Inorganica Chimica Acta, 201 (1992) 165–176

Synthesis and coordination chemistry of trifunctional phosphono-bis-carbonyl alkane ligands

G. S. Conary, R. L. Meline, R. Schaeffer, E. N. Duesler and R. T. Paine*

Department of Chemistry, University of New Mexico, Albuquerque, NM 87131 (USA)

(Received March 11, 1992; revised May 29, 1992)

Abstract

Trifunctional ligands, 1-phosphono-1-carbamoyl-n-alkyl ester alkanes $[(RO)_2P(O)][C(O)NEt_2]C(H)[(CH_2)_n$-$C(O)OR']$ (n = 1–3) were prepared from metathesis reactions of the metallated anions $[(RO)_2P(O)][C(O)NEt_2]CH^-$ and bromoalkyl esters. The ligands were fully characterized and selected coordination chemistry with La(III), Er(III), UO_2^{2+} and Th(IV) was examined. The molecular structures of three coordination complexes were determined by single crystal X-ray diffraction techniques. The 1:1 complex, $Er(NO_3)_3\{[(i$-$PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_2C(O)OMe]\}$, crystallizes in the monoclinic space group, $P2_1/c$ with $a=9.418(4)$, $b=15.547(7)$, $c=18.259(8)$ Å, $\beta=92.29(4)°$, $Z=4$, $V=2671(2)$ Å^3 and $\rho_{calc}=1.787$ g cm^{-3}. The structure was solved by heavy atom methods and full matrix least-squares refinements converged at $R_F=3.52\%$ and $R_{wF}=4.84\%$ on 4086 reflections with $F>6\sigma(F)$. The compound forms a polymeric structure in which each Er(III) is nine-coordinate. The Er atom is bonded to three bidentate nitrate ions and the bidentate carbamoylmethyl phosphonate fragment of one trifunctional ligand. It is also bridge bonded to the ester carbonyl group in a second molecular unit. The 2:1 complex, $Er(NO_3)_3\{[(i$-$PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_2C(O)OMe]\}_2$, crystallizes in the monoclinic space group $P2_1/n$ with $a=16.090(8)$, $b=19.114(9)$, $c=17.166(8)$ Å, $\beta=108.01(4)°$, $Z=4$, $V=5021(4)$ Å^3 and $\rho_{calc}=1.434$ g cm^{-3}. The structure was solved by direct methods and refinement converged at $R_F=4.00\%$ and $R_{wF}=4.89\%$ on 5109 independent reflections with $F>6\sigma(F)$. The compound contains isolated molecules in which the Er(III) is nine-coordinate and bonded to three bidentate nitrate ions, the bidentate carbamoylmethyl phosphonate fragment of one ligand and the phosphonate of a second ligand. The 1:1 complex, $UO_2(NO_3)_2\{[(i$-$PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_3C(O)OEt]\}$, crystallizes in the monoclinic space group $P2_1/c$ with $a=8.855(2)$, $b=16.257(5)$, $c=20.603(6)$ Å, $\beta=92.07(2)°$, $Z=4$, $V=2964(1)$ Å^3, $\rho_{calc}=1.765$ g cm^{-3}. The structure was solved by direct methods and refinement converged at $R_F=7.82\%$ and $R_{wF}=7.77\%$ on 3906 independent reflections with $F>3\sigma(F)$. The compound contains a linear UO_2^{2+} ion bonded to two bidentate nitrate ions and the bidentate carbamoylmethyl phosphonate fragment of the trifunctional ligand. The structures of these complexes are compared with structural data for complexes containing related 1-phosphono-1-carbamoyl-n-carbamoyl alkanes and 1,1-bis-phosphono-n-carbamoyl alkanes.

Introduction

Bifunctional 1-phosphono-1-carbamoyl methanes $[(RO)_2P(O)][C(O)NEt_2]CH_2$ [1, 2]** (CMPs) and 1-phosphono-1-alkyl ester methanes $[(RO)_2P(O)]$-$[C(O)OR']CH_2$ [3], have been known for a number of years. The coordination chemistry of these compounds has been partially explored and, with oxophilic metal ions, they usually behave as neutral, bidentate ligands [4–6]. From a practical perspective, trivalent f-element coordination complexes with CMP ligands formed under liquid–liquid extraction conditions are sufficiently strong that the metal ions are efficiently transferred from highly acidic, aqueous solutions to an organic solvent phase containing the ligand. On the other hand, the extraction complexes are weak enough that the metal ions may be back-extracted into water by pH variation. The efficacy of bifunctional CMP ligands in extractions has led us to explore routes to the synthesis of related trifunctional ligands and examine their extraction properties.

Both 1-phosphono-1-carbamoyl methanes and 1-phosphono-1-alkyl ester methanes are easily deprotonated at the methyl group bridging the phosphoryl and carbonyl units [3, 7–9], and the resulting carbanions have been used as synthons for the preparation of a variety of other organic compounds. In our group, we have observed that the carbanions $[(RO)_2P(O)][C(O)NEt_2]$-CH^- (R = Me, Et, i-Pr, Hx), when combined with *N,N*-diethylchloroacetamide, produce trifunctional ligands,

---

*Author to whom correspondence should be addressed.

**Previous nomenclature used with these ligands includes dialkyl-*N,N*-dialkylcarbamoylmethyl phosphonates.

0020-1693/92/$5.00

1-phosphono-1-carbamoyl-2-carbamoyl ethanes $[(RO)_2P(O)][C(O)NEt_2]CHCH_2[C(O)NEt_2]$ [9]. The coordination chemistry of this family of ligands has proven to be diverse. Surprisingly, structural studies of several lanthanide complexes indicate that the trifunctional ligand has difficulty adopting either a tridentate chelate bonding mode or a bidentate chelate mode accompanied by bridge binding through the long arm amide [10–12]. In most cases, only bidentate chelation through the 1-phosphono-1-carbamoyl methane fragment is found. However, molecular modelling has suggested that polydentate coordination conditions might be obtained with derivatives that contain longer coordination arms capable of adopting less strained chelate rings.

In the present paper, we describe the syntheses of a series of trifunctional ligands, $[(RO)_2P(O)][C(O)NEt_2]CH[(CH_2)_nC(O)OR]$, that contain the relatively weakly donating alkyl ester group at the end of a long arm alkane chain ($n = 1, 2, 3$). The coordination chemistry of the ligands has been surveyed and molecular structure determinations for three complexes are described.

Experimental

Methylbromo acetate, methylbromo propionate, ethylbromo butyrate, triethyl phosphite and sodium hydride were purchased from Aldrich Chemical Co. and used as received. Solvents were purchased from Fisher Scientific Co. and purified by standard methods. Metal nitrates were purchased from Strem Chemical Co. or Alfa (Ventron) Chemical Co. All reactions, unless specified otherwise, were performed under dry nitrogen by using standard Schlenk techniques and glove bag enclosures. IR spectra were obtained from a Nicolet model 6000 FT-IR spectrometer, mass spectra were recorded with a Finnegan model 4600 GC/MS spectrometer, and NMR spectra were recorded with Varian FT-80A, Nicolet/GE-360 and JEOL GSX-400 NMR spectrometers. Standards were Me_4Si (^{13}C, ^1H) and 85% H_3PO_4 (^{31}P). Analytical data were obtained from the UNM microanalytical facility and from Galbraith Laboratories.

Preparations of the ligands 1a–c, 2a–c and 3b

All ligands were prepared by the same procedure, and a general outline is provided. The sodium salts $Na^+\{[(RO)_2P(O)][C(O)NEt_2]CH^-\}$ were prepared as described in the literature [8]. Typically, $(RO)_2P(O)CH_2C(O)NEt_2$ (80 mmol) was weighed into a 250 ml Schlenk vessel and combined under dry nitrogen at 0 °C with a slurry containing ~100 mmol of NaH in 150 ml of dry THF. The mixture was warmed to room temperature, stirred for several hours, and filtered to remove excess NaH. The filtrate was then added dropwise over 1 h to 80 mmol of the appropriate alkylbromo ester held at 0 °C. It is important to note that this addition is done in reverse order compared with the procedure described previously for the 1-phosphono-1-carbamoyl-n-carbamoyl alkanes [9]. It is believed that excess $[(RO)_2P(O)][C(O)NEt_2]CH^-$ present when the ester is added to the sodium salt results in ester cleavage and unusually low yields for the trifunctional ligand. After addition is complete, the reaction mixture is warmed to 23 °C and stirred for 1 h. The resulting mixture was centrifuged, the THF solution collected and evaporated, leaving colorless oils, which were purified by vacuum distillation.

