

Model Fluorogenic Ligand—Actinide and Lanthanide Coordination Chemistry. Formation and Crystal and Molecular Structure of $[(i-C_3H_7O)_2P(O)CH(CH_2C_6H_4NO_2-p)C(O)N(C_2H_5)_2]UO_2(NO_3)_2$

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(Received July 29, 1987)

Abstract

The ligands $(i-C_3H_7O)_2P(O)CH(CH_2C_6H_4NO_2-p)-C(O)N(C_2H_5)_2$ (1), $(i-C_3H_7O)_2P(O)CH(CH_2C_6H_4NH_2-p)C(O)N(C_2H_5)_2$ (2) and $(i-C_3H_7O)_2P(O)CH(CH_2C_6H_4N(CH_3)_2-p)C(O)N(C_2H_5)_2$ (3) have been prepared and characterized by spectroscopic methods. Coordination chemistry of the ligands with $UO_2(NO_3)_2 \cdot 6H_2O$, $La(NO_3)_3 \cdot 6H_2O$ and $Er(NO_3)_3 \cdot 5H_2O$ has been surveyed and the complexes $La(NO_3)_3 \cdot (1)_2$, $Er(NO_3)_3 \cdot (1) \cdot H_2O$, $UO_2(NO_3)_2 \cdot (1)$ and $UO_2(NO_3)_2 \cdot (2)$ have been isolated and characterized. A single crystal X-ray diffraction analysis of $UO_2(NO_3)_2[(i-C_3H_7O)_2P(O)CH(CH_2C_6H_4NO_2-p)-C(O)N(C_2H_5)_2]$ has been completed at 25 °C. The complex crystallized in the triclinic space group $P\bar{1}$ with $a = 9.524(2)$, $b = 10.111(2)$, $c = 17.692(2)$ Å, $\alpha = 70.27(1)$, $\beta = 72.48(2)$, $\gamma = 70.01(2)^\circ$, $Z = 2$, $V = 1473.5$ Å³, and $D_x(\text{calc.}) = 1.82$ g/cm³. The structure was solved by using heavy atom techniques and least-squares refinement converged at $R_F = 5.4\%$, $R_{wF} = 6.6\%$ on 2936 independent reflections with $I > 2\sigma(I)$. The molecular structure was found to have a linear UO_2^{2+} ion bonded to six equatorial oxygen atoms contributed by two bidentate nitrate ions and a bidentate carbamoylmethylphosphonate ligand. Important bond distances include U—O(uranyl)_{avg.} 1.73(1) Å, U—O(P) 2.40(1) Å, U—O(C) 2.39(1) Å, P—O 1.49(1) Å and C—O 1.28(2) Å.

Introduction

Bifunctional carbamoylmethylphosphonates (CMP) [1, 2], $(RO)_2P(O)CH_2C(O)NR_2'$, are known to be effective liquid–liquid extractants for lanthanide and actinide ions under selected conditions [3–7], and the fundamental coordination chemistry of representative ligands has been examined in our laboratory [8–14]. The ligand chemistry is varied, and it is clear that many new and potentially useful

extractant systems may be designed by expanding upon the themes established in these earlier studies.

One extraction concept which warrants additional attention for analytical detection of Ln(III) and An(III) ions in process systems involves the utilization of selective fluorogenic ligands. Indeed, many fluorogenic ligands have been prepared and employed in metal ion detection schemes [15, 16]; however, applications of these ligands in Ln and An analyses are relatively uncommon. In fact, most of the well known fluorogenic ligands are anticipated to have little selective utility for Ln and An ions because these reagents appear to indiscriminately bind many metal ions. An alternative approach involves derivatization of an extractant known to be selective for trivalent Ln and An ions with a luminescent chromophore. Since CMP ligands are known to be good extractants for these ions it appeared appropriate to base a search for luminescent extractants on the backbone of this ligand. Three sites are available for derivatization: the phosphonate RO group, the amide R' group and the central methyl carbon center, $P(O)CH_2C(O)$. We report here the preparation of model CMP ligands derivatized with *p*-nitrobenzyl, *p*-aminobenzyl and *p*-dimethylaminobenzyl fragments at the methylene carbon center: $(i-PrO)_2P(O)CH(CH_2C_6H_4X-p)C(O)NEt_2$ (X = NO₂, NH₂, NMe₂). Limited coordination chemistry of the ligands was explored in order to determine if derivatization hindered coordination, and the single crystal X-ray diffraction analysis of a uranyl complex is also reported.

Experimental

General

$(i-C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2$ and $Na(i-C_3H_7O)_2P(O)CHC(O)N(C_2H_5)_2$ were prepared by literature methods [17]. *p*-O₂NC₆H₄CH₂Br was purchased from Aldrich Chemical Co. and $UO_2(NO_3)_2 \cdot 6H_2O$,

La(NO₃)₃·6H₂O and Er(NO₃)₃·5H₂O were purchased from Alfa Products (Ventron). Infrared spectra were recorded on a Nicolet 6000 FTIR spectrometer. The samples were prepared as KBr pellets. Vis–UV spectra were recorded on a Perkin-Elmer Model 330 spectrometer from aqueous solutions. The NMR spectra were recorded on a Varian FT-80A spectrometer or a Nicolet NT-360 spectrometer. The spectral standards were 85% H₃PO₄ (³¹P) and (CH₃)₄Si (¹³C, ¹H) and resonances downfield of the standard were assigned positive chemical shifts, δ. Elemental analyses were obtained from R. Ju of the UNM Chemical Analysis Laboratory.

