Formation and Crystal and Molecular Structures of Dioxouranium(VI) Complexes Containing Bidentate Carbamoylmethylphosphinate and Phosphine Oxide Ligands

L. J. CAUDLE, E. N. DUESLER and R. T. PAINE*

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

Received March 11, 1985

Abstract

The ligands $(C_6H_5)(C_2H_5O)P(O)CH_2C(O)N-(C_2H_5)_2$ (1) and $(C_6H_5)_2P(O)CH_2C(O)N(C_2H_5)_2$ (2) have been prepared and characterized by spectroscopic methods, and the coordination complexes, $UO_2(NO_3)_2[(C_6H_5)(C_2H_5O)P(O)CH_2C(O)N(C_2H_5)_2]$ (3) and $UO_2(NO_3)_2[(C_6H_5)_2P(O)CH_2C(O)N(C_2H_5)_2]$ (4), have been isolated and characterized by elemental analyses and spectroscopic methods. A single crystal X-ray diffraction analysis of 3 has been completed at 20 °C, and the complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.141(3)$ Å, $b = 13.281(2)$ Å, $c = 13.918(3)$ Å, $\beta = 116.79(2)°$, $Z = 4$, $V = 2168.5(8)$ Å^3, and $\rho_{calcd} = 2.07$ g × cm^{-3}. The structure was solved by heavy-atom methods and blocked least-squares refinement converged with $R_F = 0.048$ and $R_{wF} = 0.046$. Single crystal X-ray diffraction analysis of 4 has been performed at 26 °C and the complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.155(3)$ Å, $b = 11.265(2)$ Å, $c = 20.317(5)$ Å, $\beta = 107.44(2)°$, $Z = 4$, $V = 2435.5(8)$ Å^3 and $\rho_{calcd} = 1.93$ g × cm^{-3}. The structure was solved by heavy atom methods and blocked least-squares refinement converged with $R_F = 0.035$ and $R_{wF} = 0.029$. The molecular structures contain linear $UO_2{}^{2+}$ ions bonded to two bidentate nitrate ions and one bidentate carbamoylmethylphosphinate or phosphine oxide ligand. The structures of these complexes are compared with the structure of $UO_2(NO_3)_2[(i-C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$.

Introduction

Although bifunctional carbamoylmethylphosphonate (CMP) ligands, $(RO)_2P(O)CH_2C(O)NR_2'$, are effective lanthanide and actinide extractants [1], there exists a great demand for improved specific ion extractants which function under a wide range of conditions. In order to design improved extractants it is helpful to understand the funda-mental coordination chemistry of existing extraction systems. In this regard, previous papers from our laboratory have described some of the solution and solid state structural chemistry of CMP extraction complexes [2–4]. Complexes of the types $UO_2-(NO_3)_2(CMP)$, $Th(NO_3)_4(CMP)_2$, $Ln(NO_3)_3(CMP)_2$ (Ln = La–Gd) and $Ln(NO_3)_3(CMP)_2·H_2O$ (Ln = Tb–Er) have been isolated and, in the first three examples, found to contain bidentate CMP ligands. In the last case, the CMP ligand is bonded to the lanthanide ion through the phosphoryl oxygen atom, while the carbonyl oxygen atom is hydrogen bonded to a lanthanide coordinated water molecule. These results have suggested several approaches for development of new bifunctional extractants. In particular, it is of interest to determine what systematic steric and electronic modifications on the CMP backbone alter the coordination properties of the ligand in a favorable way.

Prior to our present work, Horwitz and coworkers [5] examined the liquid-liquid extraction of Am(III) and Fe(III) with a series of phosphonate, phosphinate, and phosphine oxide ligands, $X_2P(O)CH_2C(O)-NR_2'$ where $X_2 = (C_6H_{13}O)_2$, $(C_6H_{13})(C_6H_{13}O)$ and $(C_6H_{13})_2$. Based upon distribution measurements they concluded that replacement of an alkoxy substituent by an alkyl chain resulted in improved hydrolytic stability and improved Am(III) extraction capability. It was suggested that enhanced extraction capability resulted from improved basicity of the phosphoryl oxygen atom. On the other hand, metal ion selectivity was degraded by this structural-electronic change, although some selectivity was subsequently recovered by introduction of a branched amide alkyl group.

In one aspect of our studies we have chosen to replace alkoxy substituents at phosphorus with phenyl groups which should likewise enhance ligand hydrolytic and radiolytic stability, as well as improve the phosphoryl base strength. The ligands $(C_6H_5)-(C_2H_5O)P(O)CH_2C(O)N(C_2H_5)_2$ (1) and $(C_6H_5)_2-P(O)CH_2C(O)N(C_2H_5)_2$ (2) have been prepared and characterized, and complexes with $UO_2(NO_3)_2$ have been isolated and structurally characterized. We report here on these findings and on the comparison

---

*Author to whom correspondence should be addressed.

of these results with those obtained for the CMP complex, $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$.

Experimental

General Information

$(C_6H_5)_2POCH_3$ and $(C_2H_5O)_2PPh$ were obtained from Aldrich Chemical Co. and used without further purification. The $ClCH_2C(O)N(C_2H_5)_2$ was obtained from Fairfield Chemical Co., and it was freshly distilled prior to reaction with the phenyl phosphates. $UO_2(NO_3)_2 \cdot 6H_2O$ was obtained from Ventron-Thiokol. Infrared spectra were recorded on a Nicolet Model 6000 FT-IR spectrometer from KBr pellets or thin films. NMR spectra were recorded on a Varian FT-80 spectrometer operating at 32.2 MHz (^{31}P, 85% H_3PO_4 std.), 20.0 MHz (^{13}C, Me_4Si std.) and 80.0 MHz (^1H, Me_4Si std.). Elemental analyses were obtained from Galbraith Laboratories, Knoxville, Tenn.

Preparation of Ligands

(a) $(C_6H_5)(C_2H_5O)P(O)CH_2C(O)N(C_2H_5)_2$ (1)

The synthesis was performed in a 250 ml Schlenk flask outfitted with a stir bar, a water-cooled consenser capped with a mercury pressure relief bubbler, and a short side arm capped with a septum. The flask was purged with nitrogen and then charged with 25 g (0.13 mol) diethylphenylphosphonite. Freshly distilled N,N-diethylchloroacetamide, 18.8 g (0.13 mol) was slowly dripped from a syringe (30 min) into the stirred phosphonite held at 130 °C. Ethyl chloride was rapidly evolved and swept from the reaction vessel by a slow stream of nitrogen. After addition was complete the flask was held at 130 °C for an additional hour. The contents were then cooled to 25 °C and vacuum distilled. The colorless product 1 collected at 131–133 °C (10^{-3} torr) (yield 60%). The ligand is soluble in benzene, toluene, tetrahydrofuran (THF) and diethyl ether. *Anal.* Calcd. for $PO_3NC_{14}H_{22}$: C, 59.39; H, 7.77; N, 4.95; O, 16.95; P, 10.94. Found: C, 59.04; H, 7.93; N, 4.96; O, 16.89; P, 10.87. Infrared spectrum (cm^{-1}, thin film) 2965(m), 1635(s, ν_{co}), 1440(m) 1229(s, ν_{po}), 1035(s), 1022(s), 950(m). NMR spectra (C_6D_6, 27 °C): $^{31}P\{^1H\}$ δ 34.6; $^{13}C\{^1H\}$ δ 163.0 ($^2J_{CP}$ = 4.9 Hz), 131.5 ($^4J_{CP}$ = 2.6 Hz), 131.4 ($^1J_{CP}$ = 123.9 Hz), 131.2 ($^2J_{CP}$ = 9.8 Hz), 127.7 ($^3J_{CP}$ = 12.8 Hz), 60.0 ($^2J_{CP}$ = 6.1 Hz), 42.0, 39.2, 36.7 ($^1J_{CP}$ = 89.1 Hz), 15.6 ($^3J_{CP}$ = 6.3 Hz), 13.3; 12.1; ^1H δ 8.0, 7.4, 3.9 ($^3J_{HH}$ = 7.0, $^3J_{HP}$ = 7.0 Hz), 3.2 ($^2J_{HP}$ = 17.8 Hz), 3.2 ($^3J_{HH}$ = 7.0 Hz), 1.1 ($^3J_{HH}$ = 7.0 Hz), 0.9 ($^3J_{HH}$ = 7.0 Hz). Mass spectrum: M^+ 283.

