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Synthesis of bifunctional phosphonates and phosphine oxides. Structural studies of 1-*N,N*-diethyl-carbamoyl-2-(4-hydroxylbenzene)-ethyl phosphonic acid and diphenyl[1-(*N,N*-diethyl-carbamoyl)-2-(phenyl)ethyl]phosphine oxide uranyl nitrate

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Abstract

Syntheses of the bifunctional ligands $Ph_2P(O)CH[CH_2C_6H_4X][C(O)NEt_2]$ (X = H, OCH_3, OH), $(EtO)_2P(O)CH[CH_2C_6H_4X][C(O)NEt_2]$ (X = H, OCH_3) and $(HO)_2P(O)CH[CH_2C_6H_4OH][C(O)NEt_2]$ from the corresponding carbanions $[Ph_2P(O)CHC(O)NEt_2^-]$ and $[(EtO)_2P(O)CHC(O)NEt_2^-]$ are described. The molecular structures of the phosphonic acid, $(HO)_2P(O)CH[CH_2C_6H_4OH][C(O)NEt_2]$ (**4c**), and of one complex, $\{Ph_2P(O)CH[CH_2C_6H_5][C(O)NEt_2]\}UO_2(NO_3)_2$ (**5a**), were determined by single crystal X-ray diffraction techniques. The phosphonic acid **4c** crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.347(2)$, $b = 11.403(2)$, $c = 12.427(1)$ Å, $\beta = 90.95(1)°$, $Z = 4$, $V = 1465.8(5)$ Å^3 and $\rho_{calc} = 1.36$ g cm^{-3}. The structure was solved by direct methods, and blocked least-squares refinement converged at $R_F = 6.37\%$ and $R_{wF} = 5.63\%$. The uranyl complex **5a** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.323(3)$, $b = 11.204(3)$, $c = 13.639(4)$ Å, $\alpha = 100.96(2)$, $\beta = 95.21(2)$, $\gamma = 98.68(2)°$, $Z = 2$, $V = 1519.3(8)$ Å^3 and $\rho_{calc} = 1.748$ g cm^{-3}. The structure was solved by Patterson methods, and blocked least-squares refinement converged at $R_F = 5.42\%$ and $R_{wF} = 3.89\%$. The ligand binds to the uranyl group in a bidentate fashion with no unusual steric congestion presented by the phenyl substituent groups. Selected bond distances include: $U{=}O_{av} = 1.740$, U–O(P) 2.347(5), U–O(C) 2.525(6), P=O 1.501(4), C=O 1.258(8) Å.

Introduction

Carbamoylmethyl phosphonates, $(RO)_2P(O)CH_2C(O)NR'_2$ (CMP), and carbamoylmethyl phosphine oxides, $R_2P(O)CH_2C(O)NR'_2$ (CMPO), coordinate effectively with trivalent lanthanide and actinide ions in acidic aqueous solutions, and selected derivatives are useful for liquid–liquid extraction processes [1–4]. In the course of studies of the coordination chemistry of these ligands, several derivatives that carry substituent groups on the central methyl carbon center, $(RO)_2P(O)CH(R'')C(O)NR'_2$ and $R_2P(O)CH(R'')C(O)NR'_2$ have been prepared. In some cases, the substituent group R″ contains a good donor center, e.g. $C(O)NR_2$ [5–8], which produces a trifunctional ligand while, in other cases, R″ is an alkyl group or an aryl group [9, 10]. In the latter case, the liquid–liquid extraction characteristics of $(C_6H_{13}O)_2P(O)CH_2C(O)N(C_2H_5)_2$ (**1**), $(C_6H_{13}O)_2P(O)CH(CH_3)C(O)N(C_2H_5)_2$ (**2**) and $(C_6H_{13}O)_2P(O)CH(CH_2C_6H_5)C(O)N(C_2H_5)_2$ (**3**) have been compared [11], and it was found that **3** behaves very differently from **1** and **2**. In particular, **1** and **2** show increasing values of *D* for extraction ($D = [M]_{org}/[M]_{aq}$) with increasing acid concentration (0.01–5 M HNO_3). In contrast, the values of *D* for **3** decrease with increasing acid strength from 0.01–1 M and then increase slightly at higher acid strengths. It was concluded that a change in mechanism for extraction occurs with the introduction of the benzyl group, although the specific nature of the change was not determined.

In an effort to learn more about substituent group effects on the coordination and extraction capabilities of CMP and CMPO ligands, a number of new ligands substituted at the phosphonate center, at the amide nitrogen and at the central methyl group have been prepared, and their coordination chemistry surveyed. We report here the formation and selected coordination chemistry of several 2-(benzene)ethyl CMP and CMPO ligands.

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Experimental

General

Boron tribromide, phosphorus tribromide, sodium hydride, benzyl bromide and anisyl alcohol were purchased from Aldrich Chemical Co. and $UO_2(NO_3)_2 \cdot 6H_2O$ was purchased from Strem Chemical Co. The reagents $(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2$, $(C_6H_5)_2P(O)CH_2C(O)N(C_2H_5)_2$, $Na^+[(C_2H_5O)_2P(O)CHC(O)N(C_2H_5)_2^-]$ and $Na^+[(C_6H_5)_2P(O)CHC(O)N(C_2H_5)_2^-]$ were prepared as described in the literature [12, 13]. All reactions were performed under dry nitrogen atmosphere, and solvents were dried and degassed. IR spectra were recorded on a Nicolet 6000 FTIR spectrometer from samples prepared as KBr pellets or oils. Mass spectra were obtained from a Finnegan model 4600 GC-mass spectrometer by using the solids probe for sample introduction. NMR spectra were obtained from Varian FT-80A, Nicolet NT-360 and JEOL GSX-400 spectrometers. ^1H and ^{13}C spectra were referenced with Me_4Si, and ^{31}P spectra were referenced with 85% H_3PO_4. Elemental analyses were obtained from the UNM microanalytical facility.