Preparation of (i-C₃H₇O)₂P(O)CH(CH₂C₆H₄NO₂-p)C(O)N(C₂H₅)₂ (1)

The synthesis was performed in a 250-ml Schlenk flask fitted with a stir bar, reflux condenser and a dropping funnel. A sample of Na(i-C₃H₇O)₂P(O)-CHC(O)N(C₂H₅)₂ (5.4 g, 18 mmol) was dissolved in 75 ml dry THF and cooled to 0 °C. To this solution was added dropwise a solution of *p*-nitrobenzylbromide (3.87 g, 18 mmol) in 75 ml dry THF. The addition was completed over 1 h under a dry nitrogen atmosphere. During the addition, the color of the reaction mixture turned from pale yellow to dark violet. The mixture was stirred for 1 h at 0 °C and then stirred overnight at 25 °C. The solvent and volatile components were vacuum evaporated (10⁻³ torr, 25 °C) and 250 ml dry Et₂O was added to the residue. The NaBr was removed by filtration and the filtrate was concentrated by vacuum evaporation. The ligand crystallized on standing at 25 °C (yield: 7.0 g, 95%) as pale yellow crystals. M.p. 73 °C. Solubility: THF, Et₂O, CHCl₃, benzene. *Anal.* Calc. for PO₆N₂C₁₉H₃₁: C, 55.06; H, 7.54; N, 6.76. Found: C, 55.37; H, 7.57; N, 6.76%. Infrared spectrum (cm⁻¹, KBr): 2985 (s), 2937 (s), 1632 (ν_{CO}, s), 1605 (m), 1517 (ν_{NO₂}, s, br), 1493 (m), 1457 (s), 1437 (m), 1384 (m), 1373 (m), 1364 (m), 1344 (ν_{NO₂}, s), 1246 (ν_{PO}, s), 1220 (m), 1181 (m), 1142 (m), 1102 (s), 1043 (m), 1010 (s), 993 (s), 937 (m), 904 (m). NMR spectra (CHCl₃/CDCl₃, 27 °C): ³¹P{¹H} δ 20.3; ¹H δ 7.62 (phenyl AA'BB' quartet), 4.64 (multiplet OCH), 3.4–2.7 (multiplets NCH₂, PCHC, CH₂C₆H₄), 1.24 (doublet, 6H, ³J_{HH} = 6.1 Hz, OCHCH₃), 1.22 (doublet, 6H, ³J_{HH} = 5.6 Hz, OCHCH₃), 0.89 (triplet, 3H, ³J_{HH} = 7.6 Hz, NCH₂CH₃), 0.70 (triplet, 3H, ³J_{HH} = 7.4 Hz, NCH₂CH₃); ¹³C{¹H} (CDCl₃, 27 °C) δ 165.9 (doublet, ²J_{PC} = 4.3 Hz, CO), 147.8, 146.9, 129.8, 123.3 (singlets, C₆H₄), 71.8 (doublet, ²J_{PC} = 6.4 Hz, OCH), 71.1 (doublet, ²J_{PC} = 7.5 Hz, OCH), 44.6 (doublet, ¹J_{PC} = 132.9 Hz, PCHCO), 42.4 (singlet, NCH₂), 41.1 (singlet, NCH₂), 33.7 (doublet, ²J_{PC} = 4.5 Hz, CH₂C₆H₄), 24.1–23.4 (multiplet, OCHCH₃), 14.1 (singlet, NCH₂CH₃), 12.6 (singlet, NCH₂CH₃). UV spectrum

(CH₂Cl₂): 273 nm (ε = 9067), 281 nm (ε = 8900). Mass spectrum: [M⁺] 414.

Preparation of (i-C₃H₇O)₂P(O)CH(CH₂C₆H₄NH₂-p)C(O)N(C₂H₅)₂ (2)

A suspension of 0.5 g of 10% Pd on charcoal in about 100 ml absolute ethanol was placed in a 500-ml Schlenk vessel. To it was added in small portions 2.34 g (62 mmol) NaBH₄ under a nitrogen atmosphere. The mixture was stirred for 5 min in a water bath, and then 12.8 g (31 mmol) (i-PrO)₂P(O)CH-(CH₂C₆H₄NO₂-p)C(O)N(C₂H₅)₂ in 150 ml absolute ethanol was added dropwise during 30 min. The resulting reaction mixture was stirred for 14 h. The solution was filtered to remove the catalyst and the ethanol was removed by vacuum evaporation. The residue was extracted with 250 ml benzene to remove unreacted NaBH₄. The benzene layer was washed with water (2 × 50 ml), dried over MgSO₄ and concentrated to give a pale yellow solid (yield: 11.0 g, 93%). M.p. 128 °C. Solubility: benzene, CHCl₃, Et₂O, THF. *Anal.* Calc. for PO₄N₂C₁₉H₃₃: C, 59.36; H, 8.65; N, 7.29. Found: C, 59.48; H, 8.65; N, 7.15%. Infrared spectrum (cm⁻¹, KBr): 3460 (ν_{NH}, w), 3356 (ν_{NH}, w), 2983 (m), 2935 (m), 1639 (ν_{CO}, s), 1517 (m), 1450 (m), 1385 (m), 1244 (ν_{PO}, m), 1105 (m), 1010 (s), 991 (s), 823 (w). NMR spectra (CDCl₃): ³¹P{¹H} δ 21.8; ¹H δ 6.77 (phenyl AA'BB' quartet), 4.75 multiplet, OCH), 3.66 (NH₂), 3.42–2.93 (multiplets NCH₂, PCHC, CH₂C₆H₄), 1.39 (doublet, 3H, ³J_{HH} = 6.0 Hz, OCHCH₃), 1.35 (doublet, 6H, ³J_{HH} = 5.2 Hz, OCHCH₃), 1.32 (doublet, 3H, ³J_{HH} = 5.8 Hz, OCHCH₃), 1.01 (triplet, 3H, ³J_{HH} = 7.1 Hz, NCH₂CH₃), 0.8 (triplet, 3H, ³J_{HH} = 7.2 Hz, NCH₂CH₃); ¹³C{¹H} (CDCl₃, 27 °C) δ 167.1 (doublet, ²J_{PC} = 4.0 Hz, CO), 145.1, 127.4, 114.8 (singlets, C₆H₄) 71.1 (doublet, ²J_{PC} = 6.9 Hz, OCH), 70.5 (doublet, ²J_{PC} = 7.5 Hz, OCH), 45.4 (doublet, ¹J_{PC} = 132.4 Hz, PCHCO), 42.3 (singlet, NCH₂), 40.9 (singlet, NCH₂), 33.2 (doublet, ²J_{PC} = 4.8 Hz, CH₂C₆H₄), 24.1–23.5 (multiplet, OCHCH₃), 13.9 (singlet, NCH₂CH₃), 12.6 (singlet, NCH₂CH₃): UV spectrum (CH₂Cl₂): 294 nm (ε = 3300). Mass spectrum: [M⁺] 384.