(b) $(C_6H_5)_2P(O)CH_2C(O)N(C_2H_5)_2$ (2)

The synthesis was performed as described for 1. Equimolar amounts of methyldiphenylphosphinite and N,N-diethyl chloroacetamide were allowed to react at 130 °C for 1 h. As methyl chloride was evolved the reaction mixture solidified as a white powder. After cooling to 25 °C the solid was washed with benzene and air dried. The ligand is soluble in $CHCl_3$ and slightly soluble in C_2H_5OH. The yield was 65%. *Anal.* Calcd. for $PO_2NC_{18}H_{22}$: C, 68.6; H, 7.0; N, 4.4; O, 10.1; P, 9.8. Found: C, 68.74; H, 6.93; N, 4.41; O, 9.92; P, 9.85. Infrared spectrum (cm^{-1}, thin film) 2960(m), 2945(m), 1630(s, ν_{CO}), 1445(m), 1435(s), 1206(s, ν_{PO}), 1115(m), 1095(m). NMR spectra ($CDCl_3$, 27 °C): $^{31}P\{^1H\}$ δ 27.9; $^{13}C\{^1H\}$ δ 165.5 ($^2J_{CP}$ = 5.0 Hz), 133.2 ($^4J_{CP}$ = 3.0 Hz), 132.4 ($^2J_{CP}$ = 9.8 Hz), 131.8 ($^1J_{CP}$ = 102.5 Hz), 129.6 ($^3J_{CP}$ = 12.4 Hz), 44.2, 41.7, 39.4 ($^1J_{CP}$ = 60.9 Hz), 15.2; 14.0. Mass spectrum: M^+ 315.

Preparation of the Complexes

The complexes were prepared by combining a warm ethanol solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (20 mmol) with a warm ethanol solution of the respective ligands (20 mmol). Yellow, ethanol insoluble products were obtained. The solids were slightly soluble in boiling acetonitrile, and they were recrystallized from this solvent. Attempts to prepare $UO_2(NO_3)_2 \cdot L_2$ complexes by addition of excess ligand resulted in the formation of the same complexes as obtained by using the 1:1 stoichiometry. Characterization data are summarized as follows: $UO_2(NO_3)_2[(C_6H_5)(C_2H_5O)P(O)CH_2C(O)N(C_2H_5)_2]$ (3). *Anal.* Calcd. for $UPO_{11}N_3C_{14}H_{22}$: C, 24.83; H, 3.25; N, 6.21; O, 25.99; P, 4.57; U, 35.15. Found: C, 25.03; H, 3.51; N, 6.46; O, 25.77; P, 4.75; U, 35.15. $UO_2(NO_3)_2[(C_6H_5)_2P(O)CH_2C(O)N(C_2H_5)_2]$ (4) Calcd. for $UPO_{10}N_3C_{18}H_{12}$: C, 30.46; H, 3.10; N, 5.92; P, 4.37; O, 22.56; U, 33.57. Found: C, 30.46; H, 3.15; N, 5.92; P, 4.39; O, 22.45; U, 33.62. Infrared spectra (cm^{-1}, KBr pellets): **3**, 2975(m). 2935(m), 1588(s, ν_{CO}), 1480(s), 1365(m), 1280(s), 1173(s), 1149(s), 1120(m), 1010(s), 980(m), 930(s), 865(m); **4**, 3050(m), 2995(m), 1595 (s, ν_{CO}), 1510(s), 1475(sh), 1440(m), 1381(w), 1360(w), 1280(s), 1218(s), 1221(w), 1165(w), 1145(s), 1125(m), 1083(m), 1045(m), 1038(m), 951(w), 925(s), 840(w), 810(w).

Crystal Structure Determination

Single crystals of 3 and 4 were grown from acetonitrile solutions; suitable crystals of each (3: 0.46 × 0.20 × 0.11 mm; 4: 0.15 × 0.20 × 0.20 mm) were glued to a glass fiber. The crystals were centered on a P3/F automated diffractometer, and the determinations of the crystal class, orientation matrix and unit cell dimensions were performed in a standard manner [2]. Data were collected in the θ–2θ mode with

TABLE I. Experimental Data for the X-Ray Diffraction Studies of $UO_2(NO_3)_2[Ph(EtO)P(O)CH_2C(O)NEt_2]$ (3) and UO_2-$(NO_3)_2[Ph_2P(O)CH_2C(O)NEt_2]$ (4).

	3	**4**
(A) Crystal Parameters	At 20 °C	At 26 °C
Crystal System	monoclinic	monoclinic
Space Group	$P2_1/n$	$P2_1/n$
a (Å)	13.141(3)	11.155(3)
b (Å)	13.281(2)	11.265(2)
c (Å)	13.918(3)	20.317(5)
β (°)	116.79(2)°	107.44(2)
Z	4	4
V (Å³)	2168.5(8)	2435.5(8)
mol. wt. (g mol^{-1})	674.4	709.13
ρ_{calcd} (g cm^{-3})	2.07	1.93
$\mu(MoK_\alpha)$ (cm^{-1})	72.3	84.8
$F(000)$	1288	1352
(B) Data Collection		
diffractometer	Syntex P3/F	
radiation	MoK_α ($\lambda = 0.71069$ Å)	
monochromator	highly oriented graphite crystal	
reflections measured	$\pm h, +k, +l$	$\pm h, +k, +l$
2θ range	$1-55°$	$1-50°$
scan type	$\theta-2\theta$	$\theta-2\theta$
scan speed	$4-30$ deg min^{-1} (in 2θ)	$4-29.3$ deg min^{-1}
scan range	from $[2\theta(K\alpha_1) - 1.1]°$ to $[2\theta(K\alpha_1) + 1.1]°$	
backgrd. meas	stationary crystal and counter; at the beginning and end of each 2θ scan each for half the total 2θ scan time	
std, reflections	2/94 reflections	3/96 reflections
unique reflec. collected	4551	4311
obsd. reflect. used in refinement	3034 with $F > 5\sigma(F)$	2942 with $F > 5\sigma(F)$
weighting scheme: $1/[\sigma(F)^2 + gF^2]$	$g = 0.00056$	$g = 0.0008$
number of parameters	271	298

use of MoK_α radiation, scintillation counter and pulse height analyser. A summary of data collection parameters appears in Table I. Inspection of the collected data for 3 and 4 revealed systematic absences $h + l = 2n + 1$ for *hol* and $k = 2n + 1$ for *oko*, and the monoclinic space group $P2_1/n$ was indicated for both compounds. Corrections for absorption were made empirically based on ψ scans: 3, agreement factor on the ψ scans 5.8% before and 4.8% after the absorption correction, max. and min. transmission 24.3% and 18.4%; 4, agreement factor on the ψ scans 5.3% before and 3.3% after absorption correction, max. and min. transmission 18.2% and 13.1%. Redundant 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

