N_2C_{18}H_{37}$: C, 55.09; H, 9.50; N, 7.14. Found: C, 56.19; H, 9.85; N, 6.76%. Mass spectrum [*m*/*e* (ion) rel. inten.]: 392 (M^+) 4; 320 ($M - NEt_2^+$) 5, 292 ($M - C(O)NEt_2^+$) 6, 278 ($M - CH_2C(O)NEt_2^+$) 4. Infrared spectrum (neat, cm^{-1}): 2977(m), 2935(m), 1645(s), 1452(m), 1433(m), 1259(m), 1005(s). NMR spectra (27 °C): $^{31}P\{^{1}H\}$ (neat) δ 22.7; $^{13}C\{^{1}H\}$ (C_6D_6) δ 168.2 (J_{PC} = 17.6 Hz, CH*C*(O)), 166.0 (J_{PC} = 3.8 Hz, CH$_2$*C*(O)), 70.2 (J_{PC} = 6.1 Hz,

---

[†] Abbreviations used in the text include: THF = tetrahydrofuran, Me = methyl, Et = ethyl, i-Pr = isopropyl, n-Hx = n-hexyl.

[‡] Infrared absorptions in the region 4000–1000 cm^{-1} are listed. Numerous absorptions below 1000 cm^{-1} appear, and these data may be obtained from the authors.

*C*HO), 69.4 (J_{PC} = 6.3 Hz, *C*HO), 42.0 (N*C*H$_2$), 41.0 (N*C*H$_2$), 40.1 (N*C*H$_2$), 39.6 (N*C*H$_2$), 38.5 (J_{PC} = 132.8, *C*HC(O)), 31.2 (CH*C*H$_2$), 23.5 (OCH*C*H$_3$), 23.2 (OCH*C*H$_3$), 23.1 (OCH*C*H$_3$), 22.8 (OCH*C*H$_3$), 13.3 (NCH$_2$*C*H$_3$), 13.0 (NCH$_2$*C*H$_3$), 12.4 (NCH$_2$ *C*H$_3$), 12.1 (NCH$_2$*C*H$_3$); ^{1}H (C$_6$D$_6$) δ 4.62 (d of q, J_{HH} = 6.3 Hz, J_{PH} = 6.4 Hz, POC*H*), 3.37 (q, J_{HH} = 5.4 Hz, NC*H*$_2$), 3.14 (q, J_{HH} = 5.4 Hz, NC*H*$_2$), 2.99 (q, J_{HH} = 5.4 Hz, NC*H*$_2$), 2.87 (q, J_{HH} = 5.4 Hz, NC*H*$_2$), 2.52 (d of d, J_{HH} = 10.2 Hz, J_{PH} = 13.2 Hz, CHC*H*$_2$C(O)), 1.13 (OCHC*H*$_3$), 0.93 (t, J_{HH} = 7.0 Hz, NCH$_2$C*H*$_3$), 0.82 (m, NCH$_2$C*H*$_3$).

(n-HxO)$_2$P(O)CH[C(O)NEt$_2$][CH$_2$C(O)NEt$_2$] (1d)

The ligand was not distilled and purities were typically greater than 98% on the basis of GC analysis. Further purification was accomplished by chromatography on silica gel (60–200 mesh) with ethyl acetate eluent. The ligand is soluble in benzene, hexane, acetone, CHCl$_3$, CH$_2$Cl$_2$ and THF. *Anal.* Calc. for PO$_5$N$_2$C$_{24}$H$_{49}$: C, 60.48; H, 10.36; N, 5.88. Found: C, 60.71; H, 10.37; N, 5.72%. Mass spectrum (*m/e* (ion) rel. inten.]: 476 (*M*$^+$) 40, 404 (*M* – NEt$_2^+$) 38, 376 (*M* – C(O)NEt$_2^+$) 58, 375 (*M* – OHx$^+$) 7. Infrared spectrum (neat, cm^{-1}): 2962(s), 2928(s), 1645(s), 1462(s), 1433(s), 1259(s), 1043(m), 997(s). NMR spectra (27 °C): ^{31}P{^{1}H} (neat) δ 24.3; ^{13}C{^{1}H} (C$_6$D$_6$) δ 169.1 (J_{PC} = 17.1 Hz, CH*C*(O)), 167.0 (J_{PC} = 4.2 Hz, CH$_2$*C*(O)), 66.7 (J_{PC} = 6.4 Hz, O*C*H$_2$), 65.9 (J_{PC} = 6.3 Hz, O*C*H$_2$), 43.0 (N*C*H$_2$), 42.0 (N*C*H$_2$), 41.7 (N*C*H$_2$), 41.1 (N*C*H$_2$), 39.0 (J_{PC} = 131.6 Hz, *C*HC(O)), 32.1 (J_{PC} = 2.8 Hz, CH*C*H$_2$C(O)), 31.7 (J_{PC} = 4.8 Hz, *C*H$_2$ CH$_2$O), 30.9 (J_{PC} = 5.8 Hz, *C*H$_2$(CH$_2$)$_2$O), 25.5 (*C*H$_2$(CH$_2$)$_3$O), 22.8 (*C*H$_2$(CH$_2$)$_4$O), 14.2 (NCH$_2$-*C*H$_3$), 14.0 (*C*H$_3$), 13.9 (NCH$_2$*C*H$_3$), 13.2 (NCH$_2$ *C*H$_3$), 13.0 (NCH$_2$*C*H$_3$). ^{1}H (C$_6$D$_6$) δ 4.13 (m, C*H*$_2$OP), 3.58 (q, J_{HH} = 7.0 Hz, NC*H*$_2$), 3.34 (m, NC*H*$_2$), 3.20 (q, J_{HH} = 6.4 Hz, NC*H*$_2$), 3.13 (q, J_{HH} = 6.9 Hz, NC*H*$_2$), 2.76 (m, CHC*H*$_2$C(O)), 1.68 (OCH$_2$C*H*$_2$), 1.4–1.3 (C*H*$_2$), 1.15 (t, J_{HH} = 6.8 Hz, NCH$_2$C*H*$_3$), 1.06 (m, NCH$_2$C*H*$_3$), 0.96 (t, J_{HH} = 7.1 Hz, C*H*$_3$).