Preparation of (i-C₃H₇O)₂P(O)CH(CH₂C₆H₄N-(CH₃)₂-p)C(O)N(C₂H₅)₂ (3)

(i-C₃H₇O)₂P(O)CH(CH₂C₆H₄NH₂-p)C(O)N(C₂H₅)₂ (2) (1.0 g, 2.6 mmol) and 0.36 g (2.6 mmol) of trimethylphosphate were placed in a 25-ml round-bottom flask equipped with a stir bar and reflux condenser. The mixture was heated under gentle reflux under dry nitrogen for 2 h. The reaction mixture was cooled to 50 °C, 5 ml of 10% aqueous NaOH solution was added, and the mixture was heated at 80 °C for 1 h. The mixture was then cooled to room temperature, 10 ml of water was added and the mixture was extracted with chloroform. The

chloroform extract was dried over anhydrous MgSO_4 and concentrated under reduced pressure to give a brownish yellow liquid (yield: 0.4 g, 37%). Solubility: benzene, chloroform, THF, ethanol. *Anal.* Calc. for $\text{PO}_4\text{N}_2\text{C}_{21}\text{H}_{39}$: C, 61.15; H, 9.04; N, 6.79. Found: C, 58.76; H, 8.97; N, 6.67%. Infrared spectrum (cm^{-1} , thin film) 2979 (m), 2934 (m), 1638 (ν_{CO} , s), 1522 (m), 1434 (ν_{NMe} , w), 1449 (m), 1249 (ν_{PO} , m), 1105 (m), 1009 (s), 989 (s), 732 (m). NMR spectra (CDCl_3): $^{31}\text{P}\{^1\text{H}\}$ δ 22.4; ^1H δ 6.8 (multiplet, 4H, C_6H_4), 4.55 (multiplet, 2H, OCH), 3.20–2.55 (multiplet, 13H, NCH₂, NCH₃, PCHC, $\text{CH}_2\text{C}_6\text{H}_4$), 1.19–1.11 (multiplet, 12H, OCHCH₃), 0.80 (triplet, 3H, $^3J_{\text{HH}} = 6.6$ Hz, NCH₂CH₃), 0.60 (triplet, 3H, $^3J_{\text{HH}} = 7.2$ Hz, NCH₂CH₃); $^{13}\text{C}\{^1\text{H}\}$ δ 167.1 (doublet, $^2J_{\text{PC}} = 3.9$ Hz, CO), 149.3, 148.0, 129.2, 112.6, 112.1 (singlets, C_6H_4), 71.0 (doublet, $^2J_{\text{PC}} = 6.6$ Hz, OCH), 70.5 (doublet, $^2J_{\text{PC}} = 6.9$ Hz, OCH), 45.5 (doublet, $^1J_{\text{PC}} = 129.6$ Hz, PCHCO), 42.2 (singlet, NCH₂), 40.8 (singlet, NCH₃), 40.4 (singlet, NCH₂), 33.2 (doublet, $^2J_{\text{PC}} = 4.7$ Hz, $\text{CH}_2\text{-C}_6\text{H}_4$), 24.0–23.4 (multiplet, OCHCH₃), 13.8 (singlet, NCH₂CH₃), 12.6 (singlet, NCH₂CH₃); UV spectrum (CH_2Cl_2): 299 ($\epsilon = 400$). Mass spectrum: $[\text{M}^+]$ 412.

Preparation of Metal Complexes

Ligand 1

Each complex was prepared in a similar fashion. The metal nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.74 g, 1.17 mmol) or $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1.0 g, 2.3 mmol) or $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 g, 2.0 mmol) was dissolved in 30–50 ml ethanol. To this solution was added an ethanol solution containing the derivatized ligand (1.17 g, 4.1 mmol; 1.92 g, 4.7 mmol; 0.9 g, 2.1 mmol, respectively). The resulting mixtures were stirred and then set aside to allow the solvent to evaporate in the air. The resulting solid residues were washed with Et_2O to remove any uncoordinated ligand. Characterization data: $\text{La}(\text{NO}_3)_3[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}(\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]_2$, pale yellow solid soluble in all common organic solvents. *Anal.* Calc. for $\text{LaP}_2\text{O}_{21}\text{N}_7\text{C}_{38}\text{H}_{62}$: C, 39.56; H, 5.42; N, 8.50. Found: C, 38.56; H, 5.54; N, 8.46%. Infrared spectrum (cm^{-1} , KBr pellet): 1601 (ν_{CO}), 1523 (ν_{asNO_2}), 1470, 1450, 1347 (ν_{sNO_2}), 1189 (ν_{PO}). NMR spectra ($\text{CHCl}_3/\text{CDCl}_3$; 27 °C): $^{31}\text{P}\{^1\text{H}\}$ δ 36.2; ^1H δ 7.69 (phenyl AA'BB' quartet), 4.81 (multiplet, OCH), 3.5–2.7 (multiplets CH, CH_2N , $\text{CH}_2\text{C}_6\text{H}_4$), 1.32 (doublet, 12H, $^3J_{\text{HH}} = 7.4$ Hz, OCHCH₃), 1.23 (doublet, 12H, $^3J_{\text{HH}} = 7.2$ Hz, OCHCH₃), 1.27 (triplet, 6H, $^3J_{\text{HH}} = 7.1$ Hz, NCH₂CH₃), 0.78 (triplet, 6H, $^3J_{\text{HH}} = 7.1$ Hz, NCH₂CH₃). UV spectrum (CH_2Cl_2): 270 nm ($\epsilon = 20\,000$), 280 nm ($\epsilon = 6400$).