Synthesis of ligands

$(C_2H_5O)_2P(O)CH[CH_2C_6H_5][C(O)N(C_2H_5)_2]$ (**4a**)

A sample of $(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2$ (5.03 g, 20 mmol) was added to a 250 ml Schlenk vessel along with 150 ml of dry tetrahydrofuran (THF). Powdered NaH (1.0 g, 40 mmol) was added, and the mixture stirred at 25 °C for 2 h. The resulting mixture was filtered into a Schlenk vessel fitted with a septum capped side arm, and benzyl bromide (3.42 g, 20 mmol) was slowly syringed into the stirred filtrate. The reaction mixture was stirred for 1 h, then filtered. The solvent was vacuum evaporated, leaving a faintly yellow oil. Yield 95%. Soluble in benzene, toluene and THF. *Anal.* Calc. for $PO_4NC_{17}H_{28}$: C, 59.80; H, 8.28; N, 4.10. Found: C, 60.01; H, 8.18; N, 3.98%. Mass spectrum: $[M^+]$ 341. IR spectrum (cm^{-1}): 2963(m), 2932(m), 1643(s), 1446(m), 1432(m), 1255(s), 1059(m), 961(m). NMR spectra (C_6D_6): $^{31}P\{^1H\}$ δ23.7; ^1H δ7.2–7.1 (C_6H_4), 4.0 ($^3J_{HH}=7.0$ Hz, $POCH_2$) 3.5 ($^3J_{HH}=3.5$ Hz, $CH_2C_6H_5$), 3.2 ($^3J_{HH}=7.0$ Hz, NCH_2), 2.6 ($PCHC$), 0.8 ($^3J_{HH}=7.0$ Hz, $POCH_2CH_3$), 0.6 ($^3J_{HH}=7.0$ Hz, NCH_2CH_3); $^{13}C\{^1H\}$ δ165.9 ($^2J_{PC}=4.0$ Hz, $-C{=}O$), 138.7 ($^3J_{PC}=17.1$ Hz, i-C_6H_5) 127.9–125.6 (C_6H_5), 61.8 ($^2J_{PC}=6.4$ Hz, $POCH_2$), 61.4 ($^2J_{PC}=6.4$ Hz, $POCH_2$), 43.8 ($^1J_{PC}=132.5$ Hz PCHC), 41.5 (NCH_2), 40.1 (NCH_2), 31.2 ($^2J_{PC}=4.7$ Hz, $CH_2C_6H_5$), 15.4 ($^3J_{PC}=6.0$ Hz, $POCH_2CH_3$), 13.0 (NCH^2CH_3), 11.7 (NCH_2CH_3).

$(C_2H_5O)_2P(O)CH[CH_2C_6H_4OCH_3][C(O)N(C_2H_5)_2]$ (**4b**)

Anisyl bromide was prepared by bromination of anisyl alcohol by using PBr_3. A sample of $CH_3OC_6H_4CH_2OH$ (90.0 g, 0.65 mol) was dissolved in 250 ml CCl_4, and 64.7 g (0.24 mol) PBr_3 was added to the solution held at 0 °C in the dark. The mixture was stirred overnight. The resulting solution was washed with 10% aqueous $NaHCO_3$ until the washings tested basic to litmus paper. The solvent was removed by vacuum evaporation and the product rapidly distilled onto $CaCO_3$ held at 0 °C. Yield 47%. The anisyl bromide is light sensitive, and it was used immediately in subsequent reactions. Decomposition is accompanied by gas evolution.

A sample of anisyl bromide (2.67 g, 13.3 mmol) was added dropwise via syringe to a stirred solution containing 13 mmol of $Na^+[(C_2H_5O)_2P(O)CHC(O)N(C_2H_5)_2]$ in 100 ml of THF held at 0 °C. After the reagents were combined, the solution was warmed to room temperature and stirred for 1 h. The resulting mixture was centrifuged, the clear solution decanted, and the solvent removed by vacuum evaporation. The resulting oil was distilled and the product collected between 145–160 °C (10 mtorr). Yield 82%. *Anal.* Calc. for $PO_5NC_{18}H_{30}$: C, 58.20; H, 8.16; N, 3.77. Found: C, 57.88; H, 7.96; N, 3.68%. Mass spectrum: $[M^+]$ 371. NMR spectra (C_6D_6): $^{31}P\{^1H\}$ δ23.0; $^{13}C\{^1H\}$ δ167 ($-C{=}O$), 159 (C_6H_4), 131.7 ($^3J_{PC}=18.1$ Hz, i-C_6H_4), 130.5 (C_6H_4), 114.3 (C_6H_4), 63.3 ($^2J_{PC}=5.1$ Hz, $POCH_2$), 62.8 ($^2J_{PC}=5.5$ Hz, $POCH_2$), 55.6 (OCH_3), 45.5 ($^1J_{PC}=130.9$ Hz, $PCHC$), 43.1 (NCH_2), 41.7 (NCH_2), 33.9 ($CHCH_2$), 17.1 ($POCH_2CH_3$), 14.7 (NCH_2CH_3), 13.4 (NCH_2CH_3).