Calculations were performed with the R3/SHELXTL structure determination package [6]. Anomalous dispersion terms were included for atoms with $Z > 2$. Least-squares refinement in this package uses a blocked-cascade algorithm with full-matrix blocks of 103 parameters [7]. The solution and refinement of the structures were based upon 3034 reflections with $F \geq 5\sigma(F)$ for 3 and 2943 reflections with $F \geq 5\sigma(F)$ for 4. Analysis of Patterson maps yielded the respective positions of the uranium atoms, and subsequent difference maps yielded the remaining nonhydrogen atom positions. Refinements of the positional and individual isotropic thermal parameters gave convergence at $R = 0.08$ and 0.07, respectively. Anisotropic refinements followed by inclusion of the hydrogen atoms in idealized positions with U_{iso} assigned at 1.3 and 1.2 times the last U_{equiv} of the parent atoms, respectively, led to final discrepancy indices $R_F = 0.048$, $R_{WF} = 0.045$, GOF = 1.29 for 3 and $R_F = 0.035$, $R_{WF} = 0.029$, GOF = 1.302 for 4. Final difference Fourier syntheses for 3 showed the first five peaks, 2.78–1.3 eÅ^{-3}, to be less than 1.06 Å from the uranium atom and the next seven peaks, 1.22–0.77 eÅ^{-3} less than 0.6 Å from C(7) or O(3). For 4, the three highest peaks, 0.93–0.62 eÅ^{-3}, were less than 1.12 Å from the

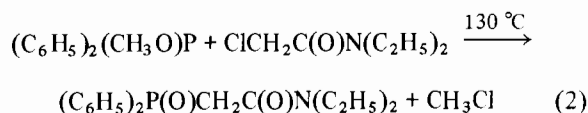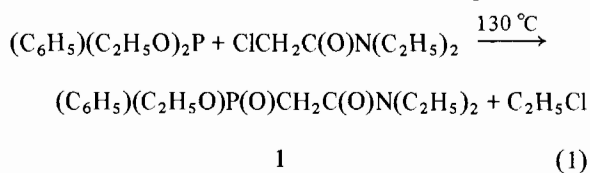TABLE II. Fractional Coordinates and Thermal Parameters[a] for $UO_2(NO_3)_2[Ph(EtO)P(O)CH_2C(O)NEt_2]$.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	−0.08418(3)	−0.03462(3)	0.14991(3)	0.0400(2)	0.0431(2)	0.0358(2)	0.0038(2)	0.0158(2)	0.0053(2)
O	−0.1806(7)	−0.1140(6)	0.1681(6)	0.072(5)	0.063(5)	0.074(5)	−0.006(5)	0.047(5)	−0.010(5)
O	0.0129(7)	0.0441(6)	0.1319(7)	0.075(6)	0.066(6)	0.078(6)	−0.008(5)	0.043(5)	−0.010(5)
O(1)	0.0447(8)	−0.0639(7)	0.3311(6)	0.084(6)	0.104(8)	0.044(5)	−0.004(4)	0.020(4)	0.050(5)
P(1)	0.1403(3)	−0.1348(3)	0.3905(2)	0.048(2)	0.068(2)	0.033(1)	0.001(1)	0.013(1)	0.015(2)
C(1)	0.2210(8)	−0.1590(8)	0.3178(8)	0.045(6)	0.052(7)	0.048(6)	0.000(5)	0.024(5)	0.001(5)
C(2)	0.1453(8)	−0.1929(8)	0.2028(7)	0.043(6)	0.048(6)	0.030(5)	0.006(5)	0.015(4)	0.009(5)
O(2)	0.0424(6)	−0.1716(6)	0.1605(5)	0.047(4)	0.057(5)	0.049(4)	−0.007(4)	0.017(4)	0.011(4)
N(1)	0.1923(7)	−0.2408(7)	0.1497(7)	0.053(5)	0.053(6)	0.037(5)	0.004(4)	0.021(4)	0.011(5)
C(3)	0.1211(10)	−0.2659(10)	0.0358(9)	0.062(8)	0.087(10)	0.048(7)	0.002(7)	0.026(6)	0.008(7)
C(4)	0.0751(12)	−0.3712(11)	0.0226(11)	0.086(10)	0.103(13)	0.072(9)	−0.028(9)	0.037(8)	−0.012(9)
C(5)	0.3141(10)	−0.2733(10)	0.1967(9)	0.069(8)	0.077(9)	0.056(7)	0.015(7)	0.038(7)	0.020(7)
C(6)	0.3885(11)	−0.1974(12)	0.1834(13)	0.068(9)	0.110(13)	0.155(15)	0.056(12)	0.074(10)	0.031(9)
O(9)	0.1043(8)	−0.2443(8)	0.4054(7)	0.031(5)	0.045(6)	0.027(5)	−0.009(4)	0.018(4)	−0.15(4)
C(7)	0.0347(18)	−0.2539(13)	0.4504(15)	0.228(24)	0.067(12)	0.102(15)	−0.22(11)	−0.25(15)	−0.009(14)
C(8)	0.0301(13)	−0.3576(14)	0.4889(11)	0.084(11)	0.163(18)	0.066(9)	−0.006(10)	0.045(9)	0.004(11)
C(11)	0.2296(9)	−0.0818(8)	0.5152(8)	0.051(6)	0.045(6)	0.035(5)	−0.008(5)	0.005(5)	0.002(5)
C(12)	0.2009(13)	0.0092(9)	0.5472(12)	0.087(10)	0.046(7)	0.091(10)	−0.007(7)	0.048(9)	0.003(7)
C(13)	0.2729(14)	0.0516(10)	0.6469(11)	0.141(14)	0.069(10)	0.074(9)	−0.021(8)	0.067(10)	−0.012(9)
C(14)	0.3678(14)	0.0004(11)	0.7121(11)	0.118(12)	0.095(11)	0.046(7)	−0.021(7)	0.030(8)	−0.045(9)
C(15)	0.3997(13)	−0.0892(13)	0.6856(10)	0.103(11)	0.101(12)	0.050(8)	−0.022(8)	0.014(8)	−0.026(10)
C(16)	0.3311(10)	−0.1336(10)	0.5916(10)	0.068(9)	0.071(9)	0.062(8)	0.002(7)	0.023(7)	−0.005(7)
N(2)	−0.2204(8)	−0.0656(7)	−0.0867(7)	0.014(6)	0.058(6)	0.043(5)	0.013(4)	0.019(5)	0.016(9)
O(4)	−0.2279(8)	0.0110(7)	−0.0367(7)	0.095(7)	0.066(6)	0.048(5)	−0.002(4)	0.009(5)	0.032(5)
O(3)	−0.1483(6)	−0.1316(5)	−0.0269(5)	0.052(4)	0.052(5)	0.044(4)	−0.001(4)	0.020(4)	0.005(4)
O(5)	−0.2773(7)	−0.0778(7)	−0.1809(6)	0.074(6)	0.097(7)	0.035(4)	−0.007(4)	0.008(4)	0.016(5)
N(3)	−0.1682(9)	0.1440(8)	0.2209(8)	0.087(8)	0.055(7)	0.069(7)	−0.001(5)	0.051(6)	0.009(6)
O(6)	−0.0852(6)	0.0915(6)	0.2842(5)	0.066(5)	0.057(5)	0.045(4)	−0.002(4)	0.018(4)	0.015(4)
O(7)	−0.2167(7)	0.1112(6)	0.1230(6)	0.076(6)	0.066(6)	0.066(5)	0.004(5)	0.029(5)	0.026(5)
O(8)	−0.2023(9)	0.2176(7)	0.2471(7)	0.131(8)	0.059(6)	0.082(6)	−0.006(5)	0.054(6)	0.032(6)

[a]The anisotropic temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \ldots 2U_{23}klb^*c^* + \ldots)$.

uranium atom. The remaining peaks were less than 0.52 $e\text{Å}^{-3}$. The observed and calculated structure factor amplitudes, hydrogen atom positional parameters, and anisotropic thermal parameters are available in supplementary material from our laboratory. The nonhydrogen atom positional parameters appear in Tables II and III.