$\text{Er}(\text{NO}_3)_3[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}(\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]_2 \cdot \text{H}_2\text{O}$, pale yellow solid soluble in

all common organic solvents. *Anal.* Calc. for $\text{ErP}_2\text{O}_{22}\text{N}_7\text{C}_{38}\text{H}_{64}$: C, 38.02; H, 5.37; N, 8.16%. Found: C, 37.52; H, 5.47; N, 7.94%. Infrared spectrum (cm^{-1} , KBr pellet): 1647 and 1606 (ν_{CO}), 1522 (ν_{NO}), 1496, 1452, 1220, 1182 (ν_{PO}). UV spectrum (CH_2Cl_2): 270 nm ($\epsilon = 21\,519$), 280 nm ($\epsilon = 16\,800$).

$\text{UO}_2(\text{NO}_3)_2[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}(\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]$, pale yellow solid appreciably soluble only in CH_2Cl_2 . *Anal.* Calc. for $\text{UPO}_{14}\text{N}_4\text{C}_{19}\text{H}_{31}$: C, 28.23; H, 3.87; N, 6.93. Found: C, 28.50; H, 4.01; N, 6.59%. Infrared spectrum (cm^{-1} , KBr pellet): 2986 (m), 2946 (m), 1604 (ν_{CO} , s), 1537 (ν_{NO_2} , s), 1519 (ν_{NO} , s), 1483 (s), 1463 (s), 1388 (s), 1351 (ν_{NO_2} , s), 1328 (m), 1282 (s), 1262 (s), 1216 (s), 1175 (ν_{PO} , s), 1145 (m), 1101 (s), 1073 (m), 1026 (s), 1009 (s), 938 (m), 897 (m). NMR spectra ($\text{CH}_2\text{Cl}_2/\text{CDCl}_3$): $^{31}\text{P}\{^1\text{H}\}$ δ 26.8; ^1H δ 7.83 (phenyl AA'BB' quartet), 5.5–5.1 (multiplets, OCH), 4.0–3.1 (multiplets, CH, CH_2N , $\text{CH}_2\text{C}_6\text{H}_4$) 1.73 (doublet, 6H, $^3J_{\text{HH}} = 6.3$ Hz, OCHCH₃), 1.64 (doublet, 3H, $^3J_{\text{HH}} = 5.9$ Hz, OCHCH₃), 1.47 (doublet, 3H, $^3J_{\text{HH}} = 6.2$ Hz, OCHCH₃), 1.26 (triplet, 3H, $^3J_{\text{HH}} = 7.1$, NCH₂CH₃), 1.17 (triplet, 3H, $^3J_{\text{HH}} = 7.0$ Hz, NCH₂CH₃). UV spectrum (CH_2Cl_2): 260 nm ($\epsilon = 17\,100$), 281 nm ($\epsilon = 7200$ nm).

Ligand 2

The only complex containing ligand 2 which was isolated was the uranyl complex. Uranyl nitrate (1.0 g, 2 mmol) was dissolved in 30 ml ethanol and this solution was added to an ethanol solution of 2 (0.84 g, 2.2 mmol). The mixture was stirred and the solvent allowed to evaporate slowly in air. A yellow residue was obtained which was washed with CHCl_3 to remove uncomplexed ligand. Characterization data: $\text{UO}_2(\text{NO}_3)_2[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}(\text{CH}_2\text{C}_6\text{H}_4\text{NH}_2\text{-}p)\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]$, yellow solid appreciably soluble only in EtOH. *Anal.* Calc. for $\text{UPO}_{12}\text{N}_4\text{C}_{19}\text{H}_{33}$: C, 29.31; H, 4.27; N, 7.20. Found: C, 28.01; H, 4.04; N, 6.44%. Infrared spectrum (cm^{-1} , KBr pellet): 3384 (ν_{NH} , vw), 2986 (m), 1601 (ν_{CO} , s), 1519 (s), 1487 (m), 1460 (m), 1388 (w), 1285 (m), 1266 (m), 1174 (ν_{PO} , m), 1094 (w), 1017 (s), 938 (s), 760 (s). NMR spectra (CDCl_3): $^{31}\text{P}\{^1\text{H}\}$ δ 27.7; ^1H δ 6.82 (phenyl AA'BB' quartet), 5.5–4.6 (multiplets OCH), 4.3–3.0 (multiplets, CH, $\text{CH}_2\text{C}_6\text{H}_4$, CH_2N), 1.8–1.0 (multiplets, CH₃).