Preparation of the Complexes of 1c

All of the lanthanide complexes were prepared by the same general procedure previously reported for the Er complex [8]. Hydrated lanthanide nitrate (La, Ce, Pr, Nd, Sm, Gd, Dy, and Yb) (2.0 mmol) was dissolved in 10 ml 95% EtOH, 4.0 mmol (1.6 g) of (i-PrO)$_2$P(O)CH[C(O)NEt$_2$][CH$_2$C(O)NEt$_2$] was dissolved in 10 ml 95% EtOH, and the two solutions were combined, stirred and allowed to evaporate overnight. The resulting viscous oil was washed with hexane (2 × 5 ml) to remove any uncomplexed ligand. Ethanol (15 ml) was added to the oil, and the EtOH was again allowed to slowly evaporate. The La, Ce, Pr, and Nd complexes were isolated as oils, and the remaining complexes were obtained as crystalline solids.

Characterization of the Complexes, Ln(NO$_3$)$_3$-{(i-PrO)$_2$P(O)CH[C(O)NEt$_2$][CH$_2$C(O)NEt$_2$]}$_2$

La

Anal. Calc. for LaP$_2$O$_{19}$N$_7$C$_{36}$H$_{74}$: C, 38.97; H, 6.72; N, 8.83. Found: C, 38.19; H, 6.75; N, 8.51%. Infrared spectrum (THF, cm^{-1}): 1647(s), 1603(m), 1472(s), 1313(m), 1290(m), 1218(m), 1201(m), 1001(s). NMR spectrum: ^{31}P{^{1}H} (H$_2$O) δ 23.4.

Ce

Anal. Calc. for CeP$_2$O$_{19}$N$_7$C$_{36}$H$_{74}$: C, 38.92; H, 6.71; N, 8.82. Found: C, 39.04; H, 6.53; N, 8.50%. Infrared spectrum (THF, cm^{-1}): 1647(s), 1602(m), 1470(s), 1302(m), 1292(m), 1218(m), 1198(m), 1002(s), NMR spectrum: ^{31}P{^{1}H} (H$_2$O) δ 24.8.

Pr

Anal. Calc. for PrP$_2$O$_{19}$N$_7$C$_{36}$H$_{74}$: C, 38.89; H, 6.71; N, 8.82. Found: C, 40.34; H, 7.27; N, 8.35%. Infrared spectrum (THF, cm^{-1}): 1647(s), 1605(m), 1465(m), 1218(m), 1203(m), 1003(s). NMR spectrum: ^{31}P{^{1}H} (CDCl$_3$) δ 53.5.

Nd

Anal. Calc. for NdP$_2$O$_{19}$N$_7$C$_{36}$H$_{74}$: C, 38.78; H, 6.69. Found: C, 37.78; H, 7.10%. Infrared spectrum (THF, cm^{-1}); 1647(s), 1616(m), 1475(m), 1219(m), 1193(m), 1005(s). NMR spectrum: ^{31}P{^{1}H} (D$_2$O) δ 53.3; ^{13}C{^{1}H} (D$_2$O/EtOH) δ 181.9 (J_{PC} = 16.7 Hz, CH*C*(O)), 178.3 (J_{PC} = 2.5 Hz, CH$_2$*C*(O)), 74.9 (J_{PC} = 6.0 Hz, OC*H*) 74.6 (J_{PC} = 5.3 Hz, O*C*H), 45.4 (N*C*H$_2$), 43.8 (N*C*H$_2$), 42.5 (N*C*H$_2$), 41.5 (N*C*H$_2$), 39.2 (J_{PC} = 93.2, *C*HC(O)), 32.3 (CH*C*H$_2$C(O)), 24.2 (m, CH$_2$*C*H$_3$), 14.4 (NCH$_2$*C*H$_3$), 14.0 (NCH$_2$*C*H$_3$), 12.5 (NCH$_2$*C*H$_3$).

Sm

Anal. Calc. for SmP$_2$O$_{19}$N$_7$C$_{36}$H$_{74}$: C, 38.57; H, 6.65; N, 8.74. Found: C, 38.41; H, 6.80; N, 8.49%. Infrared spectrum (THF, cm^{-1}) 1648(s), 1616(m), 1501(m), 1218(m), 1194(s), 1005(s). NMR spectrum: ^{31}P{^{1}H} (H$_2$O) δ 22.0; ^{13}C{^{1}H} (H$_2$O/EtOH) δ 170.1 (J_{PC} = 14.8 Hz, CH$_2$*C*(O)), 169.1 (J_{PC} = 3.3 Hz, CH*C*(O)), 74.1 (J_{PC} = 7.4 Hz, O*C*H), 44.1 (N*C*H$_2$), 43.1 (N*C*H$_2$), 42.1 (N*C*H$_2$), 41.5 (N*C*H$_2$), 39.0 (J_{PC} = 141.5 Hz, *C*HC(O)), 32.4 (CH*C*H$_2$C(O)), 23.9 (m, OCH*C*H$_3$), 14.0 (NCH$_2$*C*H$_3$), 12.8 (NCH$_2$-*C*H$_3$), 12.6 (NCH$_2$*C*H$_3$).

Gd

Anal. Calc. for GdP$_2$O$_{20}$N$_7$C$_{36}$H$_{76}$: C, 37.72; H, 6.68. Found: C, 37.58; H, 6.75%. Infrared spectrum (THF, cm^{-1}) 1648(s), 1616(m), 1497(s), 1300(s), 1215(s), 1197(m) 1006(s).

Dy

Anal. Calc. for $DyP_2O_{20}N_7C_{36}H_{76}$: C, 37.55; H, 6.65; N, 8.52. Found: C, 37.56; H, 6.74; N, 8.26%. Infrared spectrum (KBr, cm^{-1}) 2985(m), 1644(s), 1611(s), 1492(m), 1384(m), 1302(s), 1212(m), 1196(s), 1020(s). NMR spectrum: $^{31}P\{^1H\}$ (H_2O) δ 21.0.

Yb

Anal. Calc. for $YbP_2O_{20}N_7C_{36}H_{76}$: C, 37.20; H, 6.59; N, 8.44. Found: C, 34.63; H, 6.07; N, 8.40%. Infrared spectrum (KBr, cm^{-1}) 2984(m), 1642(s), 1610(s), 1494(s), 1384(m), 1308(m), 1214(m), 1200(m), 1021(s). NMR spectrum: $^{31}P\{^1H\}$ (H_2O) δ 21.3.