$(HO)_2P(O)CH[CH_2C_6H_4OH][C(O)N(C_2H_5)_2]$ (**4c**)

This reaction was performed in a manner similar to that described by Felix [14]. A sample of **4b** (1.71 g, 4.6 mmol) was dissolved in 60 ml of CH_2Cl_2 and 3.76 g (15.0 mmol) BBr_3 in 20 ml of CH_2Cl_2 was added at 0 °C. The mixture was stirred overnight, and the reaction was quenched with water. The resulting solution was vacuum evaporated and the residue dissolved in 100 ml CH_3OH containing ~1 g of H_2SO_4. The $B(OCH_3)_3$ and solvent were removed by vacuum evaporation until 20 ml remained. $BaCl_2$ (2.2 g) in 40 ml water was added, the mixture was filtered and the filtrate evaporated to dryness. The residue was recrystallized from C_2H_5OH. Yield 62%. *Anal.* Calc. for $PO_5NC_{13}H_{20}$: C, 51.82; H, 6.69; N, 4.65. Found: C, 52.10; H, 7.36; N, 4.48%. Mass spectrum: $[M^+]$ 301. IR spectrum (cm^{-1}): 3206(m), 1616(m), 1596(m), 1554(m), 1519(s), 1222(s), 1192(m), 1035(s), 1015(s), 964(s). NMR spectra:

$^{31}P\{^1H\}$ δ23.1; $^{13}C\{^1H\}$ δ169.4 ($^3J_{CP}$ = 3.9 Hz, −C=O), 156.4 (C_6H_4), 131 (C_6H_4), 130.1 (C_6H_4), 115.4 (C_6H_4), 45.9 ($^1J_{PC}$ = 131.1 Hz, P-CH-C), 43.0 (NCH$_2$), 41.4 (NCH$_2$), 33.6 ($^3J_{PC}$ = 3.7 Hz, CHCH$_2$), 13.6 (NCH$_2$CH$_3$), 12.3 (NCH$_2$CH$_3$).

$(C_6H_5)_2P(O)CH[CH_2C_6H_5][C(O)N(C_2H_5)_2]$ (5a)

This compound was prepared in a fashion analogous to that of **4a** from $(C_6H_5)_2P(O)$-$CH_2C(O)N(C_2H_5)_2$ [13]. The compound was isolated as a white crystalline solid, recrystallized from C_2H_5OH, with a yield of 85%. *Anal.* Calc. for $PO_2NC_{25}H_{28}$: C, 74.05; H, 6.96; N, 3.45. Found: C, 73.94; H, 7.39; N, 3.24%. Mass spectrum: [M^+], 405. NMR spectra (C_6D_6): $^{31}P\{^1H\}$ δ32.4; $^{13}C\{^1H\}$ δ174.1 (−C=O), 135–125 (C_6H_5), 49.9 (P-CH-C), 41.9 (NCH$_2$), 40.5 (NCH$_2$), 34.2 (CHCH$_2$), 12.9 (NCH$_2$CH$_3$), 12.0 (NCH$_2$CH$_3$).

$(C_6H_5)_2P(O)CH[CH_2C_6H_4OCH_3]$-$[C(O)N(C_2H_5)_2]$ (5b)

This compound was prepared in a fashion identical to that described for **4b** by using $(C_6H_5)_2P(O)CH_2C(O)N(C_2H_5)_2$ as the starting material. The compound was isolated as a white crystalline solid in 89% yield. *Anal.* Calc. for $PO_3NC_{26}H_{30}$: C, 71.71; H, 6.94; N, 3.22. Found: C, 71.56; H, 7.40; N, 3.17%. Mass spectrum: [M^+] 435. NMR spectra (C_6D_6): $^{31}P\{^1H\}$ δ32.2. $^{13}C\{^1H\}$ δ167.8 (−C=O), 159–125 (C_6H_4), 54.9 (OCH$_3$), 50.2 (PCHC), 42.0 (NCH$_2$), 40.6 (NCH$_2$), 33.5 (CHCH$_2$), 13.2 (NCH$_2$CH$_3$), 12.2 (NCH$_2$CH$_3$).

$(C_6H_5)_2P(O)CH[CH_2C_6H_4OH][C(O)N(C_2H_5)_2]$ (5c)

This compound was prepared in a fashion identical to that described for **4c** by using $(C_6H_5)_2P(O)CH_2C(O)N(C_2H_5)_2$ as the starting material. In this case, only the anisyl group undergoes cleavage. The compound was isolated as a white crystalline solid. Yield 80%. *Anal.* Calc. for $PO_3NC_{25}H_{28}$: C, 71.24; H, 6.70; N, 3.32. Found: C, 71.26; H, 6.97; N, 3.20%. NMR spectrum (D_2O): $^{31}P\{^1H\}$ δ28.0.

Synthesis of the complex $\{(C_6H_5)_2P(O)CH[CH_2C_6H_5]$-$[C(O)N(C_2H_5)_2]\}UO_2(NO_3)_2$

Ligand **5a** (3 mmol) was combined with $UO_2(NO_3)_2 \cdot 6H_2O$ (3 mmol) in 100 ml C_2H_5OH. The solvent was allowed to evaporate slowly and a yellow

TABLE 1. Experimental data for the X-ray diffraction study of $\{(HO)_2P(O)CH[CH_2C_6H_4OH][C(O)NEt_2]\}$ (**4c**) and $\{Ph_2P(O)CH[CH_2C_6H_5][C(O)NEt_2]\}UO_2(NO_3)_2$