Crystal Structure Determination

Single crystals of $\text{UO}_2(\text{NO}_3)_2[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}(\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]$ were grown from a CH_2Cl_2 /hexane (2:1 mixture) and a suitable crystal (0.06 × 0.12 × 0.24 mm) was glued to a glass fiber. Room temperature data were collected by variable speed θ – 2θ scans on an Enraf Nonius CAD-4 diffractometer equipped with a graphite monochromator and using $\text{Mo K}\alpha$ radiation. Cell param-

TABLE I. X-ray Data of [(i-C₃H₇O)₂P(O)CH(CH₂C₆H₄-NO₂-p)C(O)N(C₂H₅)₂]UO₂(NO₃)₂

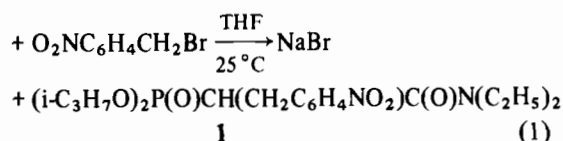
Chemical formula	C ₁₉ H ₃₁ N ₄ O ₁₄ PU
Crystal system	triclinic
Space group	<i>P</i> 1
<i>a</i> (Å)	9.524(2)
<i>b</i> (Å)	10.111(2)
<i>c</i> (Å)	17.692(2)
α (°)	70.27(1)
β (°)	72.48(2)
γ (°)	70.01(2)
<i>V</i> (Å ³)	1473.5
<i>Z</i>	2
<i>D_x</i> (g/cm ³)	1.82
λ (Mo K α ₁)	0.70930
Temperature (°C)	23
Xtl color	light yellow
Xtl dimensions (mm)	0.06 × 0.12 × 0.24
Absolute coefficient (cm ⁻¹)	53.4
Absolute correction type	<i>f</i> * sphere
Sphere radius (mm)	0.2
Transmission (Min, Max)	0.32, 0.49
Average peak width (ω) ∞	0.7
Scan range (2θ max)	45°
Scan type	θ - 2θ
Scan rate	variable, $\sigma(I)/I = 0.015$, max time = 90 s
($-h$, $+h$), ($-k$, $+k$), ($-l$, $+l$)	(9, 9), (0, 10), (17, 19)
Total no. collected	4100
No. unique reflections	3836
No. $I \geq 2\sigma(I)$	2936
<i>R_F</i> equivalent reflections (%)	2.2
<i>R_F</i> observed reflections (%)	5.4
<i>R_{wF}</i> observed reflections (%)	6.6

eters, additional information relevant to the data collection process and crystallographic *R* values are given in Table I. The structure was solved by using standard Patterson and difference Fourier methods and refined to the observed data ($I \geq 2\sigma(I)$) with full-matrix least-squares methods using appropriate neutral scattering factors and anomalous scattering terms [18]. Refinements included anisotropic thermal parameters for uranium and a correction for secondary extinction [19]. Final Fourier difference maps failed to show peaks which could be interpreted as hydrogen atoms. The Los Alamos Crystal Structure Codes [20] were used for all calculations. Data were corrected for absorption using the relative intensity of a low angle reflection measured as a function of ψ (mapped to ϕ) multiplied by a spherical correction using a radius calculated from the average distance between the three most prominent directions of crystal development. The function minimized was $R_F = \sum w^2 [F_o - F_c]^2$ and weights were calculated as $w^2 = 4F^2 / \sigma^2(I)$ where $\sigma(I) = \sigma_c(I) + (0.030 \times I)^2$; $\sigma_c(I)$ is the error based on counting statistics. Coordinates, bond distances and bond angles are

given in Tables II, III and IV, respectively. An ORTEP projection with appropriate atom numbering scheme is given in Fig. 1.

Results and Discussion

The ligand (i-C₃H₇O)₂P(O)CH(CH₂C₆H₄NO₂-p)-C(O)N(C₂H₅)₂ (**1**) was prepared in good yield by using a metathesis reaction between the NaCMP salt, Na[(i-C₃H₇O)₂P(O)CHC(O)N(C₂H₅)₂] [17] and O₂NC₆H₄CH₂Br, as shown in eqn. (1). The slightly Na[(i-C₃H₇O)₂P(O)CHC(O)N(C₂H₅)₂]



yellow crystalline ligand was characterized by elemental analysis and infrared, UV and NMR spectroscopic data. In particular, the carbonyl stretching frequency ($\nu_{\text{CO}} = 1632 \text{ cm}^{-1}$) and phosphoryl stretching frequency ($\nu_{\text{PO}} = 1246 \text{ cm}^{-1}$) are similar to the respective frequencies in the precursor bifunctional ligand (i-C₃H₇O)₂P(O)CH₂C(O)N(C₂H₅)₂, ($\nu_{\text{CO}} = 1644 \text{ cm}^{-1}$ and $\nu_{\text{PO}} = 1253 \text{ cm}^{-1}$ [17]) and in the benzyl-derivatized CMP ligand (C₂H₅O)₂P(O)CH(CH₂C₆H₅)C(O)N(C₂H₅)₂ ($\nu_{\text{CO}} = 1643 \text{ cm}^{-1}$ and $\nu_{\text{PO}} = 1255 \text{ cm}^{-1}$ [21]). The small differences in ν_{CO} and ν_{PO} in these ligands suggest that the nitro group does not exert a large electronic effect on the bifunctional ligand base sites. In addition, **1** shows strong, broad absorptions at 1517 and 1344 cm^{-1} characteristic of ν_{as} and ν_{s} (NO₂) frequencies in nitro aryl compounds. The ligand shows a single ³¹P{¹H} resonance at δ 20.3 which compares favorably with the resonance positions in (i-C₃H₇O)₂P(O)CH₂C(O)N(C₂H₅)₂ (δ 20.2) and in (C₂H₅O)₂P(O)CH(CH₂C₆H₅)C(O)N(C₂H₅)₂ (δ 23.8). The UV spectrum of the ligand shows two strong bands at 273 nm ($\epsilon = 9067$) and 281 nm ($\epsilon = 8900$) while (i-C₃H₇O)₂P(O)CH₂C(O)N(C₂H₅)₂ and (C₂H₅O)₂P(O)CH(CH₂C₆H₅)C(O)N(C₂H₅)₂ show no UV absorption in this region.