Results and Discussions

The ligands 1 and 2 were prepared under an inert atmosphere in good yields from the Arbusov rearrangement in a fashion related to the synthesis of CMP ligands [8]. The ligands were identified by elemental analyses, observation of a parent ion

$$(C_6H_5)(C_2H_5O)_2P + ClCH_2C(O)N(C_2H_5)_2 \xrightarrow{130\,°C}$$

$$(C_6H_5)(C_2H_5O)P(O)CH_2C(O)N(C_2H_5)_2 + C_2H_5Cl$$

$$\mathbf{1} \qquad\qquad (1)$$

$$(C_6H_5)_2(CH_3O)P + ClCH_2C(O)N(C_2H_5)_2 \xrightarrow{130\,°C}$$

$$(C_6H_5)_2P(O)CH_2C(O)N(C_2H_5)_2 + CH_3Cl \qquad (2)$$

$$\mathbf{2}$$

in mass spectra and characteristic infrared and NMR spectroscopic signatures. In particular, 1 and 2 display carbonyl stretching frequencies at 1635 and 1630 cm^{-1}, respectively. These appear in positions comparable with ν_{CO} in $Ph_2P(O)CH_2C(O)Ph$ [9], 1630 cm^{-1} and in $(EtO)_2P(O)CH_2C(O)NEt_2$ [10], 1615 cm^{-1}. The phosphoryl stretching frequencies for 1 and 2 appear at 1229 and 1205 cm^{-1}, respectively. These can be compared with ν_{PO} measured for $(EtO)_2P(O)CH_2C(O)NEt_2$ [10], 1260 cm^{-1}. A similar down-frequency shift in ν_{PO} with increasing aryl substitution has been observed in a related series of bifunctional ligands [11]: $(EtO)_2P(O)CH_2$-CO_2H, 1257 cm^{-1}; $(EtO)(Ph)P(O)CH_2CO_2H$, 1177 cm^{-1}; $Ph_2P(O)CH_2CO_2H$, 1168 cm^{-1}. Ethoxy groups would be expected to exert a greater electron withdrawing influence relative to a phenyl

TABLE III. Fractional Coordinates and Thermal Parameters[a] for UO$_2$(NO$_3$)$_2$[Ph$_2$P(O)CH$_2$C(O)NEt$_2$].

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.05862(3)	0.13356(3)	−0.17314(1)	0.0289(1)	0.0375(2)	0.0387(2)	0.0013(2)	0.0020(1)	−0.0014(2)
P(1)	−0.23957(17)	0.15175(18)	−0.30645(10)	0.0298(10)	0.0407(13)	0.0404(11)	0.0030(10)	0.0026(8)	−0.0001(9)
Oa	0.1246(5)	0.0281(5)	−0.2146(3)	0.045(3)	0.056(4)	0.061(4)	−0.002(3)	0.015(3)	−0.010(3)
Ob	−0.0060(5)	0.2417(5)	−0.1327(3)	0.048(3)	0.063(4)	0.052(3)	−0.007(3)	0.011(3)	−0.014(3)
O(1)	−0.1443(4)	0.0880(4)	−0.2484(2)	0.033(3)	0.050(3)	0.046(3)	0.009(3)	−0.003(2)	−0.004(2)
O(2)	0.0219(4)	0.2551(5)	−0.2746(3)	0.034(3)	0.064(4)	0.054(3)	0.018(3)	0.010(3)	−0.001(3)
O(3)	0.2289(4)	0.2790(4)	−0.1744(3)	0.036(3)	0.045(3)	0.076(4)	0.005(3)	0.005(3)	−0.004(3)
O(4)	0.2725(5)	0.1649(5)	−0.0874(3)	0.048(3)	0.081(5)	0.076(4)	0.022(4)	−0.019(3)	−0.025(3)
O(5)	0.4084(5)	0.2966(6)	−0.0974(4)	0.045(4)	0.109(6)	0.107(6)	0.002(5)	−0.010(4)	−0.043(4)
O(6)	−0.0574(5)	−0.0239(5)	−0.1299(3)	0.046(3)	0.062(4)	0.053(4)	0.010(3)	−0.001(3)	−0.013(3)
O(7)	0.1283(5)	0.0086(5)	−0.0659(3)	0.056(4)	0.088(5)	0.063(4)	0.028(4)	−0.015(3)	−0.019(4)
O(8)	0.0161(7)	−0.1289(7)	−0.0373(4)	0.117(6)	0.104(6)	0.095(5)	0.054(5)	−0.009(5)	−0.049(5)
N(1)	−0.0436(5)	0.3749(6)	−0.3668(3)	0.042(4)	0.053(4)	0.045(4)	0.009(4)	0.013(3)	−0.008(4)
N(2)	0.3087(6)	0.2494(6)	−0.1182(4)	0.036(4)	0.061(5)	0.074(5)	0.001(4)	−0.002(4)	−0.004(4)
N(3)	0.0292(7)	−0.0511(7)	−0.0758(4)	0.66(5)	0.065(5)	0.063(5)	0.009(4)	0.001(4)	−0.021(4)
C(1)	−0.1953(7)	0.3053(7)	−0.3088(4)	0.044(5)	0.044(5)	0.046(5)	0.005(4)	0.002(4)	−0.004(4)
C(2)	−0.0650(7)	0.3115(7)	−0.3175(4)	0.033(4)	0.041(4)	0.051(5)	−0.008(4)	0.002(4)	−0.008(4)
C(5)	−0.1418(8)	0.4408(7)	−0.4211(4)	0.058(6)	0.059(6)	0.042(5)	0.010(5)	−0.000(4)	0.004(5)
C(6)	−0.1596(8)	0.5645(7)	−0.3994(5)	0.077(7)	0.058(6)	0.085(7)	0.020(6)	−0.001(6)	−0.002(5)
C(3)	0.0858(7)	0.3801(8)	−0.3715(4)	0.048(5)	0.078(7)	0.065(6)	0.016(6)	0.017(4)	−0.006(5)
C(4)	0.1120(9)	0.2879(10)	−0.4175(5)	0.082(8)	0.134(10)	0.085(8)	−0.017(8)	0.044(7)	0.015(7)
C(11)	−0.3932(6)	0.1517(6)	−0.2952(3)	0.035(4)	0.038(5)	0.035(4)	0.008(4)	0.004(3)	−0.004(4)
C(12)	−0.4402(7)	0.2472(7)	−0.2696(4)	0.050(5)	0.041(5)	0.060(6)	0.002(4)	0.021(4)	−0.007(4)
C(13)	−0.5577(8)	0.2399(8)	−0.2598(5)	0.059(6)	0.036(5)	0.091(7)	0.005(5)	0.038(5)	0.006(5)
C(14)	−0.6252(7)	0.1354(9)	−0.2737(4)	0.042(5)	0.075(7)	0.080(6)	0.025(7)	0.024(5)	−0.006(6)
C(15)	−0.5801(8)	0.0393(8)	−0.2998(4)	0.050(6)	0.049(6)	0.061(6)	0.011(5)	0.009(5)	−0.022(5)
C(16)	−0.4632(7)	0.0458(7)	−0.3120(4)	0.039(5)	0.040(5)	0.050(5)	0.005(4)	0.004(4)	0.002(4)
C(21)	−0.2461(7)	0.0862(7)	−0.3871(4)	0.033(4)	0.049(5)	0.040(4)	0.001(4)	−0.002(4)	0.002(4)
C(22)	−0.3396(7)	0.1176(7)	−0.4478(4)	0.050(5)	0.055(6)	0.056(5)	0.000(5)	0.006(4)	0.014(5)
C(23)	−0.3421(9)	0.0658(8)	−0.5099(5)	0.079(7)	0.077(7)	0.046(6)	−0.002(5)	−0.014(5)	0.026(6)
C(24)	−0.2541(12)	−0.0143(11)	−0.5119(5)	0.140(11)	0.126(10)	0.054(7)	−0.024(7)	0.011(7)	0.065(9)
C(25)	−0.1599(12)	−0.0433(12)	−0.4527(6)	0.146(12)	0.163(13)	0.080(8)	−0.040(9)	−0.009(8)	0.110(10)
C(26)	−0.1561(9)	0.0037(10)	−0.3906(5)	0.089(8)	0.113(9)	0.049(6)	−0.004(6)	−0.001(5)	0.059(7)