Crystallographic Measurements and Structure Solutions

$(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]$

A suitable crystal (0.25 × 0.28 × 0.51 mm), shaped as a rectangular prism, was mounted in a glass capillary. 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 [4]. Data were collected at 17 °C in the θ–2θ scan mode with use of Mo Kα radiation, a scintillation counter, and pulse height analyzer. The data collection parameters are summarized in Table I. Axial photographs and a limited diffraction data set were found to be con-

TABLE I. Experimental Data for the X-ray Diffraction Study of $(i\text{-}C_3H_7O)_2P(O)CH[C(O)N(C_2H_5)_2][CH_2C(O)N(C_2H_5)_2]$ (**1c**) and $Gd(NO_3)_3\{(i\text{-}C_3H_7O)_2P(O)CH[C(O)N(C_2H_5)_2][CH_2C(O)N(C_2H_5)_2]\}_2\cdot H_2O$ (**3**)

	1c	**3**
(a) Crystal parameters		
Chemical formula	$PO_5N_2C_{18}H_{37}$	$GdP_2O_{20}N_7C_{36}H_{76}$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14, C^5_{2h})	$P2_1/n$ (No. 14)
a (Å)	15.589(6)	13.524(5)
b (Å)	9.783(4)	22.033(4)
c (Å)	16.283(7)	19.604(4)
β (deg)	110.90(3)	106.22(2)
V (Å^3)	2320(2)	5609(3)
Z	4	4
D_{calc} (g Å^{-3})	1.12	1.36
Molecular wt.	392.5	1146.3
μ (cm^{-1})	1.39	13.4
F(000)	856	2380
(b) Data collection		
Diffractometer	Syntex P3/F	
Radiation	Mo Kα (λ = 0.71069 Å)	
Monochromator	highly oriented graphite crystal	
Reflections measured	$\pm h, k, l$	$h, k, \pm l$
2θ range (°)	1–50	1–50
Scan type	θ–2θ	θ–2θ
Scan speed (deg min^{-1})	4–30	4–30
Scan range (deg)	$2\theta(K\alpha 1) - 1.2°$ to $2\theta(K\alpha 2) + 1.3°$	
Background measurement	stationary crystal and counter; at the beginning and end of 2θ scan, each for 1/2 of the total scan time	
Standard reflections	[10, 0, 0; 1, 5, 0; 0, 0, 6] 3 measured every 141 reflections	[3, 2, 0; 0, 8, 0; 0, 2, 5] 3 measured every 141 reflections
Total reflections collected	4660	10913
Unique reflections collected	4064	9893
Observed reflections used in refinement	2266; $F > 4\sigma(F)$	5275; $F > 4\sigma(F)$
Weighting scheme	$w = 1/[\sigma(F)^2 + \lvert g \rvert F_o{}^2]$ g = 0.00006	$w = 1/[\sigma^2(F)]$
No. of parameters	235	593
Goodness-of-fit	1.670	1.876

sistent with a monoclinic space group $P2_1/c$ (No. 14, C_{2h}^5, unique axis b)[*]. 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 2.05% and 2.03%[**]. The estimated maximum and minimum transmissions were 0.868 and 0.843. Redundant and equivalent data were averaged and converted to $|F_o|$ values and then scaled on the standard reflections after corrections for Lorentz and polarization effects.

All calculations were performed with the R3/SHELXTL structure determination package [11a][†]. Least-squares refinements in the package use a blocked-cascade algorithm with full matrix blocks of 103 parameters[††]. The structure was solved by direct methods, and all but four non-hydrogen atoms appeared in the best E-maps. The remaining non-hydrogen atoms were located in a subsequent Fourier map. Isotropic refinement on all twenty-six non-hydrogen atoms gave $R_F = 13.5\%$. Anisotropic refinements on these atoms converged with $R_F = 9.5\%$. Hydrogen atoms were included in idealized positions with a fixed C–H distance, 0.95 Å, with their positions riding on those of their parent atom. The hydrogen atom U_{iso}s were fixed at 1.2 times the last U_{equiv} of their parent atom. Final refinements [12] converged at $R_F = 5.7\%$ and $R_{wF} = 4.4\%$ on 2266 unique reflections with $F > 4\sigma(F)$. A final difference map showed no peaks greater than 0.22 e Å^{-3}. See also 'Supplementary Material'. The non-hydrogen atom positional parameters are listed in Table II.

TABLE II. Fractional Coordinates for $(i\text{-PrO})_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]$ (e.s.d.s in parentheses)

Atom	x/a	y/b	z/c
P(1)	0.29307(6)	0.28651(9)	0.75716(6)
O(1)	0.37724(14)	0.2652(2)	0.73901(14)
O(2)	0.20281(13)	0.2814(2)	0.67299(12)
O(3)	0.27200(15)	0.1797(2)	0.81977(14)
O(4)	0.23558(13)	0.6213(2)	0.70641(14)
O(5)	0.28293(15)	0.6055(2)	0.94931(15)
N(1)	0.38907(17)	0.6112(3)	0.77255(17)
N(2)	0.12904(17)	0.6261(3)	0.90061(18)
C(1)	0.2897(2)	0.4450(3)	0.8131(2)
C(2)	0.3032(2)	0.5671(3)	0.7606(2)
C(3)	0.1992(2)	0.4625(3)	0.8287(2)
C(4)	0.2076(2)	0.5715(3)	0.8975(2)
C(5)	0.4746(2)	0.5552(4)	0.8351(2)
C(6)	0.5093(3)	0.6356(4)	0.9198(2)
C(7)	0.3988(2)	0.7229(3)	0.7167(2)
C(8)	0.4005(3)	0.6714(4)	0.6299(2)
C(9)	0.0374(2)	0.5954(3)	0.8374(2)
C(10)	0.0098(3)	0.6907(4)	0.7589(3)
C(11)	0.1342(2)	0.7258(4)	0.9685(2)
C(12)	0.1195(3)	0.6637(4)	1.0465(2)
C(13)	0.2028(2)	0.3329(4)	0.5888(2)
C(14)	0.2184(3)	0.2168(4)	0.5369(3)
C(15)	0.1122(3)	0.4032(4)	0.5448(3)
C(16)	0.2986(3)	0.0373(3)	0.8227(3)
C(17)	0.3646(4)	0.0087(5)	0.9116(3)
C(18)	0.2145(3)	−0.0457(4)	0.8011(3)

$Gd(NO_3)_3\{(i\text{-}PrO)_2P(O)CH_2[C(O)NEt_2][CH_2C(O)NEt_2]\}_2 \cdot H_2O$

A crystal of dimensions 0.23 × 0.43 × 0.46 mm was sealed in a glass capillary, and data collection was performed at 20 °C as described above. Data collection parameters are summarized in Table I. A short data set indicated the monoclinic space group $P2_1/n$ (No. 14 alt. set.). The redundant and equivalent reflections were averaged and converted to unscaled $|F_o|$ values after correction for Lorentz and polarization effects. A small empirical absorption correction was applied based on ψ scans. The agreement factor for averaging the azimuthal scan data before and after the absorption correction were 2.51% and 1.48%. The estimated maximum and minimum transmissions were 0.443 and 0.394.