Attempts to prepare an anilino derivative via a metathesis reaction related to the chemistry described in eqn. (1) were unsuccessful; however, it was found that (i-C₃H₇O)₂P(O)CH(CH₂C₆H₄NH₂-p)C(O)N(C₂H₅)₂ (**2**) could be prepared in high yield by selective reduction of the nitro group in **1** by using a Pd/C/NaBH₄ reductant.

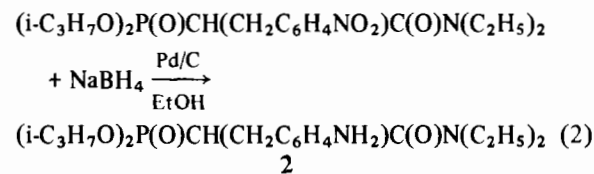


TABLE II. Fractional Coordinates and Thermal Parameters^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
U(1)	0.19018(7)	0.09582(6)	0.23824(4)	5.73(4)	3.05(4)	5.50(4)	-2.39(5)	-2.34(5)	-2.66(5)
O(1)	0.352(1)	0.124(1)	0.165(1)	7.8(8)	5.7(7)	7.2(8)	-4.8(12)	-3.2(12)	-2.6(12)
O(2)	0.027(1)	0.067(1)	0.312(1)	10.2(9)	5.0(7)	6.4(7)	-5.9(13)	0.0(13)	-2.4(12)
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
O(3)	0.079(1)	0.353(1)	0.215(1)	4.7(2)	C(1)	0.084(2)	0.476(2)	0.220(1)	3.6(3)
N(1)	-0.028(1)	0.591(1)	0.202(1)	4.2(3)	C(2)	-0.031(2)	0.740(2)	0.199(1)	5.2(4)
C(3)	-0.117(2)	0.775(2)	0.282(1)	7.7(5)	C(4)	-0.168(2)	0.576(2)	0.183(1)	5.7(4)
C(5)	-0.140(3)	0.598(3)	0.093(1)	8.8(6)	C(6)	0.218(2)	0.479(2)	0.248(1)	4.0(3)
C(7)	0.367(2)	0.456(2)	0.181(1)	4.6(3)	C(8)	0.356(2)	0.574(2)	0.103(1)	4.2(3)
C(9)	0.404(2)	0.692(2)	0.093(1)	6.7(4)	C(10)	0.390(2)	0.815(2)	0.018(1)	7.2(5)
C(11)	0.333(2)	0.794(2)	-0.035(1)	7.0(5)	C(12)	0.294(2)	0.675(2)	-0.034(1)	7.7(5)
C(13)	0.305(2)	0.557(2)	0.043(1)	6.1(4)	N(2)	0.687(2)	0.071(2)	0.119(1)	9.8(5)
O(4)	0.702(2)	0.117(2)	0.164(1)	13.5(6)	O(5)	0.668(2)	-0.033(2)	0.102(1)	12.6(6)
P(1)	0.2370(5)	0.3305(4)	0.3394(2)	4.14(8)	O(6)	0.259(1)	0.185(1)	0.328(1)	4.5(2)
O(7)	0.093(1)	0.376(1)	0.403(1)	5.9(3)	C(14)	-0.026(3)	0.298(3)	0.445(1)	8.9(6)
C(15)	0.032(4)	0.188(4)	0.514(2)	16.5(12)	C(16)	-0.163(3)	0.407(3)	0.473(2)	11.7(8)
O(8)	0.372(1)	0.343(1)	0.366(1)	6.1(3)	C(17)	0.477(3)	0.214(3)	0.413(1)	8.6(6)
C(18)	0.622(5)	0.208(5)	0.354(3)	17.8(13)	C(19)	0.470(4)	0.258(4)	0.486(2)	14.3(10)
O(9)	0.142(1)	-0.019(1)	0.150(1)	5.7(2)	N(3)	0.070(2)	0.092(2)	0.106(1)	6.0(3)
O(10)	0.031(1)	0.093(1)	0.047(1)	7.6(3)	O(11)	0.046(1)	0.212(1)	0.125(1)	5.8(2)
O(12)	0.354(1)	-0.090(1)	0.335(1)	6.7(3)	N(4)	0.367(2)	-0.193(2)	0.309(1)	7.0(4)
O(13)	0.291(1)	-0.177(1)	0.259(1)	6.6(3)	O(14)	0.452(2)	-0.321(2)	0.337(1)	10.7(5)

^aAnisotropic thermal motion is defined by $\exp(-2p_i \times p_j)(U'_{11}hh + U'_{22}kk + U'_{33}ll + U'_{12}hk + U'_{13}hl + U'_{23}kl)$ where $U'_{ij} = U_{ij} \times b_i \times b_j$ and U_{ij} is multiplied by 100 in the Table.