Characterization data

IR and NMR spectroscopic data are summarized in Table 1.

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

Distillation: 110–124 °C (10 mtorr); colorless oil. Yield 76%. *Anal.* Calc. for $C_{13}H_{26}NO_6P$: C, 48.29; H, 8.11; N, 4.33. Found: C, 48.33; H, 8.50; N, 4.37%. Mass spectrum: [M^+] 323.

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

Distillation: 115–130 °C (10 mtorr); colorless solid, m.p. 60–62 °C. Yield 72%. *Anal.* Calc. for $C_{15}H_{30}NO_6P$: C, 51.27; H, 8.61; N, 4.00. Found: C, 51.34; H, 8.71; N, 3.79%. Mass spectrum: [M^+] 351.

$[(HxO)_2P(O)][C(O)NEt_2]CH[CH_2C(O)(OMe)]$ (1c)

Distillation: 145–155 °C (10 mtorr); colorless oil. Yield 71%. *Anal.* Calc. for $C_{21}H_{42}NO_6P$: C, 57.91; H, 9.72; N, 3.22. Found: C, 57.81; H, 10.08; N, 3.31%. Mass spectrum: [M^+] 435.

$[(EtO)_2P(O)][C(O)NEt_2]CH[(CH_2)_2C(O)(OMe)]$ (2a)

Distillation: 120–130 °C (10 mtorr); colorless solid, m.p. 50–52 °C. Yield 79%. *Anal.* Calc. for $C_{14}H_{28}NO_6P$: C, 49.84; H, 8.37; N, 4.15. Found: C, 49.71; H, 8.16; N, 4.18%. Mass spectrum: [M^+] 337.

$[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_2C(O)(OMe)]$ (2b)

Distillation: 145–155 °C (10 mtorr); colorless oil. Yield 70%. *Anal.* Calc. for $C_{16}H_{32}NO_6P$: C, 52.59; H, 8.83; N, 3.83. Found: C, 52.45; H, 9.02; N, 3.86%. Mass spectrum: [M^+] 365.

TABLE 1. Characterization data for ligands

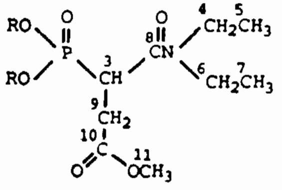
Compound	IR (cm^{-1}) $\nu(CO)/\nu(PO)$	NMR				
		$^{31}P(^1H)$	$^{13}C\{^1H\}^a$		^1H	
$[(EtO)_2P(O)][C(O)NEt_2]C(H)[CH_2C(O)(OMe)]$ **(1a)**	1739, 1642/1244	23.2	171.9 (C_{10}, $J_{PC}=21.2$) 166.1 (C_8, $J_{PC}=4.5$) 63.0 (C_2, $J_{PC}=6.1$) 62.1 (C_2', $J_{PC}=6.4$) 51.5 (C_{11}) 42.7 (C_4)	40.9 (C_6) 38.4 (C_3, $J_{PC}=131.2$) 32.6 (C_9, $J_{PC}=3.0$) 16.3 (C_1) 13.7 (C_5) 12.8 (C_7)	3.47 (HC_2, $J_{HH}=6.9$, $J_{PH}=6.8$) 3.16 (HC_4, $J_{HH}=7.6$) 3.00 (HC_{11}) 2.93 (HC_6, $J_{HH}=6.6$) 2.69 (HC_9) 2.58 (HC_9)	2.08 (HC_3) 0.69 (HC_1, $J_{HH}=6.6$) 0.47 (HC_5, $J_{HH}=6.9$) 0.47 (HC_7, $J_{HH}=6.9$)
$[(i\text{-}PrO)_2P(O)][C(O)NEt_2]C(H)[CH_2C(O)(OMe)]$ **(1b)**	1736, 1637/1252	22.3	170.5 (C_{10}, $J_{PC}=20.1$) 164.8 (C_8, $J_{PC}=4.1$) 70.5 (C_2, $J_{PC}=6.6$) 69.5 (C_2', $J_{PC}=7.2$) 50.3 (C_{11}) 41.4 (C_4)	39.7 (C_6) 37.3 (C_3, $J_{PC}=135.3$) 31.0 (C_9, $J_{PC}=2.5$) 22.4 (C_1) 12.4 (C_5) 11.4 (C_7)	4.26 (HC_2) 3.44 (HC_4) 3.24 (HC_{11}) 3.16 (HC_6) 2.83 (HC_9) 2.30 (HC_3)	0.93 (HC_1, $J_{HH}=5.4$) 0.90 (HC_1', $J_{HH}=6.1$) 0.71 (HC_5, $J_{HH}=6.8$) 0.70 (HC_7, $J_{HH}=6.8$)
$[(HxO)_2P(O)][C(O)NEt_2]C(H)[CH_2C(O)(OMe)]$ (1c)	1742, 1646/1254	22.2	171.0 (C_{10}, $J_{PC}=20.2$) 165.3 (C_8, $J_{PC}=4.7$) 66.3 (C_{2e}, $J_{PC}=6.7$) 65.8 (C_{2e}', $J_{PC}=7.0$) 50.8 (C_1) 41.8 (C_4) 40.3 (C_6) 37.3 (C_3, $J_{PC}=132.6$)	31.5 (C_9, $J_{PC}=3.3$) 30.2 (C_{2c}) 29.6 (C_{2d}, $J_{PC}=5.8$) 24.2 (C_{2b}) 21.6 (C_{2a}) 13.0 (C_1) 12.8 (C_5) 11.8 (C_7)	3.52 (HC_{2e}) 3.29 (HC_4) 3.11 (HC_{11}) 3.04 (HC_6) 2.75 (HC_9) 2.71 (HC_9') 2.20 (HC_3) 1.15 (HC_{2d})	0.78 ($HC_{2a,2c}$) 0.59 ($HC_{5,7}$, $J_{HH}=6.0$) 0.36 (HC_1)
$[(EtO)_2P(O)][C(O)NEt_2]C(H)[(CH_2)_2C(O)(OMe)]$ **(2a)**	1736, 1640/1251	23.6	173.0 (C_{10}) 166.8 (C_8, $J_{PC}=4.5$) 62.8 (C_2, $J_{PC}=6.1$) 61.8 (C_2', $J_{PC}=6.4$) 51.2 (C_{11}) 42.6 (C_4) 41.3 (C_3, $J_{PC}=131.4$)	41.0 (C_6) 31.8 (C_{9b}, $J_{PC}=14.5$) 24.0 (C_{9a}, $J_{PC}=5.1$) 16.4 (C_1, $J_{PC}=5.8$) 14.4 (C_5) 13.0 (C_7)	3.95 (HC_2) 3.49 (HC_4) 3.42 (HC_{11}) 3.35 (HC_6) 3.06 (HC_{9b}) 2.35 (HC_{9a})	2.10 (HC_3) 1.10 (HC_1, $J_{HH}=7.0$) 0.96 (HC_5, $J_{HH}=7.3$) 0.94 (HC_7, $J_{HH}=6.7$)
$[(i\text{-}PrO)_2P(O)][C(O)NEt_2]C(H)[(CH_2)_2C(O)(OMe)]$ **(2b)**	1737, 1640/1248	21.7	173.0 (C_{10}) 166.8 (C_8, $J_{PC}=4.4$) 71.2 (C_2, $J_{PC}=7.3$) 70.3 (C_2', $J_{PC}=6.6$) 51.0 (C_{11}) 42.6 (C_4) 41.8 (C_3, $J_{PC}=132.6$)	41.0 (C_6) 31.8 (C_{9b}, $J_{PC}=14.5$) 23.9 (C_1) 23.6 (C_{9a}, $J_{PC}=5.8$) 14.4 (C_5) 13.0 (C_7)	4.63 (HC_2) 3.53 (HC_4) 3.40 (HC_{11}) 3.36 (HC_6) 3.02 (HC_{9b}) 2.33 (HC_3) 2.20 (HC_{9a}) 1.24 (HC_1, $J_{HH}=5.9$)	1.19 (HC_1', $J_{HH}=6.6$) 1.16 (HC_2, $J_{HH}=6.6$) 0.96 (HC_5, $J_{HH}=6.6$) 0.93 (HC_7, $J_{HH}=6.6$)