Calculations were performed as described above and the structure solution was obtained independent of the structure solution for 2 [8]. The structure was solved by interpretation of a Patterson map on trial positions for the Gd and P atoms. Phasing on these atoms was sufficient to give the positions of the remaining non-hydrogen atoms. Isotropic refinement on the heavy atoms gave $R_F = 9.4\%$. Subsequent anisotropic refinement on all heavy atoms gave $R_F = 6.2\%$. Hydrogen atoms were inserted in idealized positions (*vide supra*), including the hydrogen atoms on the water molecule, and least-squares refinements were performed with U_{iso}s fixed at 1.2 times the U_{equiv} of the parent atom. The position of C(28) (previously refined anisotropically) now gave unusually large Us (0.3–0.6 Å^2); examination showed that the atom was disordered over three sites. The three sites were included, each with 1/3 occupancy factor fixed in positions found in the difference map with a common variable U_{iso}. The hydrogen atoms on C(27) and C(28) were not included in the final refinements, and the other hydrogen atoms were included in idealized positions

---

[*] Space group notation given in ref. 10.

[**] The empirical absorption correction uses an ellipsoidal model fitted to azimuthal scans and then applied to the intensity data.

[†] SHELXTL uses absorption, anomalous dispersion, and scattering data compiled in ref. 11b. Anomalous dispersion terms were included for all atoms with atomic numbers greater than 2.

[††] A general description of the least-squares algebra is found in ref. 12. The least-squares refinement minimizes $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F)^2 + gF^2]$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_{wF} = [\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, and $GOF = [\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where NO = number of observations and NV = number of variables.

TABLE III. Fractional Coordinates for $Gd(NO_3)_3\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}_2 \cdot H_2O$ (e.s.d.s in parentheses)

Atom	*x/a*	*y/b*	*z/c*
Gd	0.21794(3)	0.12082(2)	0.84150(2)
P(1)	−0.07257(17)	0.11818(12)	0.76364(11)
O(1)	0.0381(3)	0.1185(2)	0.7973(2)
O(2)	−0.1318(4)	0.0786(3)	0.8046(3)
O(3)	−0.1236(4)	0.1811(2)	0.7540(3)
O(4)	0.0188(4)	0.1248(3)	0.6216(3)
O(5)	−0.2044(4)	0.0010(3)	0.5788(3)
N(1)	−0.1375(5)	0.1680(3)	0.5834(3)
N(2)	−0.0645(5)	−0.0582(3)	0.5920(3)
C(1)	−0.1070(5)	0.0879(3)	0.6753(4)
C(2)	−0.0718(7)	0.1288(4)	0.6246(4)
C(3)	−0.0594(6)	0.0257(3)	0.6759(4)
C(4)	−0.1153(6)	−0.0123(4)	0.6110(4)
C(5)	−0.0971(7)	0.2070(4)	0.5346(5)
C(6)	−0.0366(9)	0.2586(5)	0.5750(6)
C(7)	−0.2456(6)	0.1787(4)	0.5812(5)
C(8)	−0.3161(7)	0.1497(5)	0.5157(5)
C(9)	0.0453(7)	−0.0726(4)	0.6242(5)
C(10)	0.1128(7)	−0.0421(5)	0.5850(5)
C(11)	−0.1199(7)	−0.0981(4)	0.5322(4)
C(12)	−0.1524(9)	−0.1579(4)	0.5561(6)
C(13)	−0.0930(8)	0.0448(5)	0.8700(5)
C(14)	−0.1577(12)	−0.0090(6)	0.8653(6)
C(15)	−0.0899(11)	0.0796(6)	0.9304(6)
C(16)	−0.1010(9)	0.2281(5)	0.8079(7)
C(17)	−0.1968(12)	0.2331(6)	0.8315(8)
C(18)	−0.0927(13)	0.2839(5)	0.7775(8)
P(2)	0.47824(17)	0.07143(9)	0.82148(11)
O(6)	0.3782(4)	0.0855(2)	0.8343(2)
O(7)	0.4927(4)	0.0035(2)	0.8069(3)
O(8)	0.5730(4)	0.0912(2)	0.8837(2)
O(9)	0.3465(4)	0.0972(2)	0.6584(2)
O(10)	0.5825(5)	0.1876(3)	0.6672(3)
N(3)	0.4831(5)	0.0513(3)	0.6367(3)
N(4)	0.4947(6)	0.2688(3)	0.6771(4)
C(19)	0.5046(5)	0.1106(3)	0.7481(3)
C(20)	0.4395(6)	0.0852(4)	0.6766(4)
C(21)	0.4876(6)	0.1793(3)	0.7518(4)
C(22)	0.5262(7)	0.2125(4)	0.6952(4)
C(23)	0.5933(7)	0.0373(5)	0.6487(5)
C(24)	0.6258(7)	−0.0220(5)	0.6842(5)
C(25)	0.4154(7)	0.0302(4)	0.5678(4)
C(26)	0.4080(7)	0.0809(4)	0.5114(4)
C(27)	0.5324(9)	0.3060(4)	0.6229(6)
C(28)	0.4944	0.2935	0.5657
P(28)	0.6227	0.3520	0.6722
R(28)	0.4572	0.2769	0.5448
C(29)	0.4258(8)	0.2983(4)	0.7105(5)
C(30)	0.3146(8)	0.2917(5)	0.6693(5)
C(31)	0.4214(8)	−0.0469(4)	0.8098(5)
C(32)	0.3611(8)	−0.0579(5)	0.7353(6)
C(33)	0.4871(9)	−0.0992(4)	0.8415(6)
C(34)	0.5715(7)	0.0974(6)	0.9576(4)
C(35)	0.6329(11)	0.1510(7)	0.9816(7)
C(36)	0.6317(12)	0.0447(7)	0.9961(6)
N(5)	0.1631(7)	−0.0065(4)	0.8457(5)
O(11)	0.1777(5)	0.0166(3)	0.7914(4)
O(12)	0.1787(5)	0.0274(3)	0.8993(3)
O(13)	0.1274(7)	−0.0569(3)	0.8466(4)
N(6)	0.2424(8)	0.1393(4)	0.9917(5)
O(14)	0.1631(6)	0.1510(3)	0.9456(4)
O(15)	0.3180(5)	0.1206(3)	0.9688(3)
O(16)	0.2530(6)	0.1418(4)	1.0550(4)
N(7)	0.2557(8)	0.2510(4)	0.8388(4)
O(17)	0.1651(6)	0.2285(3)	0.8240(4)
O(18)	0.3276(5)	0.2120(3)	0.8528(3)
O(19)	0.2708(6)	0.3048(3)	0.8389(4)
O(20)	0.2044(4)	0.1326(3)	0.7199(2)