[a]The anisotropic temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \ldots 2U_{23}klb^*c^* + \ldots)$.

group on a P=O group, thereby reducing the base strength of the oxygen atom but increasing the P=O bond strength. This picture is qualitatively consistent with the trends in the ν_{PO} frequencies listed here.

The ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra for 1 and 2 have been fully assigned, and several important observations are outlined here. The ^{31}P resonances for 1 and 2 appear at 34.6 and 27.9 ppm, and these compare with the resonance in (EtO)$_2$P(O)CH$_2$C(O)-NEt$_2$ [10], 23.7 ppm. It is noteworthy that these shifts do not indicate a smooth variation in electronic effects about the phosphorus atom as ethoxy groups are replaced by phenyl groups. Similar trends can be found, however, in several related series of phosphoryl compounds, OP(OZ)$_2$R, OP(OZ)R$_2$, OPR$_3$ where the phosphine oxide typically appears upfield of the phosphinate [12]*.
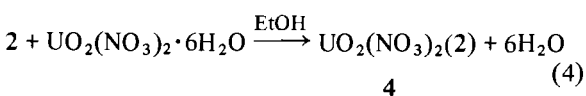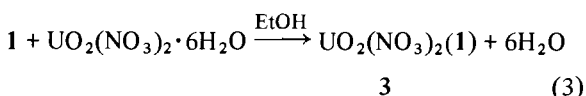
---

*Phosphonates typically appear at highest field, the phosphinates at lowest field, and phosphine oxides at intermediate field.

The ^{1}H NMR spectra show two broadened resonances in the phenyl region: 1, 8.0 and 7.4 ppm and 2 7.6 and 7.2 ppm, and a single doublet for the bridging methylene group, >P(O)CH$_2$C(O)−: 1 3.2 ppm, $^2J_{PH}$ = 17.8 Hz and 2 3.3 ppm, $^2J_{PH}$ = 15.7 Hz. The ^{1}H spectra also indicate two amide alkyl group environments in the methylene region, NCH$_2$ 3.2–3.1 ppm and in the methyl region, NCH$_2$CH$_3$ 0.9–0.7 ppm. This requires that there is hindered rotation about the carbamide C–N bond. The ^{13}C NMR data reveal resonances for each of the four nonequivalent carbon atom environments in the phenyl rings (133–127 ppm), the carbonyl atom: 1 163.0 ppm, J_{PC} = 4.9 Hz and 2 165.5 ppm and J_{PC} = 5.0 Hz, and the bridging methylene group: 1 36.7 ppm, J_{PC} = 89.1 Hz and 2 39.4 ppm, J_{PC} = 60.9 Hz. The nonequivalent amide group environments are also detected in the ^{13}C{^{1}H} spectra: NCH$_2$ 1 42.0, 39.2 ppm, 2 44.2, 41.7 ppm, NCH$_2$ CH$_3$, 1 13.3, 12.1 ppm, 2 15.2, 14.0 ppm. These data, including the evidence for hindered rotation

in the carbamide group, agree with extensive data collected on a series of CMP ligands with R = Me, Et, i-Pr, Bu and Hx [13].

Myasoedov and coworkers [14], Rozen and coworkers [15] and others [16] have extensively studied the extraction chemistry of diphosphine oxides, including methylene bis-phosphine oxides, $R_2P(O)$-$CH_2P(O)R_2$. Unlike monofunctional phosphine oxides, it has been noticed that replacement of alkyl R groups with phenyl groups leads to enhanced extraction ability for the bifunctional ligands. This is contrary to the expectation that the more electron releasing alkyl groups should enhance the phosphoryl oxygen base strength, and the so-called 'aryl strengthening effect' has been rationalized in terms of entropic influences [16]. During the course of our studies Horwitz [5] reported that, as expected, alkyl replacement of alkoxy groups on CMP ligands, $(RO)_2P(O)CH_2C(O)NR'_2$, resulted in higher extraction coefficients for trivalent actinides. Furthermore, Horwitz [17] has subsequently found that the phenyl substituted phosphine oxide (n-octyl)-$(Ph)P(O)CH_2C(O)N(i-Bu)_2$, is a particularly powerful extractant for trivalent actinides. It was with this background that we prepared 1 and 2 and studied the coordination chemistry of the ligands with uranyl ion and several lanthanide ions. The results of the chemistry with UO_2^{2+} is described here.

Combination of $UO_2(NO_3)_2 \cdot 6H_2O$ with 1 or 2 in a 1:1 mol ratio in warm ethanol resulted in the formation of yellow solids, 3 and 4, which are soluble only in hot acetonitrile. Elemental analyses confirmed the proposed compositions in which a uranyl ion

$$1 + UO_2(NO_3)_2 \cdot 6H_2O \xrightarrow{\text{EtOH}} UO_2(NO_3)_2(1) + 6H_2O$$

$$3 \qquad (3)$$

$$2 + UO_2(NO_3)_2 \cdot 6H_2O \xrightarrow{\text{EtOH}} UO_2(NO_3)_2(2) + 6H_2O$$

$$4 \qquad (4)$$

is coordinated with two nitrate ions and a single neutral bifunctional ligand. Attempts to prepare complexes with greater ligand stoichiometries were unsuccessful. The complexes have such low solubilities that it was impractical to obtain solution infrared or NMR spectra.