(*continued*)

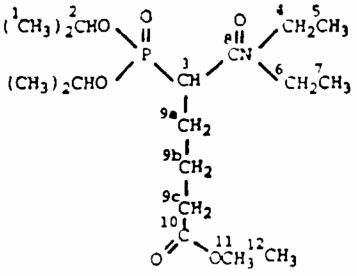
TABLE 1 (*continued*)

Compound	IR (cm^{-1}) $\nu(CO)/\nu(PO)$	NMR $^{31}P(^1H)$	$^{13}C\{^1H\}^a$		^1H	
[$(HxO)_2P(O)$][$C(O)NEt_2$]$C(H)$[$(CH_2)_2C(O)(OMe)$] (**2c**)	1739, 1642/1252	23.2	171.7 (C_{10})	30.4 (C_{2c})	3.96 (HC_{2e})	1.50 (HC_{2d})
			165.4 (C_8, $J_{PC}=4.3$)	29.6 (C_{2d}, $J_{PC}=6.0$)	3.96 (HC_6)	1.23 (HC_{2c})
			65.4 (C_{2e}, $J_{PC}=6.5$)	24.2 (C_{2b})	3.53 (HC_4)	1.15 ($HC_{2a,2b}$)
			64.7 (C_{2e}', $J_{PC}=6.7$)	22.7 (C_{9a}, $J_{PC}=3.8$)	3.42 (HC_{11})	0.97 (HC_5, $J_{HH}=6.7$)
			49.9 (C_{11})	21.5 (C_{2a})	3.25 (HC_{9b})	0.97 (HC_7, $J_{HH}=6.0$)
			41.4 (C_4)	13.2 (C_5)	2.25 (HC_{9a})	0.78 (HC_1, $J_{HH}=7.0$)
			39.9 (C_3, $J_{PC}=131.7$)	12.7 (C_1)	2.15 (HC_3)	
			39.8 (C_6)	11.7 (C_7)		
			30.5 (C_{9b}, $J_{PC}=14.8$)			
[$(i\text{-}PrO)_2P(O)$][$C(O)NEt_2$]$C(H)$[$(CH_2)_3C(O)(OEt)$] (3)	1735, 1642/1249	22.0	172.4 (C_{10})	28.1 (C_{9a}, $J_{PC}=5.4$)	4.73 (HC_2, $J_{PH}=7.3$, $J_{HH}=6.1$)	2.08 (HC_3)
			167.1 (C_8, $J_{PC}=4.2$)	24.0 (C_{9b}, $J_{PC}=20.5$)	4.65 (HC_2', $J_{PH}=7.3$, $J_{HH}=6.1$)	1.89 (HC_{9a}')
			71.2 (C_2, $J_{PC}=6.3$)	23.9 (C_1)	3.92 (HC_{11}, $J_{HH}=7.3$)	1.77
			70.1 (C_2', $J_{PC}=6.7$)	14.6 (C_5)	3.48 (HC_4, $J_{HH}=7.3$)	1.65 (HC_{9b})
			59.9 (C_{11})	14.2 (C_{12})	3.36 (HC_6, $J_{HH}=7.3$)	1.49 (HC_{9b}')
			43.0 (C_3, $J_{PC}=132.8$)	13.0 (C_7)	3.07 (HC_{9c})	1.30 (HC_1, $J_{HH}=6.1$)
			42.6 (C_4)		2.90	1.20 (HC_1', $J_{HH}=6.1$)
			41.0 (C_6)		2.25 (HC_{9a})	1.18 (HC_1'', $J_{HH}=6.1$)
			34.1 (C_{9c})			1.17 (HC_1'', $J_{HH}=6.1$)
						0.99 (HC_{12}, $J_{HH}=6.1$)
						0.99 (HC_5, $J_{HH}=7.3$)
						0.89 (HC_7, $J_{HH}=7.3$)

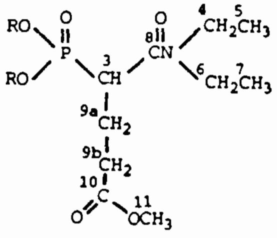
[a] Numbering scheme



1



2



3

a RO = EtO: $^1CH_3{}^2CH_2O$
b RO = i-PrO: $(^1CH_3)_2{}^2CH$
c RO = HxO: $^1CH_3{}^{2a}CH_2{}^{2b}CH_2{}^{2c}CH_2{}^{2d}CH_2{}^{2e}CH_2$

[(HxO)$_2$P(O)][C(O)NEt$_2$]CH[(CH$_2$)$_2$C(O)(OMe)] (2c)

Distillation: 155–175 °C (10 mtorr); colorless oil. Yield 64%. *Anal.* Calc. for $C_{22}H_{44}NO_6P$: C, 58.78; H, 9.87; N, 3.12. Found: 58.71; H, 10.16; N, 3.03%. Mass spectrum: [M^+] 449.

[(i-PrO)$_2$P(O)][C(O)NEt$_2$]CH[(CH$_2$)$_3$C(O)OEt)] (3b)

Distillation: 150–165 °C; colorless oil. Yield 23%. *Anal.* Calc. for $C_{18}H_{36}NO_6P$: C, 54.95; H, 9.22; N, 3.56. Found: C, 54.84; H, 9.65; N, 3.57%. Mass spectrum: [M^+] 393.

Preparation of complexes: ligands 1b, 2b and 3b

The ligands were combined with $UO_2(NO_3)_2 \cdot 6H_2O$ and $Th(NO_3)_4 \cdot 4H_2O$ in a 1:1 ratio and with $La(NO_3)_3 \cdot 5H_2O$ and $Er(NO_3)_3 \cdot 5H_2O$ in 1:1 and 2:1 ratios in ethanol. The solvent was allowed to evaporate overnight, and the residue was recrystallized slowly from a 1:1 CH_2Cl_2/hexane solution. The resulting solids were washed with diethyl ether and vacuum dried. Elemental analysis data and IR spectroscopic data are given in Table 2.

X-ray diffraction analysis

Single crystals of $UO_2(NO_3)_2 \cdot$**3b** were grown by slow evaporation of a CH_2Cl_2/hexane solution of the complex. A yellow crystal (0.16×0.22×0.23 mm) was glued to a fiber, and data collection was performed in a θ–2θ scan mode by using a Nicolet R3m/V automated diffractometer equipped with a graphite monochromator, Mo Kα radiation (λ = 0.71073 Å), scintillation counter and pulse height analyzer. The data collection parameters are summarized in Table 3. A small absorption correction was applied, based upon Ψ scans*. Redun-