Crystal parameters (293 K)		
Formula	$C_{13}H_{20}NO_5P$	$C_{25}H_{28}N_3O_{10}PU$
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	10.347(2)	10.323(3)
b (Å)	11.403(2)	11.204(3)
c (Å)	12.427(1)	13.639(4)
α (°)		100.96(2)
β (°)	90.95(1)	95.21(2)
γ (°)		98.68(2)
V (Å^3)	1465.8(5)	1519.3(8)
Z	4	2
Molecular weight (g mol^{-1})	301.3	799.5
ρ_{calc} (g cm^{-3})	1.36	1.748
μ (mm^{-1})	0.21	5.169
F (000)	640	772
Data collection		
2θ range (°)	2–50	2–50
Scan type	2θ–θ	2θ–θ
Scan speed (min^{-1}) (°)	variable 5–30	variable 4–30
Reflections collected	6208	14112
Independent reflections	2603	7023
Observed reflections	2142 ($F > 3\sigma(F)$)	5777 ($F > 3\sigma(F)$)
Min./max. transmission	0.847/0.906	0.7861/0.9682
R_F (%)	6.37	5.42
R_{wF} (%)	5.63	3.89
$w^{-1} = \sigma^2(F) + \lvert g \rvert F^2$		
g	0.0003	0.00022

crystalline solid was isolated. *Anal.* Calc. for $UPO_{10}N_3C_{25}H_{28}$: C, 37.56; H, 3.53; N, 5.26. Found: C, 37.37; H, 3.41; N, 5.18%.

Crystal structure determinations

Single crystals of the ligand **4c** (0.16×0.35×0.58 mm) and the complex $UO_2(NO_3)_2 \cdot$(**5a**) (0.09×0.16×0.16 mm) were lodged in glass capillaries. The crystals were centered on a Nicolet R3M/V or Siemens R3M/V automated diffractometer, and the determinations of the crystal class, orientation matrix, and unit cell dimensions were performed in a standard manner. Data were collected at 20 °C in the θ–2θ scan mode with use of Mo Kα radiation, scintillation counter, and pulse height analyzer. A summary of data collection parameters appears in Table 1. Corrections for adsorption were made empirically based on Ψ scans. Reduntant and equivalent data were averaged and converted to unscaled $|F_o|$ values following corrections for Lorentz and polarization effects.

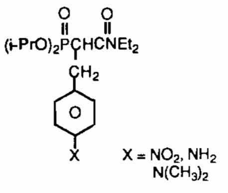
Solution and refinement of the structures

Solution of the structure for **4c** was made with direct methods, and all calculations were performed with the R3 SHELXTL structure determination package [15]. Anomalous dispersion terms were included for all atoms with $Z > 2$. Least-squares refinement* in this package uses a blocked-cascade algorithm with full matrix blocks of 103 parameters [16]. Anisotropic refinement on all non-hydrogen atoms with most hydrogens in fixed positions (riding model) resulted in the final R values listed in Table 1. The positions of hydrogens on O(2), O(3) and O(5) were allowed to vary. The final difference map showed no peaks greater than the trough amplitude. Atomic positional parameters and anisotropic thermal factors are provided in Table 2.

Solution and refinement for $UO_2(NO_3)_2 \cdot$(**5a**) were accomplished by heavy atom techniques, and all calculations were performed with a modified R3 system with SHELXTL Plus (Microvax II version). Anisotropic refinements were performed on all non-hydrogen atoms with hydrogens in fixed positions (riding model) and fixed U_{iso}s. Atomic positional parameters and anisotropic thermal factors are provided in Table 3.

Results and discussion

In previous papers, we reported formation of compounds of the general types I and II [10, 11]. The compounds with $X = NO_2$ and $Y = CH_3$ and $CH_2C_6H_5$ were prepared from metathesis reactions utilizing the respective sodium salts of the parent CMP ligands, $Na^+[(RO)_2P(O)CHC(O)NEt_2]$. In the present study, a set of related 2-(benzene)ethyl CMP and CMPO ligands has been obtained from metathesis reactions or subsequent derivatization of a 2-(benzene)ethyl compound as shown in eqns. (1)–(4). The new ligands are obtained in good yields in pure states, as indicated by satisfactory elemental analyses.



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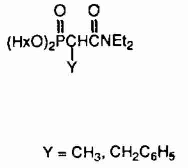

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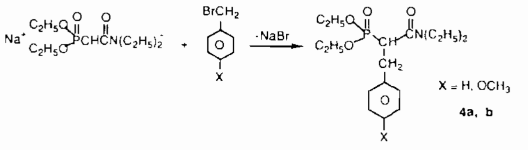

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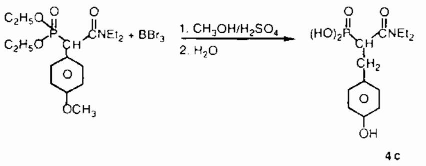

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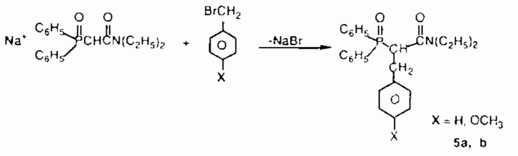

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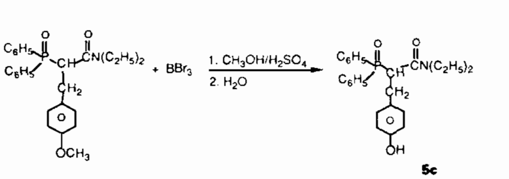

(4)