Infrared spectra of 3 and 4 recorded in KBr pellets show strong carbonyl frequencies at 1588 and 1595 cm^{-1}, respectively. These bands are shifted to lower frequency than ν_{CO} in the free ligands: $\Delta\nu_{CO}$ −47 and −35 cm^{-1}. These coordination shifts can be compared with the coordination shifts in $UO_2(NO_3)_2$-$[(i-PrO)_2P(O)CH_2C(O)NEt_2]$ [4] 5 −41 cm^{-1}, UO_2-$(NO_3)_2[CH_3CH_2C(O)NH_2]_2$ [18] − 20 cm^{-1}, UO_2-$(NO_3)_2[CH_3C(O)N(C_2H_5)_2]$ [19] −47 cm^{-1} and $UO_2(NO_3)_2-[C_6H_5C(O)N(C_2H_5)_2]$ [19] − 70 cm^{-1}. Shifts of these magnitudes have been invoked in the

past as evidence for carbonyl oxygen atom coordination to the uranyl ion, and the shifts in 3 and 4 support this mode of binding of 1 and 2 to UO_2^{2+}. Bands at 1173 cm^{-1} in 3 and 1145 cm^{-1} in 4 are assigned to ν_{PO}, and these frequencies represent −56 and −60 cm^{-1} coordination shifts. These shifts can be compared with shifts in 5 [4] −61 cm^{-1}, $UO_2(NO_3)_2[Ph_2P(O)CH_2P(O)Ph_2]$ [20] −49 and −88 cm^{-1} and $UO_2(NCS)_2[Ph_3P(O)]_2[CH_3C(O)CH_3]$ [21] −67 cm^{-1}. The large phosphoryl coordination shifts in 3 and 4 provide evidence that 1 and 2 bond to UO_2^{2+} through the phosphoryl oxygen atoms.

The asymmetric uranyl stretch in 3 and 4 appears at 930 and 925 cm^{-1}, respectively. These compare with related bands in 5 [4] 943 cm^{-1}, $UO_2(NO_3)_2$-$[CH_3CH_2C(O)NH_2]_2$ [18] 937 cm^{-1}, $UO_2(NO_3)_2$-$[Ph_3P(O)]_2$ [22] 929 cm^{-1} and $UO_2(NCS)_2[Ph_3$-$P(O)]_2[CH_3C(O)CH_3]$ [21] 923 cm^{-1}. Carnall [23] and Peppard [24] have noted that the uranyl asymmetric stretch can be qualitatively related to the U—O bond distance and to the electron density in 'secondary' bonds formed between the uranyl group and its ligands. Further, it has been suggested that as the uranyl—ligand coordinate bond strength increases the U—O bond distances should increase and the uranyl vibrational frequency should decrease. If this argument is valid and if 3, 4 and 5 are structurally related, then a comparison of ν_{O-U-O} should give a qualitative measure of the complexation strength of the respective phosphine oxide ligands. Interestingly, the highest uranyl stretching frequency is found in 5 and the lowest in 4, and this is in agreement with the expectation that sequential replacement of alkoxy groups in the CMP ligands with aryl groups should enhance the coordinate bond strength between the extractant and UO_2^{2+}.

Crystal structure determinations for 3 and 4 confirm the compositions of the complexes as UO_2-$(NO_3)_2(L)$, as well as the proposed bidentate coordination mode for the phosphine oxide ligands. Views of the molecules are shown in Figs. 1 and 2.
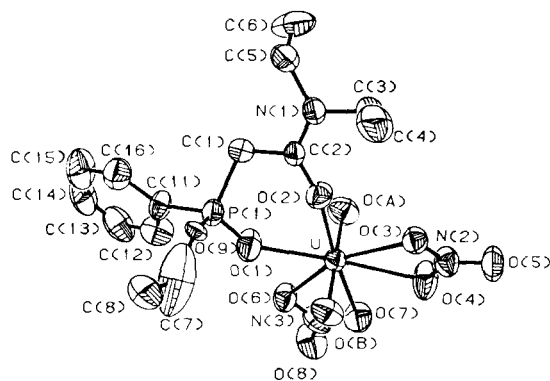

Fig. 1. Molecular geometry and atom labelling scheme for $UO_2(NO_3)_2[Ph(EtO)P(O)CH_2C(O)NEt_2]$ (50% ellipsoids).
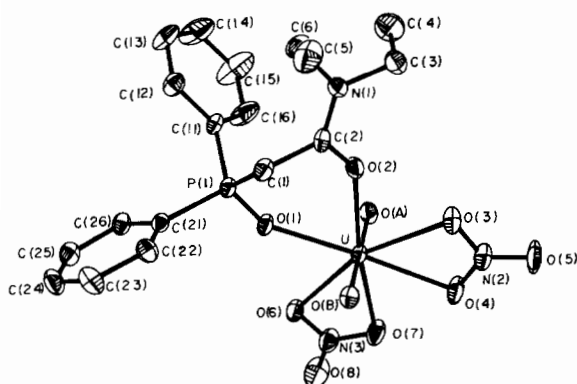
Fig. 2. Molecular geometry and atom labelling scheme for $UO_2(NO_3)_2[Ph_2P(O)CH_2C(O)NEt_2]$ (50% ellipsoids).

TABLE IV. Selected Interatomic Distances (Å).

(3) $UO_2(NO_3)_2[Ph(EtO)P(O)CH_2C(O)NEt_2]$

U–O(B)	1.754(10)
U–O(A)	1.752(10)
U–O(1)	2.351(7)
U–O(2)	2.426(8)
U–O(5)	2.561(7)
U–O(4)	2.503(7)
U–O(7)	2.515(9)
U–O(8)	2.517(9)
P(1)–O(1)	1.487(9)
P(1)–O(3)	1.572(10)
P(1)–C(1)	1.795(14)
P(1)–C(11)	1.746(9)
O(9)–C(7)	1.328(30)
C(7)–C(8)	1.489(26)
C(11)–C(12)	1.396(19)
C(12)–C(13)	1.399(18)
C(13)–C(14)	1.351(20)
C(14)–C(15)	1.365(24)
C(15)–C(16)	1.342(17)
C(16)–C(11)	1.453(15)
C(1)–C(2)	1.520(12)
C(2)–O(2)	1.243(12)
C(2)–N(1)	1.320(16)
N(1)–C(3)	1.473(13)
N(1)–C(5)	1.496(15)
C(3)–C(4)	1.502(20)
C(5)–C(6)	1.471(22)
N(2)–O(3)	1.283(11)
N(2)–O(4)	1.264(14)
N(2)–O(5)	1.192(11)
N(3)–O(6)	1.258(12)
N(3)–O(7)	1.294(14)
N(3)–O(8)	1.198(16)

(4) $UO_2(NO_3)_2[Ph_2P(O)CH_2C(O)NEt_2]$

U–O(A)	1.742(6)
U–O(B)	1.742(6)
U–O(1)	2.377(4)
U–O(2)	2.404(5)
U–O(3)	2.515(5)
U–O(4)	2.522(5)

TABLE IV. (continued)

U–O(6)	2.505(6)
U–O(7)	2.514(6)
P(1)–O(1)	1.512(5)
P(1)–C(1)	1.803(8)
P(1)–C(11)	1.796(8)
P(1)–C(21)	1.778(8)
C(2)–O(2)	1.264(8)
C(11)–C(12)	1.366(11)
C(12)–C(13)	1.385(13)
C(13)–C(14)	1.380(13)
C(14)–C(15)	1.365(14)
C(15)–C(16)	1.400(13)
C(16)–C(11)	1.411(10)
C(21)–C(22)	1.401(9)
C(22)–C(23)	1.384(13)
C(23)–C(24)	1.342(16)
C(24)–C(25)	1.377(15)
C(25)–C(26)	1.357(17)
C(26)–C(21)	1.386(14)
C(1)–C(2)	1.518(12)
C(2)–N(1)	1.309(11)
N(1)–C(3)	1.476(10)
N(1)–C(5)	1.497(9)
C(3)–C(4)	1.484(15)
C(5)–C(6)	1.493(12)
N(2)–O(3)	1.264(8)
N(2)–O(4)	1.269(10)
N(2)–O(5)	1.191(8)
N(3)–O(6)	1.264(8)
N(3)–O(7)	1.258(10)
N(3)–O(8)	1.212(11)