riding on their parent carbon atom with U_{iso}s fixed at 1.2 times U_{equiv}. The final agreement factors were $R_F = 5.9\%$ and $R_{wF} = 4.1\%$ on 5275 reflections with $F > 4\sigma(F)$. A final difference map showed the highest peak to be 0.75 e Å^{-3} which was 0.93 Å from the Gd atom. The rest of the peaks were no greater than the troughs (−0.65 e Å^{-3}). The non-hydrogen atom positional parameters are listed in Table III, see also 'Supplementary Material'.

Results and Discussion

The ligands $(RO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]$, R = Me, Et, i-Pr, Hx (**1a–d**) have been prepared in high yield and purity by addition of the respective sodium salts of the bifunctional CMP ligands [9], $Na[(RO)_2P(O)CHC(O)NEt_2]$, to the chloroacetamide, $ClCH_2C(O)NEt_2$. The ligands are very soluble in common organic solvents, and, with the exception of **1d**, they are soluble in water. It is interesting to note that the water solubility of **1c** is dramatically inversely proportional with temperature: at 25 °C, solubility ~ 1 g/ml; at 75 °C, solubility < 0.01 g/ml. This behavior is, in fact, useful for purification/recrystallization of the ligand. The ligands were characterized by elemental analyses, by observation of a parent ion and expected fragmentation patterns in mass spectra, and by characteristic infrared and NMR data. In particular, the ligands display carbonyl and phosphoryl stretching frequencies in the regions 1645–1642 cm^{-1} and 1261–1259 cm^{-1}, respectively. The carbonyl bands are sufficiently broad that only one absorption is resolved, except for **1c** which, in a KBr pellet, shows two absorptions at 1651 and 1638 cm^{-1}. The carbonyl frequencies are similar to those found for bifunctional CMP ligands [4] and for tertiary carbamides [13]. The positions of the phosphoryl stretching frequencies and the P–O–C stretching frequencies, 997–1053 cm^{-1}, in **1** are also in agreement with the frequencies found for CMP ligands [4].

The $^{31}P\{^1H\}$ NMR spectra of **1** show single resonances in a range, δ 26.7–22.7, expected for dialkyl alkylphosphonates [4, 14]. The ^1H and $^{13}C\{^1H\}$ NMR spectra are complex, yet nearly complete assignments have been accomplished. Some important aspects are summarized here. The methine carbon, P(O)*C*H, resonance appears in the region δ 39.9–38.3 with J_{PC} = 132.9–131.6 Hz. The resonances are 4–5 ppm downfield of the related CMP ligands, and similar downfield shifts are found for alkyl methine substituted CMP derivatives [15]. The methylene carbon, $P(O)CH[CH_2C(O)NEt_2]$, resonance has been assigned to a doublet centered in the region δ 33.4–31.9, J_{PC} = 2.8–2.3 Hz. These shifts can be compared to methylene carbon resonances adjacent to carbamide groups in $CH_3CH_2C(O)NEt_2$, δ 26.3 and $C_2H_5CH_2$-$C(O)NEt_2$, δ 35.1 [16]. Two closely spaced carbonyl doublets are found for each ligand in the regions δ 169.1–168.2, J_{PC} = 17.6–17.1 Hz, and δ 167.0–166.0, J_{PC} = 4.3–3.8 Hz. On the basis of the magnitudes of J_{PC}, the low field doublet is assigned to the short-leg carbamide group, $CH[C(O)NEt_2]$, and the higher field doublet is identified with the long-leg carbamide group, $CH[CH_2C(O)NEt_2]$.

Both ^1H and $^{13}C\{^1H\}$ NMR spectra at 27 °C show four resonances in the amide methylene region: ^1H δ 3.6–3.0, $^{13}C\{^1H\}$ δ 44.2–40.4. Four resonances are also found in the amide methyl region: ^1H δ 1.4–0.81; $^{13}C\{^1H\}$ δ 15.3–12.8. These resonance features are consistent with inequivalent methylene and methyl groups resulting from hindered amide group rotation. Similar effects have been found in bifunctional CMP ligands [4, 15] and organic acetamide compounds [13, 16–19].

The coordination chemistry of **1c** has been examined with lanthanide nitrates, $Ln(NO_3)_3$ Ln = La, Pr, Nd, Sm, Gd, Dy, and Yb, by combination of the ligand and metal in a 2:1 ratio in EtOH. The complexes were obtained by evaporation of the solvent. The La, Ce, Pr, and Nd complexes were isolated as oils, and the remaining complexes were isolated as crystalline solids. Elemental analyses of the complexes containing the early lanthanides, La–Nd, were found to be consistent with a formulation $Ln(NO_3)_3$-$\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}_2$ while analyses of the latter lanthanides, Gd–Yb, were more consistent with a formulation*, $Ln(NO_3)_3\{(i\text{-}PrO)_2$-$P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}_2 \cdot H_2O$.