TABLE III. Selected Interatomic Distances (Å)

Uranyl sphere		CMP ligand	
U–O1	1.73(1)	P–O6	1.49(1)
U–O2	1.74(1)	P–O7	1.54(1)
U–O3	2.39(1)	P–O8	1.56(1)
U–O6	2.40(1)	P–C6	1.80(1)
U–O9	2.45(1)	Cl–C6	1.52(2)
U–O11	2.50(1)	Cl–O3	1.28(2)
U–O12	2.52(1)	Cl–N1	1.30(2)
U–O13	2.52(1)	N2–C11	1.66(3)
		N2–O4	1.12(3)
		N2–O5	1.28(3)
		C6–C7	1.56(2)
		C7–C8	1.49(2)
Nitrate ions			
N4–O9	1.24(2)	N3–O12	1.24(2)
N4–O10	1.22(2)	N3–O13	1.23(2)
N4–O11	1.28(2)	N3–O14	1.29(2)

Compound **2** is a pale yellow solid. The compound shows strong absorptions at 1639 and 1244 cm^{-1} which can be assigned to ν_{CO} and ν_{PO} vibrations, respectively. In addition, the band assigned to the ν_{asNO_2} vibration is absent. A sharp medium intensity band is present at 1517 cm^{-1} ; however, it is assumed to belong to aryl ring vibrations. The nitro group bands are replaced by broad weak bands centered

at 3460 and 3356 cm^{-1} which are assigned to ν_{NH_2} . The anilino derivative shows a single $^{31}\text{P}\{^1\text{H}\}$ resonance at δ 21.8. The UV spectrum of **2** shows a single absorption at 294 nm ($\epsilon = 3300$).

The *N,N*-dimethylaniline derivative was obtained in fair yield from **2** by using trimethylphosphate as the methylation reagent. The ligand was isolated as a brown yellow liquid. The compound displays bands at 1638 and 1249 cm^{-1} which are assigned to ν_{CO} and ν_{PO} , respectively. The N–H stretches are replaced by typical bands for an NMe_2 group. The $^{31}\text{P}\{^1\text{H}\}$ resonance appears at δ 22.4, slightly downfield of the resonance for **2**. The presence of the NMe_2 group is indicated in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum by a sharp singlet at δ 40.8. The UV spectrum of **3** displays a broad and weaker intensity absorption compared to the spectrum for **2**.

Combination of the ligand **1** with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and of ligand **2** with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ each dissolved in ethanol results in the formation of complexes with the following compositions; $\text{UO}_2(\text{NO}_3)_2(\mathbf{1})_2$ (**4**), $\text{La}(\text{NO}_3)_3(\mathbf{1})_2$ (**5**), $\text{Er}(\text{NO}_3)_3(\mathbf{1})_2 \cdot \text{H}_2\text{O}$ (**6**) and $\text{UO}_2(\text{NO}_3)_2(\mathbf{2})$ (**7**). Infrared spectra obtained from KBr pellets display ν_{CO} and ν_{PO} bands as follows: **4**, 1604 and 1175 cm^{-1} ; **5**, 1601 and 1189 cm^{-1} ; **6**, 1647, 1606 and 1182 cm^{-1} ; and **7**, 1601 and 1174 cm^{-1} . For the uranyl complex **4**, the coordination

TABLE IV. Selected Interatomic Angles (°)

Uranyl sphere			
O1-U-O2	179.7(5)	O6-U-O9	173.8(4)
O1-U-O3	90.7(4)	O6-U-O11	134.8(4)
O1-U-O6	90.1(4)	O6-U-O12	63.3(4)
O1-U-O9	88.1(4)	O6-U-O13	113.4(4)
O1-U-O11	87.4(4)		
O1-U-O12	90.1(4)	O9-U-O11	51.1(4)
O1-U-O13	91.3(4)	O9-U-O12	110.7(4)
		O9-U-O13	60.7(4)
O1-U-O3	89.5(4)		
O2-U-O6	89.8(4)	O11-U-O12	161.7(4)
O2-U-O9	92.0(4)	O11-U-O13	111.8(4)
O2-U-O11	92.9(4)	O12-U-O13	50.1(4)
O2-U-O12	89.6(4)		
O2-U-O13	88.5(4)		
O3-U-O6	70.2(4)		
O3-U-O9	115.8(3)		
O3-U-O11	64.7(4)		
O3-U-O12	133.5(4)		
O3-U-O13	175.8(4)		
Nitrate ions			
O9-N3-O10	123(2)	O12-N4-O13	120(2)
O9-N3-O11	115(1)	O12-N4-O14	119(2)
O10-N3-O11	121(2)	O13-N4-O14	120(2)
CMP ligand			
O6-P-C6	114.2(6)	O6-P-O7	113.4(6)
O7-P-O8	106.2(6)	O6-P-O8	114.2(6)
O7-P-C6	104.4(7)		
O8-P-C6	103.4(6)		
C1-C6-P	106(1)	C6-C7-C8	123(1)
C1-C6-C7	111(1)	O4-N2-O5	151(3)
C7-C6-P	110(1)	O4-N2-C11	106(2)
N1-C1-O3	119(1)	O5-N2-C11	103(2)
O3-C1-C6	118(1)		

shift $\Delta\nu_{\text{CO}} = 28 \text{ cm}^{-1}$ is similar to but on the low end of the range of carbonyl coordination shifts typically found in uranyl-CMP complexes [12]. The $\Delta\nu_{\text{PO}}$ coordination shift, 71 cm^{-1} , on the other hand, is slightly larger than normally encountered in uranyl CMP complexes (normal range $55\text{--}65 \text{ cm}^{-1}$). The data suggest that **1** is bonded in a bidentate fashion to the UO_2^{2+} center; however, the coordinate interaction may be more phosphoryl in character than that found in related complexes. It is interesting that the coordination shifts for the second uranyl complex **7** are essentially identical to those of complex **4**. In the lanthanum complex **5**, the carbonyl coordination shift $\Delta\nu_{\text{CO}} = 31 \text{ cm}^{-1}$ is slightly smaller and phosphoryl coordination shift $\Delta\nu_{\text{PO}} = 57 \text{ cm}^{-1}$ is slightly greater than the respective shifts (55 and 47 cm^{-1}) in the early lanthanide complex $\text{Sm}[(i\text{-PrO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{N}(\text{Et})_2](\text{NO}_3)_3$ [22], which was shown to contain bidentate CMP ligands in the solid state. Similarly,