Selected interatomic distances and angles are given in Tables IV and V. The structures of the two molecules are closely related to the structure of 5 [4]. In each case the UO_2^{2+} group is bonded to two bidentate nitrate ions and one bidentate phosphine oxide ligand. These six oxygen atoms from the ligands form an approximately planar belt* which is perpendicular to the UO_2^{2+} vector and the eight oxygen atoms form an approximate hexagonal bipyramid. It is important to note that the bidentate nature of the carbamoylmethyl phosphine oxide ligands forces a *cis* orientation for the coordinated P=O and C=O groups. In

*The equations for the least-squares planes and atomic deviations (Å) from the planes are listed here. The equations are given in orthogonal coordinates x_o, y_o, z_o from crystal coordinates a, b, c for positions at x/a, y/b, z/c; $x_o = (x/a) a \sin \beta$, $y_o = (y/b)b$, $z_o = (x/a)a \cos \beta + (z/c)c$.
3: $0.640 x_o + 0.589 y_o - 0.494 z_o = -2.184$; deviations: U 0.004, O(1) = -0.124, O(2) = 0.181, O(3) = -0.209, O(4) = 0.143, O(6) = 0.057, O(7) = -0.52
4: $-0.396 x_o + 0.689 y_o - 0.608 z_o = -1.484$; deviations: U 0.017, O(1) = 0.002, O(2) = -0.062, O(3) = 0.068, O(4) = -0.016, O(6) = -0.062, O(7) = -0.077.

TABLE V. Selected Interatomic Angles (°).

TABLE V. (continued)

(1) $UO_2(NO_3)_2[Ph(EtO)P(O)CH_2C(O)NEt_2]$

O(A)–U–O(B)	179.7(5)
O(A)–U–O(1)	91.8(4)
O(A)–U–O(2)	86.1(4)
O(A)–U–O(3)	96.3(4)
O(A)–U–O(4)	88.0(3)
O(A)–U–O(6)	87.5(4)
O(A)–U–O(7)	91.1(4)
O(B)–U–O(1)	88.0(3)
O(B)–U–O(2)	93.6(4)
O(B)–U–O(3)	83.7(3)
O(B)–U–O(4)	92.2(3)
O(B)–U–O(6)	92.6(4)
O(B)–U–O(7)	89.2(4)
O(1)–U–O(2)	70.6(3)
O(3)–U–O(4)	50.0(3)
O(6)–U–O(7)	50.4(2)
O(3)–U–O(1)	135.5(3)
O(4)–U–O(1)	174.4(3)
O(6)–U–O(1)	63.6(3)
O(7)–U–O(1)	113.8(3)
O(3)–U–O(2)	66.5(2)
O(4)–U–O(2)	114.9(3)
O(6)–U–O(2)	133.5(2)
O(7)–U–O(2)	174.9(3)
O(6)–U–O(3)	160.0(2)
O(7)–U–O(3)	109.7(2)
O(6)–U–O(4)	110.8(3)
O(7)–U–O(4)	60.7(3)
U–O(2)–C(2)	140.7(7)
U–O(1)–P(1)	136.2(6)
P(1)–C(1)–C(2)	111.9(8)
O(1)–P(1)–C(1)	115.5(5)
C(11)–P(1)–O(5)	110.5(5)
C(11)–P(1)–C(1)	109.2(5)
O(5)–P(1)–C(1)	101.4(6)
C(11)–P(1)–O(1)	108.2(5)
O(5)–P(1)–O(1)	115.5(5)
O(2)–C(2)–C(1)	119.1(11)
N(1)–C(2)–O(2)	121.8(8)
N(1)–C(2)–C(1)	119.1(9)
O(3)–N(2)–O(4)	114.3(8)
O(3)–N(2)–O(5)	123.3(9)
O(4)–N(2)–O(5)	122.4(9)
O(6)–N(3)–O(7)	114.2(11)
O(6)–N(3)–O(8)	124.5(10)
O(7)–N(3)–O(8)	121.3(9)

(2) $UO_2(NO_3)_2[Ph_2P(O)CH_2C(O)NEt_2]$

O(A)–U–O(B)	178.6(3)
O(A)–U–O(1)	90.0(2)
O(A)–U–O(2)	87.8(2)
O(A)–U–O(3)	90.6(2)
O(A)–U–O(4)	88.9(2)
O(A)–U–O(6)	91.4(2)
O(A)–U–O(7)	88.4(2)
O(B)–U–O(1)	90.3(2)
O(B)–U–O(2)	91.0(2)
O(B)–U–O(3)	88.3(2)

O(B)–U–O(4)	90.9(2)
O(B)–U–O(6)	90.0(2)
O(B)–U–O(7)	92.7(2)
O(1)–U–O(2)	71.8(2)
O(3)–U–O(4)	49.8(2)
O(6)–U–O(7)	50.0(2)
O(3)–U–O(1)	135.3(2)
O(4)–U–O(1)	174.8(2)
O(6)–U–O(1)	65.2(2)
O(7)–U–O(1)	115.1(2)
O(3)–U–O(2)	63.6(2)
O(4)–U–O(2)	113.3(2)
O(6)–U–O(2)	136.9(2)
O(7)–U–O(2)	172.2(2)
O(6)–U–O(3)	159.4(2)
O(7)–U–O(3)	109.6(2)
O(6)–U–O(4)	109.7(2)
O(7)–U–O(4)	59.8(2)
U–O(2)–C(2)	141.0(5)
U–O(1)–P(1)	135.3(3)
P(1)–C(1)–C(2)	111.9(8)
O(1)–P(1)–C(1)	110.0(3)
C(11)–P(1)–C(21)	109.9(3)
C(11)–P(1)–O(1)	112.0(3)
C(11)–P(1)–C(1)	106.4(4)
C(21)–P(1)–O(1)	110.3(3)
C(21)–P(1)–C(1)	108.1(4)
O(2)–C(2)–C(1)	117.3(7)
N(1)–C(2)–O(2)	121.7(7)
N(1)–C(2)–C(1)	121.0(6)
O(3)–N(2)–O(4)	113.7(6)
O(3)–N(2)–O(5)	122.1(7)
O(4)–N(2)–O(5)	124.1(7)
O(6)–N(3)–O(7)	114.5(7)
O(6)–N(3)–O(8)	121.9(7)
O(7)–N(3)–O(8)	123.6(7)

$UO_2(NO_3)_2L_2$ complexes containing monodentate ligands the oxygen atoms of the L donors typically occupy *trans* coordination sites.

The uranyl bond distances in **3** are U–O(B) 1.754(10) Å and U–O(A) 1.752(10) Å and in **4** are U–O(A) 1.742(6) Å and U–O(B) 1.742(6) Å, and the bond angles O(A)–U–O(B) are 179.7(5)° and 178.6(3)°. These parameters can be compared with the similar parameters in **5**, 1.757(5) Å, 1.755(6) Å and 179.5(2)°. There appears to be a trend toward decreasing U–O bond length with increasing degree of aryl substitution. This would be in direct opposition to the expected trend. However, within a 3σ standard deviation test the uranyl bond distances U–O(A) and U–O(B) in **3**, **4** and **5** must be considered to be identical, and an accurate test of the U–O bond distance/ligand base strength correlation, mentioned above, unfortunately can not be confidently made here. It is noteworthy that the U–O bond distances calculated from the U–O asymmetric stretch-

ing frequency relationship proposed by Carnall are 3, 1.75 Å, 4, 1.75 Å and 5 1.74 Å. Clearly, based upon this model these ligands may not be expected to provide a particularly large variation in U–O bond distances in the linear UO_2^{2+} unit.