The molecular structures of the lanthanide–trifunctional bis-carbamoylethylphosphonate complexes are of interest with respect to our efforts to design improved extractants. It is important to recall that our previous studies of lanthanide-bifunctional CMP ligand complexes [4] showed that earlier lanthanides (La–Gd) formed complexes, $Ln(NO_3)_3$-$(CMP)_2$, in which the CMP ligands were bonded to the lanthanide in a bidentate fashion. The late lanthanides (Tb–Yb), on the other hand, formed complexes, $Ln(NO_3)_3(CMP)_2 \cdot H_2O$, in which the CMP ligands were coordinated to the lanthanide in a monodentate fashion through Ln–O=P phosphonate bonding. Further, the two carbonyl groups in these latter complexes were hydrogen bonded to the hydrogen atoms of a lanthanide coordinated water molecule. The latter interaction was also indicated in solid and solution infrared spectroscopic studies by intermediate magnitude carbonyl stretching frequency shifts.

A previous report [8] on the coordination chemistry of **1c** with $Er(NO_3)_3$ from our group revealed that two trifunctional ligands bonded to the late lanthanide in a fashion related to the behavior of the CMP ligands with late lanthanides. In this complex **2**, the Er bonded only to the phosphoryl oxygen atoms, while the two short-leg carbonyl groups, $CH[C(O)$-$NEt_2]$, were hydrogen bonded to a Er coordinated water molecule. The two long-leg carbonyl groups pointed away from the Er ion. The determination of a structure for an earlier lanthanide ion complex of **1c** was important in light of the CMP studies.

The elemental analyses of the complexes, Ln = La–Eu, and the expected coordination numbers suggested, in fact, that the trifunctional ligand **1c** was acting as a bidentate ligand through phosphoryl and short-leg carbonyl coordination. Unfortunately, none of these complexes formed crystals; the lightest lanthanide which formed a crystalline product was Gd. On the basis of the CMP coordination studies, it was expected that the Gd complex of **1c** would display bidentate ligand coordination; however, elemental analyses suggested the presence of a coordinated water molecule. This ambiguity led us to determine the structures of the ligand **1c** and its Gd complex, **3**.

The molecular structure of the trifunctional ligand **1c** is shown in Fig. 1, and selected bond distances and angles are summarized in Table IV. The phosphoryl P=O distance, 1.459(3) Å, falls within the range, 1.38–1.56 Å (avg. 1.46 Å), observed for tetrahedral phosphates [20]. The average i-PrO–P distance, 1.575(3) Å, falls within the range, 1.56–1.64 Å (avg. 1.59 Å), found in other phosphonates [20]. The bond angles about phosphorus are also normal. The carbonyl distances in the short-leg carbamide group, $CH[C(O)NEt_2]$ C(2)–O(4) 1.228(3) Å and in the long-leg carbamide group $[CH_2C(O)NEt_2]$ C(4)–O(5) 1.223(3) Å are identical and comparable with the average distance, 1.23 Å,

---

*Given the accuracy of elemental analyses and the molecular weights of the complexes, the formulae are not unambiguously determined by the analytical data. Selected determinations of water content in the Nd and Gd complexes, however, support the proposed formulations.

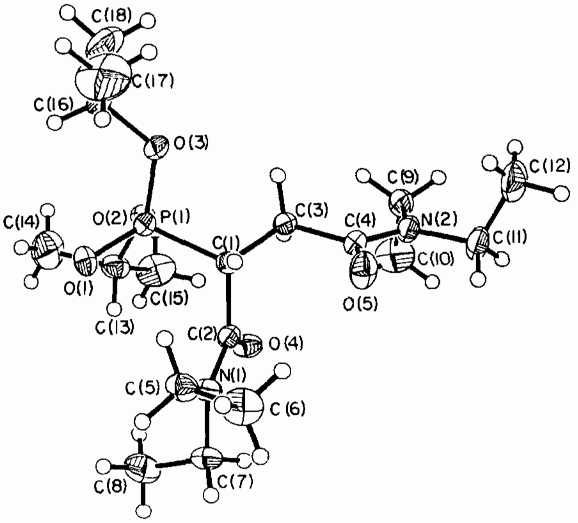

Fig. 1. Molecular geometry and atom labelling scheme for $(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]$ (25% probability ellipsoids).

TABLE IV. Selected Bond Distances and Angles for $(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]$

Distances (Å)	
P(1)–O(1)	1.459(3)
P(1)–O(2)	1.576(2)
P(1)–O(3)	1.574(3)
C(2)–O(4)	1.228(3)
C(4)–O(5)	1.223(3)
C(2)–N(1)	1.353(4)
C(4)–N(2)	1.353(5)
P(1)–C(1)	1.808(3)
Angles (°)	
P(1)–O(2)–C(13)	120.4(2)
P(1)–O(3)–C(16)	122.4(3)
C(1)–P(1)–O(1)	114.5(1)
P(1)–C(1)–C(2)	110.7(2)
P(1)–C(1)–C(3)	112.0(2)
O(3)–P(1)–O(2)	102.4(1)

found in a variety of ketones and aldehydes [21]. The amide distances C(2)–N(1) and C(4)–N(2) are identical, 1.353(4) Å, and shorter than found in alkyl amines, 1.47 Å. However, the distances are typical of carbamides which possess partial $C\overset{\cdot\cdot\cdot}{-}N$ multiple bonding, 1.32 Å [21].

The molecular structure determination for the Gd complex 3 reveals that the composition is $Gd(NO_3)_3\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}_2\cdot H_2O$, and the complex is isostructural with the erbium complex [8] 2, $Er(NO_3)_3\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}_2\cdot H_2O$. A view of the molecule is shown in Fig. 2, and a partial list of bond distances and angles is given in Table V. The coordi-

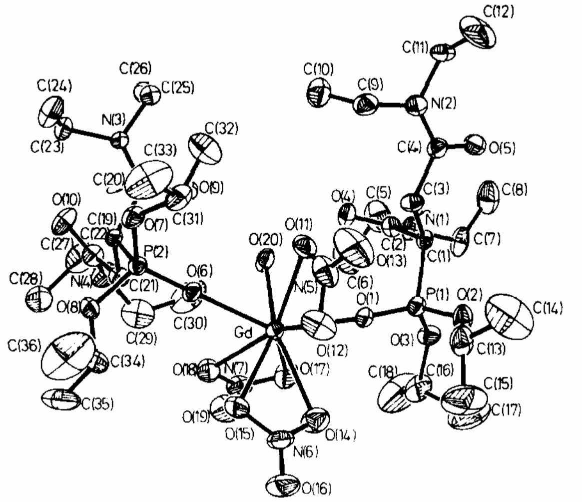

Fig. 2. Molecular geometry and atom labelling scheme for $Gd(NO_3)_3\{(i\text{-}PrO)_2P(O)CH_2[C(O)NEt_2][CH_2C(O)NEt_2]\}_2\cdot H_2O$ (25% probability ellipsoids).