TABLE 2. Characterization data for complexes

Complex	IR spectrum (KBr, cm^{-1})			Elemental analyses: calc. (found)		
	Ester ν(CO)/$\Delta\nu$(CO)	Amide ν(CO)/$\Delta\nu$(CO)	ν(PO)/$\Delta\nu$(PO)	C	H	N
$La(NO_3)_3 \cdot$**1b**	1711/−25	1606/−31	1182/−70 1210/−42			
$Er(NO_3)_3 \cdot$**1b**	1713/−23	1610/−27	1187/−65	25.57 (24.56)	4.29 (4.13)	7.95 (7.69)
$La(NO_3)_3 \cdot$**2b**	1690/−47	1595/−45	1178/−70 1210/−38			
$Er(NO_3)_3 \cdot$**2b** (**5**)	1686/−51	1593/−47	1176/−72 1211/−37	26.74 (26.66)	4.49 (4.86)	7.80 (7.45)
$La(NO_3)_3 \cdot$**3b**	1680/−55	1595/−47	1185/−64 1196/−53			
$Er(NO_3)_3 \cdot$**3b**	1657/−60	1597/−45	1174/−75 1187/−62			
$La(NO_3)_3 \cdot$(**1b**)$_2$	1729/−7	1605/−22 1641/+4	1184/−58 1215/−37	35.06 (35.50)	5.88 (5.98)	6.81 (6.38)
$La(NO_3)_3 \cdot$(**2b**)$_2$	1742/+5	1597/−44	1180/−68 1210/−38			
$Er(NO_3)_3 \cdot$(**1b**)$_2$	1740/+4	1614/−23 1641/+4	1185/−57 1214/−38	34.12 (34.34)	5.73 (5.94)	6.63 (6.25)
$Er(NO_3)_3 \cdot$(**2b**)$_2$ (**6**)	1744/+7	1593/−47	1176/−72 1211/−37	35.45 (37.08)	5.95 (6.30)	6.46 (6.14)
$UO_2(NO_3)_2 \cdot$**1b**	1747/+11	1602/−35	1211/−41 1221/−31	24.17 (23.55)	4.06 (4.15)	5.64 (5.70)
$UO_2(NO_3)_2 \cdot$**2b**	1739/+2	1593/−47	1160/−88	28.06 (26.75)	5.03 (4.97)	4.46 (4.47)
$UO_2(NO_3)_2 \cdot$**3b** (**4**)	1734/−15	1605/−37	1167/−82 1183/−66	29.42 (27.93)	5.06 (4.77)	5.15 (5.34)
$Th(NO_3)_4 \cdot$**1b**	1735/−1	1606/−31	1207/−45 1221/−31			
$Th(NO_3)_4 \cdot$**2b**	1730/−7	1596/−44	1153/−95	22.73 (22.61)	5.03 (4.97)	4.46 (4.47)
$Th(NO_3)_4 \cdot$**3b**	1725/−10	1594/−48	1183/−66 1195/−53	26.62 (24.48)	4.58 (4.69)	7.76 (6.93)

---

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

TABLE 3. X-ray data

Complex	$UO_2(NO_3)_2\cdot$**3**	$Er(NO_3)_3\cdot$**2b**	$Er(NO_3)_3\cdot$(**2b**)$_2$
Chemical formula	$C_{18}H_{36}N_3O_{14}PU$	$C_{16}H_{32}N_4O_{15}PEr$	$C_{32}H_{64}N_5O_{21}P_2Er$
Formula weight	787.5	718.7	1084.1
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	8.855(2)	9.418(4)	16.090(8)
b (Å)	16.257(5)	15.547(7)	19.114(9)
c (Å)	20.603(6)	18.259(8)	17.166(8)
β (°)	92.07(2)	92.29(4)	108.01(4)
V (Å^3)	2964(1)	2671(2)	5021(4)
Z	4	4	4
T (°C)	20	22–24	22–24
λ (Å)	0.71073	0.71073	0.71073
ρ_{calc} (g cm^{-3})	1.765	1.787	1.434
μ (cm^{-1})	0.5306	0.3313	0.1826
Transmission coefficient	0.129–0.078	0.619–0.944	0.832–0.954
R_F	7.82	3.52	4.00
R_{wF}	7.77	4.84	4.89

TABLE 4. Atomic coordinates ($\times 10^4$) for $UO_2(NO_3)_2\cdot$**3**

	x/a	y/b	z/c
U(1)	1879(1)	2376(1)	2206(1)
O(1)	3021(9)	2994(6)	1727(5)
O(2)	778(11)	1728(6)	2682(6)
P	497(4)	4158(2)	3051(2)
O(3)	1621(12)	3474(6)	2961(5)
O(4)	1226(12)	4883(6)	3432(5)
C(13)	2795(18)	4964(11)	3634(9)
C(14)	3185(26)	5853(11)	3657(11)
C(15)	3052(27)	4554(14)	4266(10)
O(5)	−974(11)	3930(6)	3384(5)
C(16)	−1124(23)	3640(15)	4054(9)
C(17)	−2765(30)	3815(14)	4194(10)
C(18)	−742(32)	2794(14)	4116(13)
C(1)	−208(16)	4541(8)	2295(6)
C(2)	−968(15)	3827(8)	1944(7)
O(6)	−273(10)	3179(5)	1875(5)
N(1)	−2401(13)	3880(7)	1730(6)
C(9)	−3106(17)	3150(10)	1401(8)
C(10)	−2820(19)	3138(12)	694(8)
C(11)	−3386(18)	4616(9)	1775(9)
C(12)	−4374(18)	4570(11)	2352(9)
C(3)	1035(16)	4881(8)	1866(7)
C(4)	454(16)	5193(9)	1212(7)
C(5)	1659(21)	5454(11)	759(9)
C(6)	2659(33)	4786(16)	548(12)
O(7)	3948(19)	4712(13)	661(9)
O(8)	1894(19)	4216(12)	233(9)
C(7)	2718(40)	3306(28)	95(15)
C(8)	3138(38)	3534(21)	−419(15)
N(2)	1282(19)	1288(9)	1076(8)
O(9)	453(13)	1910(6)	1199(5)
O(10)	2304(18)	1151(7)	1498(7)
O(11)	1039(16)	868(8)	602(7)
N(3)	4758(22)	1904(13)	2900(10)
O(12)	3928(15)	2512(7)	3085(6)
O(13)	4166(17)	1515(8)	2435(8)
O(14)	5903(22)	1745(12)	3169(10)

TABLE 5. Atomic coordinates ($\times 10^4$) for $Er(NO_3)_3\cdot$**2b**

	x/a	y/b	z/c
Er(1)	2166(1)	1858(1)	2852(1)
P(1)	4531(2)	3571(1)	3106(1)
N(1)	4335(5)	1223(3)	1946(3)
O(1A)	3638(4)	1891(2)	1772(2)
O(1B)	3917(5)	834(3)	2507(2)
O(1C)	5319(6)	988(3)	1598(3)
N(2)	−120(6)	2363(3)	3710(3)
O(2A)	−313(5)	2000(3)	3091(3)
O(2B)	1139(5)	2545(3)	3898(2)
O(2C)	−1108(6)	2522(4)	4100(3)
N(3)	2460(6)	547(3)	3907(3)
O(3A)	1459(5)	554(3)	3431(2)
O(3B)	3246(5)	1194(3)	3943(2)
O(3C)	2636(7)	−61(3)	4331(3)
N(4)	2640(6)	3981(3)	1413(3)
O(1)	−275(5)	571(3)	933(2)
O(2)	836(4)	1193(3)	1889(2)
O(3)	4047(4)	2674(2)	3201(2)
O(4)	1670(4)	3155(2)	2271(2)
O(5)	5647(4)	3654(3)	2520(3)
O(6)	5101(5)	3965(3)	3828(2)
C(1)	3181(5)	4275(3)	2724(3)
C(2)	2115(6)	4606(3)	3267(3)
C(3)	1152(7)	5295(3)	2893(3)
C(4)	−92(6)	722(4)	1651(3)
C(5)	683(9)	1032(5)	455(5)
C(6)	2453(5)	3778(3)	2095(3)
C(7)	3645(8)	4663(4)	1181(4)
C(8)	2996(10)	5524(5)	1091(5)
C(9)	1911(8)	3480(4)	831(3)
C(10)	486(8)	3799(6)	629(5)
C(11)	8136(8)	3875(5)	2735(5)
C(12)	7043(6)	3229(4)	2512(4)
C(13)	7199(9)	2892(6)	1760(5)
C(14)	4320(12)	3259(8)	4894(5)
C(15)	5557(8)	3452(5)	4474(3)
C(16)	6658(9)	3969(6)	4875(5)