It is worth noting that the anisyl derivatives **4b** and **5b** were prepared from the relatively unstable p-$BrCH_2C_6H_4OCH_3$. The ligands, however, are stable and well-behaved. The formation of the 4-hydroxybenzene derivatives **4c** and **5c** was accomplished by reaction of the respective anisyl derivatives with BBr_3 followed by destruction of the intervening complex with $MeOH/H_2SO_4$, which releases $B(OMe)_3$ and water. Unfortunately, the strenuous reaction con-

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*A general description of the least-squares algebra is found in ref. 16. The least-squares refinement minimizes $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma(F)^2 + gF^2]$, $R_F = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$, $R_{wF} = [\Sigma|F_o| - [F_c|)^2/\Sigma wF_o]^{1/2}$, and the goodness of fit $GOF = [w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

TABLE 2. Atomic coordinates ($\times 10^4$) and anisotropic displacement coefficients (Å$\times 10^3$) for $(HO)_2P(O)CH[CH_2C_6H_4OH][C(O)N(C_2H_5)_2]$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	213(1)	−763(1)	1513(1)	48(1)	58(1)	49(1)	−5(1)	9(1)	−7(1)
O(1)	−605(2)	276(2)	1249(2)	50(1)	79(1)	54(1)	10(1)	6(1)	−6(1)
O(2)	541(2)	−1507(2)	514(2)	75(1)	62(1)	53(1)	−2(1)	10(1)	−8(1)
O(3)	−430(3)	−1580(3)	2329(2)	93(2)	68(2)	69(2)	−29(2)	29(1)	−13(1)
C(1)	1734(3)	−338(2)	2139(2)	48(2)	45(2)	45(2)	6(1)	6(1)	6(1)
C(2)	1503(3)	344(3)	3170(2)	44(2)	46(2)	61(2)	1(1)	3(1)	−2(1)
O(4)	1058(3)	1347(2)	3093(2)	125(2)	61(2)	93(2)	39(2)	−9(2)	−11(1)
C(3)	2535(3)	402(3)	1347(2)	54(2)	79(2)	56(2)	−8(2)	−3(2)	17(2)
C(4)	3897(3)	624(3)	1723(2)	53(2)	64(2)	40(2)	−7(2)	7(1)	14(1)
C(5)	4904(3)	−82(3)	1375(2)	64(2)	64(2)	44(2)	−16(2)	7(1)	1(2)
C(6)	6165(3)	114(3)	1689(2)	53(2)	60(2)	52(2)	0(2)	13(1)	1(2)
C(7)	6467(3)	1038(3)	2360(2)	55(2)	58(2)	42(2)	−7(1)	4(1)	6(1)
C(8)	5468(3)	1737(3)	2726(2)	62(2)	58(2)	56(2)	−7(2)	8(2)	−7(2)
C(9)	4223(3)	1532(3)	2413(3)	55(2)	60(2)	62(2)	2(2)	9(2)	9(2)
O(5)	7698(2)	1329(2)	2673(2)	50(1)	86(2)	61(1)	−7(1)	1(1)	−13(1)
N	1764(2)	−116(2)	4118(2)	63(2)	57(2)	45(1)	1(1)	3(1)	−6(1)
C(10)	1556(4)	609(4)	5086(3)	82(3)	90(3)	59(2)	−7(2)	7(2)	−22(2)
C(11)	2671(5)	1409(5)	5356(4)	103(4)	112(3)	115(4)	−16(3)	2(3)	−61(3)
C(12)	2221(4)	−1329(3)	4304(3)	118(3)	76(2)	50(2)	−10(2)	−2(2)	3(2)
C(13)	3653(4)	−1381(4)	4386(4)	108(4)	118(4)	80(3)	33(3)	−18(3)	−23(3)

The anisotropic displacement exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12})$.

ditions also result in displacement of the phosphonate ester groups of **4b** and the resulting product **4c** is a previously unknown phosphonic acid derivative.

Since compound **4c** is novel and well-formed crystals are obtained from the synthesis, a single crystal X-ray diffraction analysis of the compound was undertaken. A view of the molecule is shown in Fig. 1 and bond distances and angles are summarized in Table 4. The structure determination confirms the identity of the molecule and no unusual metrical parameters are revealed. The P=O distance, 1.489(2) Å, is shorter than the average P−OH distance, 1.541 Å, and falls within a range of P−O distances, 1.38–1.56 Å (av. 1.46 Å) observed for tetrahedral phosphates [17]. The C=O distance, 1.235(4) Å, is similar to those found in the trifunctional ligand $(i\text{-}PrO)_2P(O)CH[CH_2C(O)NEt_2][C(O)NEt_2]$, 1.228(3) and 1.223(3) Å [8], and they are comparable with the average carbonyl distance, 1.23 Å, found in a large group of amides and ketones [18]. The C(2)–N distance, 1.314(4) Å, is shorter than the distances in the trifunctional ligand, 1.353 (Å), or in alkyl amines 1.47 Å. This short distance suggests that the amide group may have a high degree of C–N multiple bonding, and this may influence the coordinating ability of the ligand. The coordination chemistry is under study; however, no structural data are presently available.

The spectroscopic data for the ligands are typical of data reported for related CMP and CMPO compounds [5, 10, 13]. The IR spectra show bands in the regions 1645–1610 and 1250–1205 cm^{-1} that may be assigned to the ν(CO) and δ(PO) stretching modes, respectively. The ^{31}P NMR spectra show single, sharp resonances in the region δ23–24 for **4a–c** and δ33–28 for **5a–c**. The shifts to lower field for the phenyl CMPO derivatives are expected [13].