TABLE V. Selected Bond Distances and Angles for $Gd(NO_3)_3\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}_2\cdot H_2O$

Distances (Å)			
Gd–O(1)	2.343(4)	Gd–O(6)	2.343(5)
Gd–O(11)	2.496(7)	Gd–O(12)	2.477(6)
Gd–O(14)	2.450(8)	Gd–O(15)	2.485(5)
Gd–O(17)	2.475(6)	Gd–O(18)	2.470(6)
Gd–O(20)	2.354(5)	P(1)–O(1)	1.458(5)
P(1)–O(2)	1.552(6)	P(1)–O(3)	1.537(6)
P(1)–C(1)	1.791(7)	O(4)–C(2)	1.246(11)
O(5)–C(4)	1.229(9)	N(1)–C(2)	1.337(10)
N(1)–C(5)	1.498(12)	C(1)–C(2)	1.514(12)
N(2)–C(4)	1.333(11)	C(3)–C(4)	1.534(10)
C(1)–C(3)	1.514(10)	P(2)–O(7)	1.546(5)
P(2)–O(6)	1.477(6)	P(2)–C(19)	1.797(7)
P(2)–O(8)	1.565(5)	O(10)–C(22)	1.189(12)
O(9)–C(20)	1.236(9)	N(4)–C(22)	1.329(10)
N(3)–C(20)	1.333(11)		
Angles (°)			
O(1)–Gd–O(6)	148.5(2)	O(6)–Gd–O(20)	77.7(2)
O(1)–Gd–O(20)	81.3(2)	O(1)–P(1)–O(3)	114.9(3)
O(1)–P(1)–O(2)	112.5(3)	O(1)–P(1)–C(1)	113.3(3)
O(2)–P(1)–O(3)	107.0(3)	O(3)–P(1)–C(1)	103.3(3)
O(2)–P(1)–C(1)	105.0(3)	P(1)–C(1)–C(2)	111.7(5)
Gd–O(1)–P(1)	175.0(3)	C(2)–C(1)–C(3)	109.4(7)
P(1)–C(1)–C(3)	109.6(5)	O(4)–C(2)–C(1)	118.9(7)
O(4)–C(2)–N(1)	120.9(8)	C(1)–C(3)–C(4)	112.2(6)
O(5)–C(4)–N(2)	123.1(7)	O(5)–C(4)–C(3)	118.7(7)
O(8)–P(2)–C(19)	100.9(3)	Gd–O(6)–P(2)	170.7(3)
P(2)–C(19)–C(20)	111.3(5)	P(2)–C(19)–C(21)	111.6(5)
C(20)–C(19)–C(21)	110.3(5)	N(3)–C(20)–C(19)	120.3(6)
O(10)–C(22)–C(21)	120.3(7)	O(10)–C(22)–N(4)	120.4(9)
O(9)–C(20)–C(19)	117.6(7)	N(4)–C(22)–C(21)	119.3(8)
C(19)–C(21)–C(22)	110.3(7)		
N(1)–C(2)–C(1)	120.2(8)		

nation polyhedron approximates a nine coordinate tricapped trigonal bipyramid with coordination positions occupied by six oxygen atoms from three bidentate nitrate ions, two phosphoryl oxygen atoms from two monodentate ligands, **1c**, and the oxygen atom of a water molecule. Apparently, steric congestion introduced by the long-leg carbamide groups prevents displacement of the last coordinated water molecule and coordination of the carbonyl groups by Gd.

The Gd–O(phosphoryl) distances are identical, 2.343(5) Å, and slightly longer than the average Er–O(phosphoryl) distances in **2**, 2.284(5) Å and in $Er(NO_3)_3[(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2]_2 \cdot H_2O$ (**4**), 2.28 Å [4]. The phosphoryl distances, P(1)–O(1) 1.458(5) Å and P(2)–O(6) 1.477(6) Å (avg. 1.468 Å), show no significant lengthening over the P=O distance in **1c**. A similar observation can be made by comparison to P=O distances in **2**.

The long-leg carbonyl distances, C(4)–O(5) 1.229(9) Å, and C(22)–O(10) 1.189(12) Å are unaffected by formation of **3**; however, the short-leg distances, C(2)–O(4) 1.246(11) Å and C(20)–O(9) 1.236(9) Å, appear slightly elongated compared to the distance in **1c**, although the differences may not be statistically significant. The short-leg carbonyl groups are pointed not at the Gd atom (Gd–O(4), Gd–O(9) > 4 Å), but directly at the hydrogen atoms of the Gd coordinated water molecule. The water hydrogen atoms (H(20a) and H(20b)) are clearly visible in the final Fourier difference map, and the Gd–water–carbonyl oxygen parameters are consistent with a formation of significant hydrogen bonding network: Gd–O(20) 2.354(5) Å, O(4)···O(20) 2.709 Å, O(9)···O(20) 2.654 Å, O(4)–H(20b) 2.06(6) Å, O(9)–H(20a) 1.86(7) Å, O(4)–H(20b)–O(20) 140.4° and O(9)–H(20a)–O(20) 173.9°. It is important to note that infrared spectroscopic shifts in ν_{PO} and ν_{CO} from **1c** and **3** are consistent with the structural picture*. Bond distances and angles along the ligand backbone and among the Gd–nitrate interactions show no unusual features.

Unfortunately, these structural studies do not provide an unambiguous structure assignment for the early lanthanide complexes. Infrared spectra for the ligand** **1c** and complexes, Ln = La, Ce, Pr and Nd, in THF solutions (0.1 g/ml) were obtained, and two distinct carbonyl bands were observed with one appearing at 1647 cm^{-1} ($\Delta\nu \sim 0$), and the second residing in the range 1616–1602 cm^{-1} ($\Delta\nu$ 47–33 cm^{-1}). The latter coordination shifts are comparable to those in the bidentate CMP–early lanthanide complexes, [4, 22] and they are also consistent with the presence of a free carbonyl group and a metal coordinated carbonyl group. The phosphoryl stretch is split in these complexes [23] with shifts of 42–41 cm^{-1} and 67–57 cm^{-1}. Such shifts are consistent with lanthanide phosphoryl coordination interactions [4, 22].