TABLE 6. Atomic coordinates ($\times 10^4$) for $Er(NO_3)_3 \cdot (\mathbf{2b})_2$[a]

	x/a	*y/b*	*z/c*
Er(1)	6738(1)	3110(1)	4432(1)
P(1)	7043(1)	2483(1)	6433(1)
O(2)	3788(7)	835(5)	4735(6)
O(3)	7336(3)	2611(3)	5714(3)
O(4)	5607(3)	3118(3)	4980(3)
O(5)	7378(3)	1773(3)	6845(3)
O(6)	7320(3)	3056(3)	7100(3)
N(1)	5884(5)	1963(5)	3435(6)
O(1A)	5901(5)	2570(4)	3167(4)
O(1B)	6225(4)	1891(3)	4186(4)
O(1C)	5561(6)	1490(4)	2984(5)
N(2)	7747(6)	4263(5)	5238(6)
O(2A)	6969(4)	4171(3)	5248(5)
O(2B)	8062(4)	3794(3)	4924(5)
O(2C)	8151(6)	4771(5)	5563(7)
N(3)	6117(6)	4122(4)	3168(6)
O(3A)	6843(4)	3835(3)	3314(4)
O(3B)	5702(4)	3967(4)	3650(5)
O(3C)	5841(5)	4521(5)	2606(6)
N(4)	5055(3)	3592(3)	5898(4)
C(1)	5871(4)	2475(3)	6228(5)
C(2)	5487(5)	1796(4)	5812(5)
C(3)	4507(5)	1747(4)	5632(6)
C(4)	4189(6)	1012(6)	5394(7)
O(1)	4405(5)	594(4)	6016(5)
C(5)	4156(10)	−126(6)	5850(9)
C(6)	5496(4)	3099(4)	5677(4)
C(7)	4820(6)	3604(5)	6662(5)
C(8)	5480(8)	3969(6)	7355(7)
C(9)	4739(5)	4190(4)	5349(6)
C(10)	3859(7)	4061(6)	4791(7)
C(12)	7968(8)	1285(6)	6623(9)
C(11A)#	8449(22)	894(15)	7452(17)
C(13A)#	7635(16)	852(13)	5939(13)
C(11B)#	8737(28)	1246(23)	7068(42)
C(13B)#	7386(26)	555(18)	6648(39)
C(14)	8598(8)	2926(7)	8266(8)
C(15)	8232(6)	3289(6)	7471(6)
C(16)	8197(9)	4039(7)	7555(9)
P(1′)	8638(1)	2467(1)	3917(1)
O(1′)	6982(6)	3883(6)	435(5)
O(2′)	7398(7)	2767(6)	607(6)
O(3′)	7831(3)	2504(3)	4157(3)
O(4′)	9799(3)	2819(3)	2640(4)
O(5′)	8751(4)	1745(3)	3564(4)
O(6′)	9488(3)	2624(3)	4620(4)
N(4′)	10010(4)	3783(3)	3425(4)
C(1′)	8630(4)	3120(4)	3155(5)
C(2′)	7978(5)	2927(4)	2326(5)
C(3′)	7761(5)	3544(5)	1751(5)
C(4′)	7357(6)	3328(8)	879(7)
C(5′)	6594(9)	3748(9)	−445(9)
C(6′)	9542(5)	3226(4)	3066(5)
C(7′)	10864(6)	3894(6)	3274(8)
C(8′)	11532(7)	3479(9)	3845(10)
C(9′)	9765(6)	4279(5)	3954(6)
C(10′)	9305(9)	4897(6)	3510(8)
C(12′)	8244(10)	1136(6)	3590(12)
C(11′)	8888(16)	566(8)	3990(11)
C(13′)	7755(10)	936(9)	2778(14)
C(14′)	9976(10)	1885(8)	5794(10)
C(15′)	9632(6)	2555(7)	5511(7)
C(16′)	10240(11)	3123(9)	5900(8)

[a]Atoms have occupancies of 1.0 except as marked with #: C(11A), 0.64; C(13A), 0.64; C(11B), 0.36; C(13B), 0.36.

dant and equivalent data were averaged and converted to unscaled $|F_o|$ values after corrections for Lorentz and polarization effects. The structure was solved by direct methods and refined by full-matrix least-squares methods using appropriate neutral atom scattering factors and anomalous dispersion terms. All calculations were performed with the Nicolet SHELXTL PLUS (MicroVax II version) structure determination package. (Nicolet SHELXTL PLUS uses absorption, anomalous dispersion and scattering data [13]. Anomalous dispersion terms were included for all atoms with atomic numbers greater than 2. Corrections for extinction were not found to be necessary and none were used. A general description of the least-squares algebra is found in ref. 14.) All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in fixed positions (C–H = 0.96 Å) and their isotropic thermal parameters U_{iso} fixed at 1.2 times the last U_{eq} of the parent carbon atom. Final refinements converged at $R_F = 7.82\%$ and $R_{wF} = 7.77\%$ on 3906 reflections with $F > 3\sigma(F)$*.

The structures of $Er(NO_3)_3 \cdot \mathbf{2b}$ (rose needle: 0.07 × 0.10 × 0.15 mm) and $Er(NO_3)_3 \cdot (\mathbf{2b})_2$ (rose needle: 0.05 × 0.05 × 0.12 mm) were determined in similar fashions using the θ–2θ scan mode on a Siemens P3/F diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). Final refinements converged at $R_F = 3.52\%$ and $R_{wF} = 4.84$ on 4086 observed reflections ($F > 6\sigma(F)$) for $Er(NO_3)_3 \cdot \mathbf{2b}$ and at $R_F = 4.00\%$ and $R_{wF} = 4.89\%$ on 5109 reflections ($F > 6\sigma(F)$) for $Er(NO_3)_3 \cdot (\mathbf{2b})_2$. Atomic coordinates for the complexes are presented in Tables 4–6. See also 'Supplementary material'.

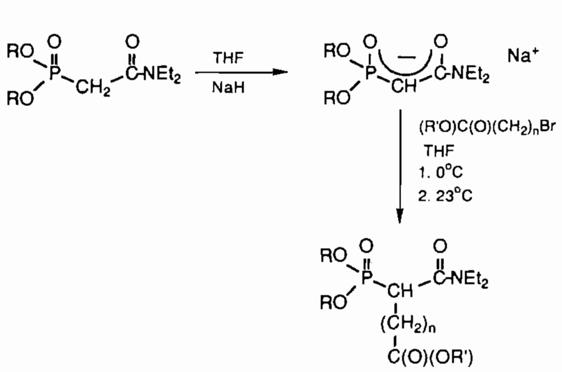
Results and discussion

Heathcock and co-workers [15] have previously reported that carbanions, $[(EtO)_2P(O)][C(O)R]CH^-$, undergo 1-alkylation by a variety of haloalkanes. Similarly, we have observed that the amide analog, $[(RO)_2P(O)][C(O)NEt_2]CH^-$ undergoes 1-alkylation with haloalkanes that contain no additional functionality, e.g. CH_3I or $C_6H_5CH_2Br$ [16], or that possess a donor group, e.g. $Et_2NC(O)CH_2Cl$ [9] or $(RO)_2P(O)(CH_2)_nBr$ [17].

By direct analogy, we find that trifunctional 1-phosphono-1-carbamoyl-n-alkyl ester alkanes $[(RO)_2P(O)][C(O)NEt_2]C(H)[(CH_2)_nC(O)OR']$ ($n = 1$–3) are formed as shown in Scheme 1.

---

*The quantity minimized in the least-squares procedures is: $\Sigma w(|F_o| - |F_c|)^2$, and the residuals are defined as $R = R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $R_w = R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o)^2]^{1/2}$.



R′	*n*	R = Et	i-Pr	Hx
Me	1	**1a**	**1b**	**1c**
Me	2	**2a**	**2b**	**2c**
Et	3		**3b**	

Scheme 1.

The new trifunctional ligands are obtained in good yield as stable, distillable oils or low melting solids. The molecular formulations have been confirmed in each case by observation of a parent ion and anticipated fragment ions in the mass spectra and by agreement of elemental analysis data. The compounds have also been characterized by IR and NMR spectroscopy, and those data are summarized in Table 1. IR spectra for **1a–c**, **2a–c**, and **3b** show an ester carbonyl stretch in the region 1742–1735 cm^{-1} comparable to $\nu(CO)$ (ester) frequencies observed for $(EtO)_2P(O)CH_2C(O)(OMe)$, 1710 cm^{-1}, $(i\text{-}PrO)_2P(O)CH_2C(O)(OMe)$, 1745 cm^{-1} [17] and $(n\text{-}BuO)_2P(O)CH_2C(O)(OMe)$ 1743 cm^{-1} [18]. The amide carbonyl stretch appears in the region 1646–1637 cm^{-1}. This range is identical to that found for the bifunctional CMP ligands [4] and the trifunctional 1-phosphino-1-carbamoyl-n-carbamoyl alkanes [9]. In addition, the phosphoryl stretching frequency is found in the range 1254–1244 cm^{-1}, and this compares with ranges observed for bifunctional CMP ligands, 1273–1250 cm^{-1} [4–6], and trifunctional analogs, 1261–1259 cm^{-1} [9, 17]. Finally, these ligands typically display bands in the region 1061–965 cm^{-1} that are assigned to P–O–C stretching modes.