The coordination chemistry of the six ligands was examined with several lanthanide salts, $Ln(NO_3)_3$, thorium nitrate, $Th(NO_3)_4$ and $UO_2(NO_3)_2$. Unlike most of the other CMP and CMPO ligand chemistry we have examined, difficulty was encountered in isolating and purifying the complexes, and it is likely that mixtures of 1:1 and 1:2 complexes, M·(L) and $M\cdot(L)_2$, are formed. One complex, $UO_2(NO_3)_2\cdot$(**5a**), was isolated and its molecular structure examined by single crystal X-ray diffraction techniques. A view of the molecule appears in Fig. 2, and selected bond distances and angles appear in Table 5. The structure confirms that a 1:1 $UO_2^{2+}\cdot L$ complex is formed and that the ligand is bonded to the uranium atom in a bidentate fashion. The two nitrate ions are also bonded to the uranium atom in a bidentate mode.

The average uranyl U=O distance, 1.740(4) Å, is identical to that in $UO_2(NO_3)_2[Ph_2P(O)CH_2C(O)NEt_2]$ (**6**), 1.742 Å, where there is no bulky 2-(phenyl)ethyl substitution [13] and in $UO_2(NO_3)_2[(i\text{-}PrO)_2P(O)CH[CH_2C_6H_4NO_2][C(O)NEt_2]$ (**7**), 1.735 Å, where there is a bulky 2-(phenyl)ethyl group [10]. The U−O(P) bond distance in **5a**, (2.347(5) Å) is slightly shorter than the related distances in **6** (2.377(4) Å) and **7** (2.40(1) Å), and

TABLE 3. Atomic coordinates ($\times 10^4$) and anisotropic displacement coefficients (Å $\times 10^3$) for $\{(C_6H_5)_2P(O)CH[CH_2C_6H_5][C(O)N(C_2H_5)_2]\}UO_2(NO_3)_2$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	1705(1)	1405(1)	2290(1)	35(1)	50(1)	40(1)	14(1)	9(1)	16(1)
O(3)	1157(5)	467(4)	1112(3)	66(3)	68(3)	46(3)	10(2)	9(2)	21(3)
O(4)	2283(4)	2314(5)	3480(3)	54(3)	81(4)	57(3)	10(3)	6(2)	21(3)
P	−920(2)	3137(1)	1816(1)	39(1)	38(1)	46(1)	14(1)	10(1)	11(1)
O(1)	452(4)	2842(4)	1837(3)	38(2)	51(3)	70(3)	25(2)	10(2)	12(2)
C(14)	−979(7)	4365(6)	2842(5)	69(5)	39(4)	44(4)	12(3)	8(3)	9(3)
C(15)	208(8)	5026(7)	3359(6)	85(6)	54(5)	54(5)	1(4)	3(4)	−4(4)
C(16)	237(12)	6006(9)	4145(7)	125(9)	74(6)	69(6)	−3(5)	0(6)	−10(6)
C(17)	−918(15)	6301(9)	4440(8)	185(13)	58(6)	66(7)	−2(5)	22(8)	28(7)
C(18)	−2128(12)	5678(10)	3954(8)	139(10)	88(7)	87(7)	3(6)	40(7)	49(7)
C(19)	−2160(8)	4695(8)	3139(6)	76(5)	72(6)	79(6)	3(5)	22(5)	25(4)
C(20)	−1389(6)	3543(5)	644(5)	39(3)	36(3)	44(4)	12(3)	6(3)	1(3)
C(21)	−2342(6)	4270(6)	532(5)	43(3)	44(4)	69(5)	24(3)	11(3)	6(3)
C(22)	−2634(7)	4580(7)	−383(6)	62(5)	63(5)	70(5)	33(4)	−1(4)	12(4)
C(23)	−1993(8)	4176(7)	−1180(6)	69(5)	77(6)	59(5)	34(4)	−7(4)	1(4)
C(24)	−1024(8)	3474(8)	−1080(6)	90(6)	90(6)	45(5)	18(4)	21(4)	9(5)
C(25)	−729(7)	3149(7)	−163(5)	60(4)	70(5)	56(5)	15(4)	17(4)	24(4)
C(1)	−2104(6)	1793(5)	1930(4)	38(3)	46(4)	44(4)	16(3)	11(3)	13(3)
C(7)	−2251(7)	767(6)	940(5)	58(4)	52(4)	50(4)	8(3)	8(3)	9(3)
C(8)	−2892(7)	−462(6)	1083(5)	57(4)	35(4)	49(4)	−5(3)	10(3)	−1(3)
C(9)	−2130(7)	−1348(6)	1212(6)	62(5)	37(4)	96(6)	0(4)	18(4)	6(3)
C(10)	−2680(10)	−2455(8)	1403(8)	86(7)	46(5)	155(10)	14(6)	10(6)	14(5)
C(11)	−4019(10)	−2734(8)	1405(8)	111(8)	39(5)	124(8)	10(5)	22(6)	1(5)
C(12)	−4799(9)	−1862(8)	1271(7)	63(5)	61(6)	125(8)	−4(5)	23(5)	−12(4)
C(13)	−4254(7)	−745(7)	1091(6)	57(5)	55(5)	83(6)	4(4)	10(4)	3(4)
C(2)	−1583(6)	1304(5)	2822(5)	42(3)	35(3)	48(4)	9(3)	6(3)	10(3)
O(2)	−417(4)	1098(4)	2867(3)	44(3)	66(3)	69(3)	33(3)	17(2)	22(2)
N(1)	−2324(5)	1073(5)	3530(4)	44(3)	59(3)	45(3)	17(3)	11(2)	16(3)
C(3)	−1740(7)	574(7)	4362(5)	63(4)	77(5)	45(4)	20(4)	12(3)	19(4)
C(4)	−2028(12)	−762(9)	4199(8)	185(12)	81(7)	110(8)	47(6)	−1(8)	30(7)
C(5)	−3735(7)	1121(8)	3510(6)	46(4)	104(6)	66(5)	31(5)	25(4)	20(4)
C(6)	−4039(9)	2154(10)	4285(8)	81(6)	170(11)	106(8)	22(8)	24(6)	64(7)
N(2)	2349(6)	−788(6)	2993(4)	77(4)	71(4)	50(4)	22(3)	14(3)	35(4)
O(5)	1220(5)	−491(5)	3031(4)	59(3)	79(4)	83(4)	39(3)	28(3)	33(3)
O(6)	3176(5)	−85(5)	2632(4)	58(3)	86(4)	102(4)	50(3)	26(3)	34(3)
O(7)	2635(6)	−1691(5)	3281(4)	110(4)	75(4)	80(4)	38(3)	20(3)	53(3)
N(3)	4027(6)	2752(7)	1610(5)	46(4)	88(5)	87(5)	39(4)	13(3)	10(4)
O(8)	4025(5)	1713(5)	1863(4)	50(3)	98(4)	100(4)	47(4)	24(3)	33(3)
O(9)	2930(5)	3112(5)	1592(4)	45(3)	80(4)	113(4)	53(3)	23(3)	22(3)
O(10)	5023(6)	3351(7)	1430(6)	52(3)	143(6)	160(7)	79(5)	31(4)	−3(4)