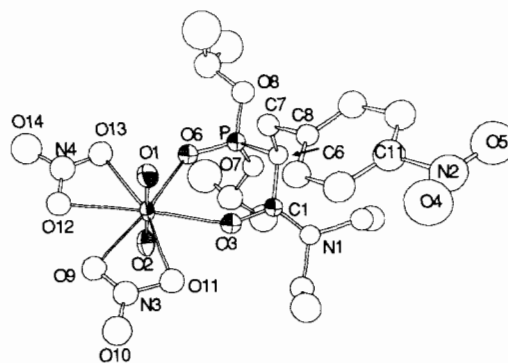


Fig. 1. Molecular geometry and atom labeling scheme for $\text{UO}_2(\text{NO}_3)_2[(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{CH}(\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]$.

the coordination shift for the erbium complex **6**, $\Delta\nu_{\text{CO}} = 26 \text{ cm}^{-1}$ (split band), is small and $\Delta\nu_{\text{PO}} = 64 \text{ cm}^{-1}$ is large, and the structure of **6** may, therefore, also resemble the monodentate ligand structure determined for $\text{Er}[(i\text{-PrO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NEt}_2]_2(\text{NO}_3)_3$ [22]. We wish to add a caution that the infrared spectra for the ligands and their complexes are especially complex in the region $1600\text{--}900 \text{ cm}^{-1}$ so assignments of ν_{PO} and ν_{NO_2} must be treated with caution.

Another indicator of the coordination strength of the ligands **1** and **2** toward uranyl ion may be found in the asymmetric uranyl stretching frequencies found in **4** (938 cm^{-1}) and **7** (939 cm^{-1}). These frequencies are comparable to the ν_{UO_2} vibrational frequencies in $\text{UO}_2(\text{NO}_3)_2[\text{RR}'\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NEt}_2]$ ($\text{R} = \text{R}' = i\text{-PrO}$, $\text{R} = \text{Ph}$, $\text{R}' = \text{EtO}$ and $\text{R} = \text{R}' = \text{Ph}$) which are 943 , 930 and 925 cm^{-1} , respectively. Based upon the empirical correlation of Carnall *et al.* [23] and Peppard *et al.* [24], it would appear that **1** and **2** exert a base strength effect on the UO_2^{2+} group comparable with $(i\text{-PrO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NEt}_2$.

The electronic spectra for these complexes, as expected, differ little from the spectra for the ligands **1** and **2**. In addition, the fluorescence intensities are found to be disappointingly weak, and it is clear that additional derivatization studies will be required to achieve an analytically useful CMP fluorescence reagent.

In order to unambiguously determine whether methyl carbon derivatization may grossly alter the coordination behavior of a CMP-like ligand, attempts were made to obtain single crystals of complexes **4**–**7**. Suitable single crystals of the uranyl complex **4** were obtained and the crystal structure was determined by single crystal X-ray diffraction methods. The structure determination verifies the proposed composition and bidentate coordination geometry of the ligand. A view of the molecule is shown in Fig. 1. The structure is closely related to the structures of $\text{UO}_2(\text{NO}_3)_2[(i\text{-PrO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NEt}_2]$ (**8**)

[10], $\text{UO}_2(\text{NO}_3)_2[(\text{EtO})(\text{Ph})\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NEt}_2]$ (**9**) [12], and $\text{UO}_2(\text{NO}_3)_2[(\text{Ph})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NEt}_2]$ (**10**) [12]. In every case, the UO_2^{2+} group is bonded to a neutral CMP ligand in a bidentate fashion and two bidentate nitrate ions. These six oxygen atoms provided by the ligands form an approximately planar belt which is perpendicular to the linear $\text{O}=\text{U}=\text{O}$ vector. The eight oxygen atoms in the coordination sphere form an approximate hexagonal bipyramid.

The average uranyl bond distances in **4**, 1.72(1) Å, appears to be slightly shorter than the average uranyl distances in **8–10**: 1.756(6), 1.75(1) and 1.742(6) Å. This bond shortening suggests a respectively weaker CMP ligand $\cdot\text{UO}_2^{2+}$ interaction and concomitant stronger $\text{U}=\text{O}$ bonds. This observation is not entirely consistent with the infrared spectroscopic data from which one might expect ν_{UO_2} for **4** to appear at a value higher than the 943 cm^{-1} found in complex **8**. The $\text{U}-\text{O}(\text{phosphoryl})$ distance in **4**, 2.40(1) Å, is intermediate between the distances in complexes **8–10**: 2.420(4), 2.351(7) and 2.377(4) Å. Similarly, the $\text{P}=\text{O}$ distance in **4**, 1.49(1) Å, is intermediate between the distances in complexes **8–10**: 1.485(5), 1.487(9) and 1.512(5) Å. The $\text{U}-\text{O}(\text{carbonyl})$ and $\text{C}=\text{O}$ distances in **4**, 2.40(1) and 1.28(2) Å, likewise are comparable to the respective distances in **8–10**: 2.406(5), 1.260(8) Å; 2.426(8), 1.241(1) Å and 2.404(5), 1.264(8) Å.

Although this initial study did not result in the development of an analytical useful fluorogenic CMP extractant, the structural results suggest that derivatization at the $\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})$ methylene carbon atom position does not dramatically alter the coordination characteristics of the modified CMP backbone. More elaborate synthetic studies of CMP ligands derivatized with fluorescent chromophores are in progress.

Acknowledgements

This work was performed under the auspices of the U.S. Department of Energy. RTP wishes to acknowledge support for SK under LANL Contract 9-X15-R78966-1, as well as support from the U.S.

DOE Office of Basic Energy Sciences, Contract 85ER40079.

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