The NMR spectra for the ligands are consistent with the proposed structures, and they have been assigned as outlined in Table 1. The $^{31}P\{^1H\}$ spectra show a single resonance in a narrow region δ 24–21, and this is comparable to the range found with bifunctional CMP compounds, δ 24.5–22.0 [4], and trifunctional bis-carbamoyl phosphono alkanes, δ 26.7–22.7 [9]. The ^{31}P shift for $(EtO)_2P(O)CH_2C(O)OCH_3$ appears at δ 23.0.

The ^1H and ^{13}C NMR spectra are complicated, and several features are worth discussion. A resonance appearing in the ^1H spectra in the range δ 3.42–3.00 is assigned to methyl ester protons. This compares well with the corresponding resonance in $(EtO)_2P(O)CH_2C(O)(OCH_3)$, δ 2.93 and with shifts for a variety of organic methyl esters [19]. The protons on the methyl carbons of the phosphonate esters and on the amide appear at δ 1.30–0.36 and δ 1.0–0.5, respectively. The methylene protons on the amide groups give rise to resonances in the region δ 4–3. These assignments are confidently made on the basis of data for related bifunctional CMP [4] and trifunctional bis-carbamoyl-phosphonate alkanes [9–12]. In some cases, the assignments of the methylene groups in the ester alkane chains are not unambiguous due to resonance overlap, and more detailed NMR studies will be required to confirm several tentative assignments. The $^{13}C\{^1H\}$ NMR spectra, on the other hand, are fully and confidently assigned, and several observations are discussed. The amide carbonyl resonance appears as a doublet centered at δ 167.1–166.1 with a coupling constant $J(PC) = 4.5$–4.1 Hz. These values correspond well with the data for bifunctional CMP ligands [4]. The ester carbonyl is assigned to resonances appearing at slightly lower field, δ 173–170. For ester alkane chains containing one methylene group, the coupling constant is $J(PC) = 21$–20 Hz, and for the longer chain compounds, no splitting of this resonance is resolved. The central methyl group bonded to phosphorus appears at δ 135.3–131.2 with $J(PC) = 135.3$–131.2 Hz.

The coordination chemistry of ligands **1b**, **2b** and **3b** with an early lanthanide, $La(NO_3)_3$, and a late lanthanide, $Er(NO_3)_3$, and actinide species $UO_2(NO_3)_2$ and $Th(NO_3)_4$ has been studied. Complexes of the general types $Ln(NO_3)_3 \cdot L$, $Ln(NO_3)_3 \cdot L_2$, $UO_2(NO_3)_2 \cdot L$ and $Th(NO_3)_4 \cdot L$ have been isolated, and the metal:ligand stoichiometries have been established by elemental analyses. In order to elucidate the nature of the metal–ligand binding in the complexes, the molecular structures of three complexes, $UO_2(NO_3)_2\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_3C(O)OEt]\}$ (**4**), $Er(NO_3)_3\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_2C(O)OMe]\}$ (**5**) and $Er(NO_3)_3\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_2C(O)OMe]\}_2$ (**6**) were determined by single crystal X-ray diffraction techniques.

The molecular structure of **4** is shown in Fig. 1 and selected metrical parameters appear in Table 7. The structure is similar to the structures of several uranyl carbamoylmethyl phosphonate complexes reported previously [5, 20]. The linear UO_2^{2+} ion (O–U–O angle 177.9(4)°) is surrounded in a planar band (maximum out-of-plane deviation is < 0.05 Å) by four oxygen atoms from two bidentate nitrate groups and two oxygen atoms from the CMP-like fragment of the trifunctional ligand **3b**. If the nitrate oxygen atoms are considered to occupy two coordination positions, the coordination polyhedron can be considered a square pyramid, while if the nitrate oxygens are considered to occupy four coordination sites, the coordination polyhedron is a hexagonal pyr-

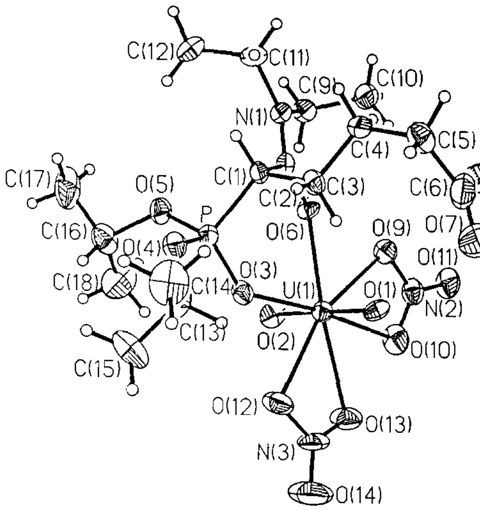


Fig. 1. Molecular structure and atom labelling scheme for $UO_2(NO_3)_2 \cdot$**3** (25% thermal ellipsoids).

TABLE 7. Selected bond distances (Å) and angles (°) for $UO_2(NO_3)_2 \cdot$**3**

Bond distances			
U(1)–O(1)	1.755(9)	P–O(3)	1.508(10)
U(1)–O(2)	1.759(11)	P–O(4)	1.544(10)
U(1)–O(3)	2.384(9)	P–O(5)	1.540(10)
U(1)–O(6)	2.388(9)	P–C(1)	1.770(13)
U(1)–O(9)	2.506(11)	C(2)–O(6)	1.232(16)
U(1)–O(10)	2.505(12)	C(6)–O(7)	1.163(33)
U(1)–O(12)	2.527(13)	C(6)–O(8)	1.307(32)
U(1)–O(13)	2.494(14)		
Bond angles			
O(1)–U(1)–O(2)	177.9(4)	O(3)–P–O(5)	116.8(6)
O(1)–U(1)–O(3)	90.5(4)	O(3)–P–C(1)	111.3(6)
O(1)–U(1)–O(6)	89.8(4)	O(3)–P–O(4)	111.0(6)
O(2)–U(1)–O(6)	92.0(4)	O(4)–P–O(5)	107.5(6)
O(3)–U(1)–O(6)	71.5(3)	O(7)–C(6)–O(8)	121.0(25)
U(1)–O(3)–P	135.4(6)		
C(1)–C(2)–N(1)	120.8(12)		

amid. The weakly basic ester carbonyl terminating the $(CH_2)_3$ chain remains uncoordinated. The average U=O distance in the uranyl unit is 1.757(11) Å, and this compares closely with the corresponding distances in $UO_2(NO_3)_2[(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2]$ (**7**) (1.756(6) Å [20]) and $UO_2(NO_3)_2[Ph_2P(O)CH_2C(O)NEt_2]$ (**8**) (1.742(6) Å [5]) which contain bifunctional CMP and CMPO ligands. The uranyl distance in $UO_2(NO_3)_2(Bu_3PO)_2$ (**9**) which contains two *cis* monodentate phosphine oxides is 1.742(7) Å [21]. The U–O(phosphoryl) distances in **4** (2.384(9) Å), **7** (2.420(4) Å) and **8** (2.377(4) Å) also are comparable, while the distance in **9** (2.347(6) Å) is slightly shorter. Similarly, the U–O(carbonyl) distances in **4** (2.388(9) Å), **7** (2.406(5) Å) and **8** (2.404(5) Å) are similar. The P=O distance in **4** is 1.508(10) Å, which falls in the range of P=O distances in **7**–**9**, 1.485(5)–1.512(5) Å. The uranyl bonded amide carbonyl distance, 1.232(2) Å, as expected, is longer than the uncoordinated ester carbonyl distance, 1.16(3) Å, and the amide distance is comparable to the amide distances in **7** (1.264(8) Å) and **8** (1.260(8) Å). The remaining bond distances and angles in this complex are similar to parameters found in related compounds [5, 20].