The anisotropic displacement exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12})$.

the U−O(C) bond distance in **5a** (2.392(4) Å) is identical to those found in **6** and **7** (2.404(5) and 2.39(1) Å). The P=O bond distance (1.501(4) Å) is long and comparable with the bond distances in **6** (1.512(5) Å) and **7** (1.49(1) Å). The C=O bond distance in **5a** (1.258(8) Å) is identical to those found in **6** (1.264(8) Å) and **7** (1.28(2) Å). These distances suggest that each ligand serves as a strong bidentate donor through the phosphoryl group and carbonyl group to UO_2^{2+}.

The results of this study and work described previously [10, 13] suggest that, at least for $Ph_2P(O)CH_2C(O)NEt_2$ and its 2-(benzene)ethyl derivatives, complexes will form with UO_2^{2+} with no obvious steric inhibition caused by the 2-(phenyl)ethyl derivatization. Unfortunately, lanthanide complexes of these ligands have not been isolated and structurally characterized so it is not possible to draw any conclusions on the binding efficacy of the ligands under the likely more sterically demanding conditions found in $Ln(NO_3)_3 \cdot L_2$ complexes. It is expected that the ligands $Ph_2P(O)CH_2C(O)NEt_2$ and $Ph_2P(O)CH[CH_2C_6H_4X][C(O)NEt_2]$ will display differing extraction abilities if for no other reasons than they should have differing competitive protonation processes depending on the basicity of X, i.e. X = H,

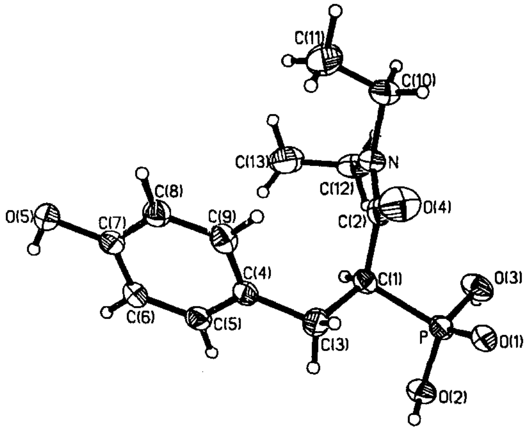

Fig. 1. Molecular structure of $(HO)_2P(O)CH[CH_2C_6H_4OH][C(O)N(C_2H_5)_2]$ (25% thermal ellipsoids).

TABLE 4. Selected structural parameters for $(HO)_2P(O)CH[CH_2C_6H_4OH][C(O)N(C_2H_5)_2]$

P–O(1)	1.489(2)	P–O(2)	1.545(2)
P–O(3)	1.537(3)	P–C(1)	1.810(3)
C(1)–C(2)	1.521(4)	C(1)–C(3)	1.547(4)
C(2)–O(4)	1.235(4)	C(2)–N	1.314(4)
C(3)–C(4)	1.499(4)	C(4)–C(5)	1.391(4)
C(4)–C(9)	1.382(4)	C(5)–C(6)	1.374(4)
C(6)–C(7)	1.376(4)	C(7)–C(8)	1.388(4)
C(7)–O(5)	1.366(3)	C(8)–C(9)	1.360(4)
N–C(10)	1.478(4)	N–C(12)	1.479(4)
C(10)–C(11)	1.505(6)	C(12)–C(13)	1.484(6)
O(1)–P–O(2)	113.1(1)	O(1)–P–O(3)	112.1(1)
O(2)–P–O(3)	107.5(1)	O(1)–P–C(1)	111.6(1)
O(2)–P–C(1)	107.0(1)	O(3)–P–C(1)	105.1(1)
P–C(1)–C(2)	110.6(2)	P–C(1)–C(3)	110.1(2)
C(2)–C(1)–C(3)	110.5(2)	C(1)–C(2)–O(4)	118.1(3)
C(1)–C(2)–N	121.2(3)	O(4)–C(2)–N	120.7(3)
C(1)–C(3)–C(4)	113.9(2)	C(3)–C(4)–C(5)	120.7(3)
C(3)–C(4)–C(9)	122.6(3)	C(5)–C(4)–C(9)	116.7(3)
C(4)–C(5)–C(6)	122.1(3)	C(5)–C(6)–C(7)	120.1(3)
C(6)–C(7)–C(8)	118.4(3)	C(6)–C(7)–O(5)	124.0(3)
C(8)–C(7)–O(5)	117.5(3)	C(7)–C(8)–C(9)	120.9(3)
C(4)–C(9)–C(8)	121.8(3)	C(2)–N–C(10)	118.4(3)
C(2)–N–C(12)	125.0(3)	C(10)–N–C(12)	116.5(3)
N–C(10)–C(11)	113.5(3)	N–C(12)–C(13)	111.4(3)