We have briefly discussed the potential effects of the long-arm carbamide group on the known, favorable extraction characteristics of the CMP ligands [8]. Extraction measurements [23], in fact, indicate that, at low acid concentrations, the ligands $(HxO)_2P(O)CH_2C(O)NEt_2$ and $(HxO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]$ have comparable extraction capabilities but, at high acid concentrations, the CMP ligand is a superior extractant for Ln(III) and An(III) ions. This observation suggests that the third functional group in **3** interferes with the normal coordination behavior of the basic CMP backbone. We have shown that it is possible to force a tridentate coordination geometry of **1c** on Er [24], and additional studies of functionally modified CMP-like ligands are warranted.

Supplementary Material

The observed and calculated structure factor amplitudes, hydrogen atom positions, anisotropic thermal parameters and full listings of bond distances and angles are available from the authors on request.

Acknowledgement

R.T.P. wishes to recognize financial support for this work from the Department of Energy, Office of Basic Energy Sciences, Contract No. 85ER-10465, as well as NSF Grants CHE-8201374 and CHE-780291 which assisted in the purchase of the high field NMR spectrometer and X-ray diffractometer.

References

1 T. H. Siddall, *J. Inorg. Nucl. Chem., 25,* 883 (1963); *26,* 1991 (1964).

2 W. W. Schulz and L. D. McIsaac, in W. Müller and R. Lindner (eds.), 'Transplutonium Elements', North-Holland, Amsterdam, 1976, p. 433; W. W. Schulz and L. D. McIsaac, in N. N. Li (ed.), 'Recent Developments in Separation Science', Vol. VII, CRC Press, Boca Raton, Fla., 1982, p. 31.

3 D. G. Kalina, G. W. Mason and E. P. Horwitz, *J. Inorg. Nucl. Chem., 43,* 159 (1981); D. G. Kalina, E. P. Horwitz, L. Kaplan and A. C. Muscatello, *Sep. Sci. Technol., 16,* 1127 (1981); A. C. Muscatello, E. P. Horwitz, D. G. Kalina and L. Kaplan, *Sep. Sci. Technol., 17,* 859 (1982).

---

*Infrared spectra for **1c** and its lanthanide complexes are very medium dependent, and coordination shifts must be interpreted with caution. For **3** in KBr ν_{PO} is split, $\Delta\nu_{PO} \sim 50$ cm^{-1}, $\Delta\nu_{CO}$ (two bands) 0 and 48 cm^{-1}. Similar shifts were observed for **2** [8].

****1c** in THF shows an infrared spectrum with ν_{CO} 1649 cm^{-1} and ν_{PO} 1260 cm^{-1}.

4 S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta, 61,* 155 (1982); S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chem., 21,* 261 (1982); S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chem., 22,* 286 (1983); L. J. Caudle, E. N. Duesler and R. T. Paine, *Inorg. Chem., 24,* 4441 (1985); S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta, 59,* 53 (1982).

5 Ya. T. Medved, M. K. Chmutova and N. P. Nesterova, *Izv. Akad. Nauk. SSSR (Khim), 9,* 2121 (1981); E. I. Matrosov, M. Yu Antipin and N. P. Nesterova, *Dokl. Akad. Nauk. SSSR, 273,* 1419 (1983); M. Yu. Antipin, T. Struchkov, E. I. Matrosov and M. I. Kabachnik, *Z. Strukt. Khim., 26,* 146 (1985).

6 B. F. Myasoedov, M. K. Chmutova and Z. K. Karalov, 'Actinide Separations', *ACS Symp. Ser., 117,* 101 (1980) and refs. therein.

7 D. J. McCabe, S. M. Bowen and R. T. Paine, *Synthesis,* 319 (1986).

8 D. J. McCabe, E. N. Duesler and R. T. Paine, *Inorg. Chem., 24,* 4626 (1985).

9 S. M. Bowen and R. T. Paine, *Inorg. Synth., 24,* 101 (1986).

10 'International Tables for X-ray Crystallography', Vol. I, D. Reidel, Dordrecht, Holland, 1983, pp. 73–346.

11 (a) G. M. Sheldrick, 'Nicolet SHELXTL Operations Manual', Nicolet XRD Corp., Cupertino, Calif., 1981; (b) 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, 1974, pp. 55–60, 99–101, 149–150.

12 F. R. Ahmed, S. R. Hall and C. P. Huber (eds.), 'Crystallographic Computing', Munksgaard, Copenhagen, 1970, p. 187.

13 R. M. Silverstein, G. C. Bassler and T. C. Morrill, 'Spectrometric Identification of Organic Compounds', 4th edn., Wiley, New York, 1981.

14 M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. Van Wazer, *Top. Phosphorus Chem., 5,* 1 (1967).

15 L. J. Caudle, *Ph.D. Thesis,* University of New Mexico, 1983.

16 H. Fritz, P. Hug, H. Sauter, T. Winkler and E. Logemann, *Org. Magn. Reson., 9,* 108 (1977).

17 M. A. Martins and R. Rittner, *Org. Magn. Reson., 14,* 522 (1980).

18 T. H. Siddall and C. A. Prohaska, *Appl. Spectros., 21,* 9 (1967).

19 W. McFarlane, *Proc. R. Soc. London, Ser. A, 306,* 185 (1968).

20 D. E. C. Corbridge, 'The Structural Chemistry of Phosphorus', Elsevier, New York, 1974.

21 A. J. Gordon and R. A. Ford, 'The Chemists Companion', Wiley, New York, 1972, pp. 107–108 and refs. therein.

22 S. M. Bowen, *Ph.D. Thesis,* University of New Mexico, 1983.

23 S. L. Blaha, K. W. Thomas and R. T. Paine, to be published; S. L. Blaha, *Ph.D. Thesis,* University of New Mexico, 1986.

24 D. J. McCabe, E. N. Duesler and R. T. Paine, submitted for publication.