The IR spectra of the uranyl complexes of **1b**, **2b** and **3b** are all very similar, suggesting that the molecular structures are the same. In particular, each complex displays an ester carbonyl stretching frequency in the range 1747–1734 cm^{-1}. These bands are shifted only slightly from the corresponding frequency in the free ligand, and this is consistent with the observation that the ester carbonyl is not bonded to the UO_2^{2+} group in the solid state structure of **4**. The amide carbonyl stretch appears in the range 1605–1593 cm^{-1} (coordination shifts 47–37 cm^{-1}), and the phosphoryl stretch falls in the range 1221–1160 cm^{-1} (coordination shifts 88–31 cm^{-1}). These are consistent with the bidentate ligand binding mode observed in the crystal structure of **4**.

The molecular structure of **5** is shown in Fig. 2, and selected bond distances and angles are summarized in Table 8. The compound is polymeric, as shown in Fig. 3, and the structure shows that the Er ion is nine-coordinate, with a tri-capped trigonal prismatic inner coordination geometry, a shown in Fig. 4. Each Er(III) ion is bonded to three bidentate nitrate ions, one trifunctional ligand, **2b**, bonded in a bidentate fashion through the phosphoryl and short leg amide carbonyl donor groups and to the ester carbonyl group in another molecule. The last interaction serves to bridge erbium ions, resulting in the polymeric structure. This structure is distinctly different from the structure of monomeric

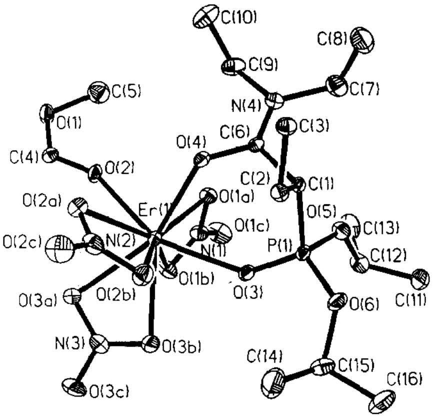


Fig. 2. Molecular structure and atom labelling scheme for $Er(NO_3)_3 \cdot$**2b** (25% thermal ellipsoids). View with one Er atom shown.

TABLE 8. Selected bond distances (Å) and angles (°) for $Er(NO_3)_3 \cdot$**2b** (**5**) and $Er(NO_3)_3 \cdot ($**2b**$)_2$ (**6**)

Compound **5**			
Bond distances			
Er(1)–O(2)	2.356(4)	P(1)–O(5)	1.535(5)
Er(1)–O(3)	2.251(4)	P(1)–O(6)	1.531(5)
Er(1)–O(4)	2.318(3)	P(1)–C(1)	1.798(5)
Er(1)–O(N)$_{av}$	2.416	O(1)–O(4)	1.336(7)
P(1)–O(3)	1.479(4)	O(2)–C(4)	1.208(7)
O(4)–C(6)	1.226(6)		
Bond angles			
O(2)–Er(1)–O(3)	148.0(1)		
O(2)–Er(1)–O(4)	87.1(1)		
O(3)–Er(1)–O(4)	77.3(1)		
Er(1)–O(2)–C(4)	152.9(4)		
Er(1)–O(3)–P(1)	137.9(2)		
Er(1)–O(4)–C(6)	132.3(3)		
Compound **6**			
Bond distances			
Er(1)–O(3)	2.317(5)	C(4)–O(1)	1.293(14)
Er(1)–O(4)	2.292(5)	P(1′)–O(5′)	1.541(6)
Er(1)–O(3′)	2.275(5)	P(1′)–O(3′)	1.481(6)
		P(1′)–O(6′)	1.548(5)
P(1)–O(3)	1.471(6)	P(1′)–C(1′)	1.804(8)
P(1)–O(5)	1.548(6)	O(1′)–C(4′)	1.335(16)
P(1)–O(6)	1.548(6)	O(2′)–C(4′)	1.180(19)
O(2)–C(4)	1.165(14)	O(4′)–C(6′)	1.224(21)
O(4)–C(6)	1.263(9)		
Er(1)–O(N)$_{av}$	2.416		
Bond angles			
O(3)–Er(1)–O(4)	76.2(2)	Er(1)–O(4)–C(6)	138.7(4)
Er(1)–O(3)–P(1)	135.9(3)	Er(1)–O(3)–P(1′)	152.0(3)

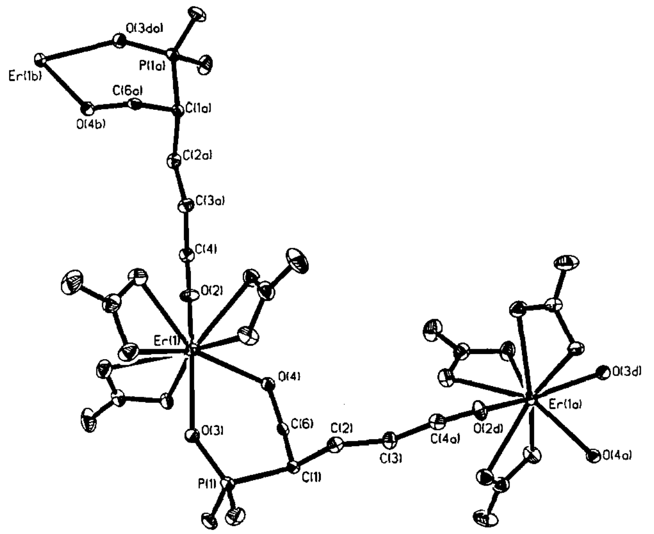


Fig. 3. Molecular structure of $Er(NO_3)_3 \cdot$**2b** with three Er atoms shown.

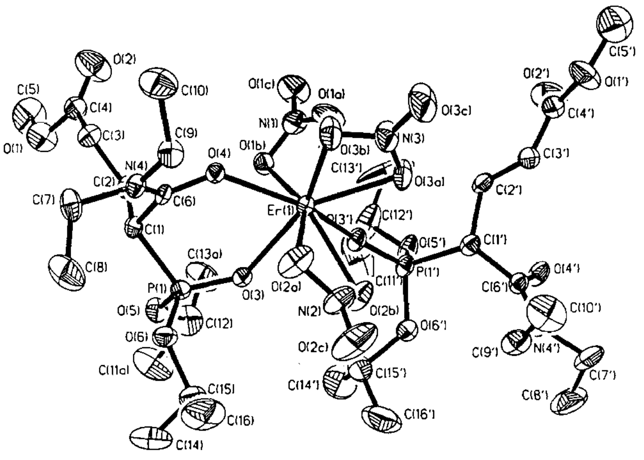


Fig. 4. Molecular structure and atom labelling scheme for $Er(NO_3)_3 \cdot ($**2b**$)_2$ (25% thermal ellipsoids).

$Er(NO_3)_3\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CHCH_2[C(O)NEt_2]\}$ [11] in which the trifunctional ligand, with one less methylene group in the pendant amide chain, adopts a tridentate coordination mode. At this point, it is not clear whether the introduction of the more weakly donating ester group of **2b** or the additional methylene group in the alkane chain of **2b** or both are responsible for disappearance of the tridentate chelation mode.

The Er–O(phosphoryl) bond distance, Er(1)–O(3) 2.251(4) Å, in **5** is shorter than the related distances in **6**, 2.317(5) Å, in $Er(NO_3)_3\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CHCH_2[C(O)NEt_2]\}$, 2.298(6) Å and in $Er(NO_3)_3\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CHCH_2[C(O)NEt_2]_2 \cdot H_2O$, 2.279(4) and 2.289(5) Å. The distance is similar to one of the related distances in the complex $Er(NO_3)_3[(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2]_2 \cdot H_2O$, 2.290(6) and 2.259(6) Å. The Er–O(amide) bond distance, Er(1)–O(4) 2.318(3) Å, is significantly shorter than the Er–O(ester) bond distance, Er(1)–O(2) 2.356(4) Å, that is involved in bridge formation to another erbium center. This distance can be compared to the two amide–erbium distances in the tridentate ligand complex $Er(NO_3)_3\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CHCH_2[C(O)NEt_2]$: Er–O (long arm amide) 2.267(8) Å and Er–O (short arm amide) 2.326(7) Å. The distance in **5** is identical to the distance in the six-membered chelate ring, but longer than the distance in the seven-membered chelate ring.