The U–O (phosphoryl) bond distances, U–O(1) for 3 and 4 are 2.351(7) and 2.377(4) Å, respectively. Although the standard deviation in the distance for 3 is large, it appears that the U–O(1) distance in 4 is unexpectedly long. However, both distances are significantly shorter than the corresponding distance in 5 [4], 2.420(4) Å. This observation is consistent with the expected lower donor strength of the $(RO)_2P(O)CH_2C(O)NR_2'$ ligand. That 4 appears to have a longer than expected U–O(1) distance may result from steric effects of the phenyl groups. The U–O (phosphoryl) distances in 3 and 4 also can be compared with related distances in $UO_2(NO_3)_2[(n-Bu)_3P(O)]_2$ [25] 2.347(6) Å, $UO_2(NCS)_2[Ph_3-P(O)]_2[MeC(O)Me]$ [21] 2.36(2) Å and $UO_2(OAc)_2-[Ph_3P(O)]_2$ [26] 2.37(3) Å. However, in these compounds the phosphoryl donor sites are *trans* to each other. The P=O bond distances, P(1)–O(1), in 3 1.487(9) Å and in 4 1.512(5) Å can be compared with the distances in 5 1.485(5) Å, and in $UO_2-(NO_3)_2[(n-Bu)_3P(O)]_2$ 1.489(7) Å, and these distances suggest that the P=O bond in 4 is most weakened by coordination with the UO_2^{2+} group and by aryl group substitution.

The U–O(carbonyl) bond distances, U–O(2), for 3 and 4 are 2.426(8) Å and 2.404(5) Å, respectively. These compare favorably with the same distance in 5, 2.406(5) Å [4] and in several other carbonyl complexes. The distances are intermediate between short and long extremes in the complexes $UO_2[(CF_3CO)_2CH]_2 \cdot THF$ [27] 2.38(2) Å (avg) and $UO_2(NCS)_2[Ph_3P(O)]_2[(Me)_2CO]$ [21] 2.56(2) Å. The C–O (carbonyl) bond distances, C(2)–O(2), in 3 and 4 are 1.243(12) Å and 1.264(8) Å, and these compare favorably with the distances in 5 [4] 1.260(8) Å and several other complexes [4].

The nitrate ions are planar and the U–O bond distances are normal, with one exception, and they appear in the range 2.503 to 2.522 Å. The U–O(3) distance in 3 is anomalously long, 2.561(7) Å, and no clear explanation is recognized. The normal distances compare favorably with the average distance in 5, 2.512 Å.

The single crystal X-ray structure determinations for 3, 4 and 5 provide proof of the stoichiometries and molecular structures of the complexes formed by a series of bifunctional carbamoylmethylphosphine oxide ligands in which alkoxy groups have been substituted by phenyl groups. Within the accuracy of the structure determinations a systematic variation in the uranyl group U–O distances with aryl substitution is not revealed; however, secondary U–O interactions between the UO_2^{2+} group and the

phosphoryl oxygen atoms do seem to indicate the effect of aryl substitution. This is evidenced by the shortened U–OP distances in 3 and 4 compared to 5. Additional structural studies in our group on uranyl complexes of bifunctional phosphine oxide ligands will provide further tests of these conclusions.

Acknowledgement

References

1 W. W. Schulz and L. D. McIsaac, in W. Müller and R. Lindner (eds.), 'Transplutonium Elements', North-Holland, Amsterdam, 1979;
   W. W. Schulz and J. D. Navratil, in N. N. Li (ed.), 'Recent Developments in Separation Science, Vol. VII', CRC Press, Boca Raton, Fla., 1982.
2 S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chem., 21*, 261 (1982).
3 S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta, 61*, 155 (1982).
4 S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chem., 22*, 286 (1983).
5 D. G. Kalina, E. P. Horwitz, L. Kaplan and A. C. Muscatello, *Sep. Sci. Technol., 16*, 1127 (1981).
6 G. M. Sheldrick, 'Nicolet SHELXTL Operations Manual', Nicolet XRD Corp., Cupertino, Calif., 1981; 'International Tables for X-ray Crystallography, Vol. IV', Kynoch Press, Birmingham, 1968.
7 F. R. Ahmed, S. R. Hall and C. P. Huber (eds.), 'Crystallographic Computing', Munksgaard, Copenhagen, 1970, p. 187.
8 T. H. Siddall, *J. Inorg. Nucl. Chem., 25*, 883 (1963).
9 J. J. Richard and C. V. Banks, *J. Org. Chem., 28*, 123 (1963).
10 S. M. Bowen, E. N. Duesler, R. T. Paine and C. F. Campana, *Inorg. Chim. Acta, 59*, 53 (1982).
11 V. E. Bel'skii, R. F. Bakeeva, L. A. Kudryavtseva, A. M. Kurguzova and B. E. Ivanov, *Izv. Akad. Nauk. SSSR Ser. Khim., 4*, 1624 (1974).
12 M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. Van Wazer, *Top. Phosphorus Chem., 5*, 1 (1967).
13 S. M. Bowen, *Ph.D. Thesis*, University of New Mexico, 1983.
14 B. F. Myasoedov, M. K. Chmutova and Z. K. Karalov, in 'Actinide Separations', ACS Symposium Series, No. 117, 1980, p. 101 and refs. therein.
15 A. M. Rozen, Z. I. Nikolotova, N. A. Kartasheva and A. S. Skotnikov, *Radiokhim., 25*, 603 (1983).
16 T. S. Lobana and S. S. Sandhu, *Coord. Chem. Rev., 47*, 282 (1982) and refs. therein.
17 E. P. Horwitz, D. G. Kalina, L. Kaplan, G. W. Mason and H. Diamond, *Sep. Sci. Technol., 17*, 1261 (1982).
18 R. Graziani, E. Bombieri, E. Forsellini, S. Degetto and G. Marvangoni, *J. Chem. Soc. Dalton Trans.*, 451 (1973).
19 K. W. Bagnall and O. V. Lopez, *J. Chem. Soc. Dalton Trans.*, 1409 (1975).

20 T. Ya. Medved, N. P. Nesterova, P. V. Petorovskii, T. D. Kirillova and M. I. Kobachnik, *Izv. Akad. Nauk, SSR. Ser. Khim., 8,* 1714 (1978).

21 G. Bombieri, E. Forsellini, G. DePaoli, D. Brown and T. C. Tso, *J. Chem. Soc. Dalton Trans.,* 2042 (1979).

22 K. W. Bagnall and M. W. Wakerly, *J. Inorg. Nucl. Chem., 37,* 329 (1975).

23 B. W. Veal, D. J. Lem, W. T. Carnall and H. R. Hoekstra, *Phys. Rev., Sect. B:, 12,* 5651 (1975).

24 L. I. Katzin, G. W. Mason and D. F. Peppard, in N. N. Li (ed.), 'Recent Developments in Separation Science, Vol. VII', CRC Press, Boca Raton, Fla., 1982, p. 207.

25 J. H. Burns, *Inorg. Chem., 20,* 3868 (1981).

26 C. Panattoni, R. Graziani, G. Bandoli, B. Zarli and G. Bombieri, *Inorg. Chem., 8,* 320 (1969).

27 G. M. Kramer, M. B. Dines, R. B. Hall, A. Kaldor, A. J. Jacobson and J. C. Scanlon, *Inorg. Chem., 19,* 1340 (1980).