OCH_3, OH, NO_2, NMe_2, and the differing organic phase solubility of the ligands with protonated substituent groups.

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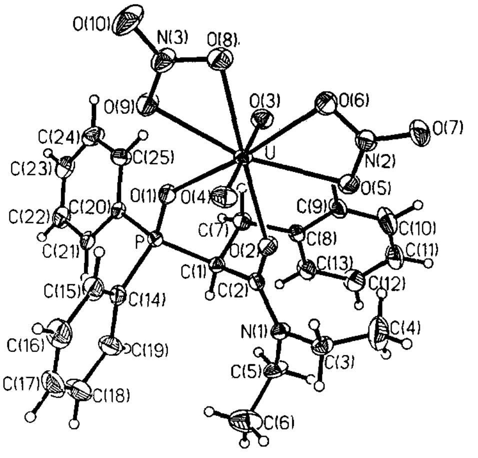

Fig. 2. Molecular structure of $\{Ph_2P(O)CH[CH_2C_6H_5][C(O)NEt_2]\}UO_2(NO_3)_2$ (20% thermal ellipsoids).

TABLE 5. Selected structural parameters for $\{Ph_2P(O)CH[CH_2C_6H_5][C(O)NEt_2]\}UO_2(NO_3)_2$

Bond lengths (Å)			
U–O(1)	2.347(5)	P–O(1)	1.501(4)
U–O(2)	2.392(4)	P–C(14)	1.779(6)
U–O(3)	1.738(4)	P–C(20)	1.788(7)
U–O(4)	1.743(4)	P–C(1)	1.831(6)
U–O(5)	2.525(6)	C(1)–C(2)	1.515(9)
U–O(6)	2.499(6)	C(2)–N(1)	1.324(8)
U–O(8)	2.505(5)	C(2)–O(2)	1.258(8)
U–O(9)	2.519(6)	C(1)–C(7)	1.576(8)
		C(7)–C(8)	1.490(9)
Bond angles (°)			
O(3)–U–O(4)	178.3(2)		
O(3)–U–O(1)	88.4(2)	P–C(1)–C(7)	109.5(4)
O(3)–U–O(2)	93.7(2)	P–C(1)–C(2)	108.3(4)
O(2)–U–O(4)	87.0(2)	C(7)–C(1)–C(2)	109.7(5)
O(1)–P–C(1)	110.6(3)	C(1)–C(2)–N(1)	121.9(5)
O(1)–P–C(14)	109.6(3)	C(1)–C(2)–O(2)	117.8(6)
O(1)–P–C(20)	109.6(3)	O(2)–C(2)–N(1)	120.3(6)
C(14)–P–C(20)	110.7(3)	C(3)–N(1)–C(5)	115.5(6)
U–O(1)–P	141.4(3)	C(2)–N(1)–C(3)	118.1(5)
U–O(2)–C(2)	148.3(5)	C(2)–N(1)–C(5)	125.9(6)

References

1 D. G. Kalina, E. P. Horwitz, L. Kaplan and A. C. Muscatello, *Sep. Sci. Tech.*, *16* (1981) 1127, and refs. therein.
2 D. G. Kalina and E. P. Horwitz, *Ion Exch. Solvent Extr.*, *3* (1985) 235.
3 E. P. Horwitz and D. G. Kalina, *Ion Exch. Solvent Extr.*, *2* (1984) 179.

4 W. W. Schulz and J. D. Navratil, in N. N. Li (ed.), *Recent Developments in Separation Science,* Vol. 7, Chemical Rubber Co., Boca Raton, FL, 1982, p. 31.

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

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

7 D. J. McCabe, E. N. Duesler and R. T. Paine, *Inorg. Chem., 27* (1988) 1220.

8 D. J. McCabe, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta, 147* (1988) 265.

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

10 S. Karthikeyan, R. T. Paine and R. R. Ryan, *Inorg. Chim. Acta, 144* (1988) 135.

11 S. L. Blaha, L. J. Caudle, G. C. Conary, R. T. Paine and K. W. Thomas, *Radiochim. Acta, 48* (1989) 59.

12 S. M. Bowen, E. N. Duesler, R. T. Paine and C. F. Campana, *Inorg. Chim. Acta, 59* (1982) 53.

13 L. J. Caudle, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta, 110* (1985) 91.

14 M. F. Felix, *J. Org. Chem., 39* (1974) 1427.

15 (a) G. M. Sheldrick, *Nicolet SHELXTL Operations Manual*, Nicolet XRD Corp., Cupertino, CA, 1981; (b) *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, UK, 1968.

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

17 D. E. C. Corbridge, *The Structural Chemistry of Phosphorus*, Elsevier, New York, 1974.

18 H. Bent, *Chem. Rev., 61* (1961) 275.