The phosphoryl bond distance in **5**, P(1)–O(3) 1.479(4) Å, is elongated relative to the distances in the related free ligand $[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CHCH_2[C(O)NEt_2]$, 1.459(3) Å, and this is consistent with direct Er–O(phosphoryl) bonding as well as the significant $\Delta\nu(PO)$ coordination shift (-72 cm^{-1}) found in the IR spectrum of **5***. The amide carbonyl distance

---

*The $\nu(PO)$ region contains two bands. This 'splitting' is observed in a number of f-element/organophosphonate complexes, and the origin is not firmly established.

C(6)–O(4) in **5**, 1.266(7) Å is longer than the amide distances in the free ligand [(i-PrO)$_2$P(O)]-[C(O)NEt$_2$]CHCH$_2$[C(O)NEt$_2$], 1.228(3) Å (short leg), 1.223(3) Å (long leg) and comparable with the distance in the tridentate ligand complex Er(NO$_3$)$_3${[(i-PrO)$_2$P(O)][C(O)NEt$_2$]CHCH$_2$[C(O)NEt$_2$]}, 1.243(10) and 1.254(12) Å. This feature is consistent with a strong Er–amide interaction and significant Δν(CO) (amide) coordination shift (-47 cm^{-1}) in the IR spectrum. The ester carbonyl distance C(4)–O(2), 1.208(7) Å, is unexpectedly short. This suggests relatively weak bridge bonding between Er(NO$_3$)$_3$·**2b** units. On the other hand, the IR coordination shift (-57 cm^{-1}) for the ester group is large, and this is consistent with a strong interaction.

Examination of the IR data for the remaining 1:1 La(III) and Er(III) complexes with ligands **2b** and **3b** indicates comparably strong ν(CO) (ester), ν(CO) (amide) and ν(PO) coordination shifts; therefore, it appears reasonable to conclude that the structures of these complexes are closely comparable to that of **5**. On the other hand, the 1:1 La(III), Er(III) and Th(IV) complexes with the shortest arm ester ligand ($n = 1$) **1b** and the 1:1 Th(IV) complex with **2b** show small ν(CO) (ester) coordination shifts. It appears likely that these complexes may have a monomeric structure with an uncoordinated ester group such as found in the uranyl complex **4**. This structural change may result from the steric crowding of the bridge coordination environment due to the short alkyl chain.

The molecular structure of **6** is displayed in Fig. 4, and selected bond distances and angles are listed in Table 8. Once again, the coordination number of the central Er ion is nine, composed of six oxygen atoms from three bidentate nitrate ions, the phosphoryl and amide oxygen atoms from one bidentate trifunctional ligand, **2b**, and the phosphoryl oxygen atom from a second ligand, and the coordination polyhedron is a tri-capped trigonal prism. The ester carbonyl group in the bidentate ligand remains uncoordinated as do the amide and ester carbonyl groups on the second ligand. The Er–O(phosphoryl) bond distances, Er(1)–O(3) and Er(1)–O(3′), are 2.317(5) and 2.275(5) Å, respectively. The shorter distance involves the monodentate ligand, and both distances are on the long end of the range of distances outlined in the description of the structure of **5** (*vide supra*). The Er–O(amide) bond distance, Er(1)–O(4) 2.292(5) Å, is slightly shorter than the related distance in **5**, and it is intermediate between the distances in Er(NO$_3$)$_3${[(i-PrO)$_2$P(O)][C(O)-NEt$_2$]CHCH$_2$[C(O)NEt$_2$]}. The P=O bond distances in **6**, P(1)–O(3) and P(1′)–O(3) are 1.471(6) and 1.481(6) Å, respectively. These are identical to the distance in **5** and consistent with the significant Δν(PO) coordination shifts. The bonded amide carbonyl distance C(6)–O(4), 1.263(9) Å, is relatively long compared to the uncoordinated amide carbonyl distance, C(6′)–O(4′), 1.224(11) Å and the uncoordinated ester carbonyl distances, C(4)–O(2), 1.165(14) Å and C(4′)–O(2′), 1.180(19) Å.

The IR spectra for the 2:1 complexes of **1b** and **2b** are all similar. They display a ν(CO) (ester) absorption with a minimal coordination shift and a ν(CO) (amide) absorption with a significant coordination shift relative to the values in the respective free ligands. Complexes of **1b** also show a band that may be assigned to the uncoordinated amide. Further, the spectra show two bands that may be tentatively assigned to the two phosphoryl environments found in the crystal structure of **6**.

Conclusions

One of the general objectives of our studies has been to design flexible, multifunctional organophosphonates that might act as polydentate ligands and as reversible liquid–liquid extractants for f-element ions. In the present study, we sought to design trifunctional phosphonobis-carbonyl alkanes, and that goal was accomplished successfully on ethane, propane and butane carbon backbones. The coordination chemistry proved to be unusually complex, and no evidence was gained that supported tridentate chelation on a single metal site. However, bidentate chelation through the 1-phosphono-1-carbamoyl methane fragment was accommodated in each complex. In addition, in two Er(III) complexes it was found that the pendant ester carbonyl functional group could act as a bridging ligand or a second ligand could displace the inner sphere water, which is typically found in related coordination complexes. These results provide guidance for the design of additional ligands that may achieve tridentate chelation, and the synthesis effort for these ligands is in progress.

Supplementary material

Full descriptions of X-ray crystallographic data and tables of bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positional parameters (128 pages) are available from author R.T.P.

Acknowledgements

R.T.P. wishes to recognize financial support for this research from the Department of Energy, Office of Basic Energy Sciences (Grant 88ER-13915) and from the DOE University Instrumentation Program (Grant

DE-FG05-86ER75294) that facilitated the purchase of the GSX-400 NMR spectrometer.

References

1 T. H. Siddall, *J. Inorg. Nucl. Chem., 25* (1963) 883; *26* (1964) 1991.
2 K. M. Kern, N. V. Nguyen and D. J. Cross, *J. Org. Chem., 46* (1981) 5188.
3 G. M. Kosolapoff and J. S. Powell, *J. Am. Chem. Soc., 72* (1950) 4198, and refs. therein.
4 S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta, 61* (1982) 155.
5 L. J. Caudle, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta, 110* (1985) 91.
6 W. E. Stewart and T. H. Siddall, *J. Inorg. Nucl. Chem., 32* (1970) 3599.
7 F. A. Cotton and R. A. Schunn, *J. Am. Chem. Soc., 85* (1963) 2394, and refs. therein.
8 S. M. Bowen, E. N. Duesler, R. T. Paine and C. F. Campana, *Inorg. Chim. Acta, 59* (1982) 53.
9 D. J. McCabe, S. M. Bowen and R. T. Paine, *Synthesis,* (1986) 319.
10 D. J. McCabe, E. N. Duesler and R. T. Paine, *Inorg. Chem., 24* (1985) 4626.
11 D. J. McCabe, E. N. Duesler and R. T. Paine, *Inorg. Chem., 27* (1988) 1220.
12 D. J. McCabe, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta, 147* (1988) 265.
13 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974, pp. 55–60, 99–101, 149–150.
14 F. R. Ahmed, S. R. Hall and C. P. Huber (eds.), *Crystallographic Computing,* Munksgaard, Copenhagen, 1970, p. 187.
15 R. D. Clark, L. G. Kozar and C. H. Heathcock, *Synthesis,* (1975) 635.
16 L. J. Caudle, *Ph.D. Thesis,* University of New Mexico, 1983.
17 D. J. McCabe, unpublished results.
18 A. A. Russell and G. S. Conary, unpublished results.
19 R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compound*, Wiley, New York, 4th edn., 1981.
20 S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chem., 22* (1983) 286.
21 J. H. Burns, *Inorg. Chem., 20* (1981) 3868.