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Synthesis and coordination chemistry of trifunctional carbamoyl-bis-phosphonate alkane ligands

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Abstract

Trifunctional ligands, 1,1-bis-phosphono-2-carbamoyl ethanes $[(RO)_2P(O)]_2CHCH_2[C(O)NEt_2]$ and 1-phosphono-1-carbamoyl-n-phosphono alkanes $[(RO)_2P(O)][C(O)NEt_2]CH(CH_2)_n[P(O)(OR)_2]$ ($n = 2$–4), were prepared from metathesis reactions of the appropriate metallated anions, $[(RO)_2P(O)]_2CH^-$ and $[(RO)_2P(O)][C(O)NEt_2]CH^-$. Selected coordination chemistry of the ligands with lanthanide nitrates was examined, and the molecular structure of $Gd(NO_3)_3\{[(i\text{-}C_3H_7O)_2P(O)][C(O)N(C_2H_5)_2]CH(CH_2)_3[P(O)(O\text{-}i\text{-}Pr)_2]$ was determined by single crystal X-ray diffraction techniques. The molecule crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.156(1)$, $b = 18.009(4)$, $c = 19.690(4)$ Å, $\beta = 96.65(1)$, $Z = 4$, $V = 3577(1)$ Å^3 and $\rho_{calc} = 1.539$ g cm^{-3}. The structure was solved by direct methods and blocked least-squares refinements converged with $R_F = 5.34\%$ and $R_{wF} = 4.57\%$ on 5102 independent reflections with $F > 3\sigma(F)$. The compound displays a polymeric structure, with each Gd atom bonded to three bidentate nitrate ions and the phosphoryl and carbonyl atoms of the carbamoylmethylphosphonate (CMP) fragment. The long arm phosphonate bridges to a second Gd atom. The coordination number of each Gd atom is nine. The Gd–O(P) and Gd–O(C) distances involving the CMP fragment are 2.332(4) and 2.396(4) Å, and the Gd–O(P) distance involving the long arm phosphonate is 2.328(4) Å.

Introduction

Syntheses for methylene diphosphonates, $(RO)_2P(O)CH_2P(O)(OR)_2$ have been extensively developed since 1953 [1–10], and the utility of the compounds as synthons in more complex organic reactions [6, 7, 10], as metal chelating ligands [9, 11, 12] and as industrial reagents [5, 13] has been actively explored. The methyl group spanning the two phosphoryl groups is relatively acidic, and it may be deprotonated with a strong base [1]. The resulting carbanions, as well as halogenated derivatives, $[(RO)_2P(O)]_2C(H)X$ and $[(RO)_2P(O)]_2CX_2$, have been utilized to prepare functionalized methylene diphosphonates $[(RO)_2P(O)]_2C(H)R$ and $[(RO)_2P(O)]_2CR_2$ [6, 7]. Carbamoylmethylphosphonates, $(RO)_2P(O)CH_2C(O)NR_2$ (CMPs), also display acidic character at the bridging methyl group, and they are easily deprotonated [14]. The resulting carbanions have been used in our group to prepare a number of trifunctional ligands of the general types $[(RO)_2P(O)][C(O)NR_2]CH[CH_2C(O)NR_2]$ [15–17] and $[(RO)_2P(O)][C(O)NR_2]CH[(CH_2)_nC(O)OR]$ [18] that, with two carbonyl and one phosphonate donor groups, display a wide range of coordination properties with hard f-element ions.

Few attempts have been made to prepare trifunctional carbamoyl-bis-phosphono alkane ligands. Quimby *et al.* [6] briefly described the formation of $[(i\text{-PrO})_2P(O)]_2C(H)R$ with $R = C(O)OR'$, $CH_2C(O)(OEt)$, $CH_2P(O)(OR')_2$ and $CH_2CH(PO_3R'_2)_2$; however, the coordination chemistry of these ligands has not been studied. In the present paper, we describe the synthesis of two groups of carbamoyl-bis-phosphono alkane ligands, $[(RO)_2P(O)]_2C(H)[CH_2C(O)NEt_2]$ and $[(RO)_2P(O)][C(O)NEt_2]C(H)[(CH_2)_nP(O)(OR)_2]$ ($n = 2$–4), and selected coordination chemistry for the latter class of ligands.

Experimental

General information

Alkyl dibromides, alkyl phosphites and sodium hydride were purchased from Aldrich Chemical Co. and used as received. Solvents were obtained from Fisher Scientific Co. and purified by standard procedures. Metal nitrates were purchased from Strem Chemical Co. and Alfa (Ventron) Chemical Co. All reactions, unless

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otherwise specified, were performed under dry nitrogen by using standard Schlenk techniques and glovebag enclosures. IR spectra were obtained from a Nicolet model 6000 FTIR, 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 (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). Analytical data were obtained from the UNM microanalytical facility and from Galbraith Laboratories. Spectroscopic data for the ligands are summarized in Table 1, and analytic and IR spectroscopic data for the complexes are presented in Table 2.

Preparations of the ligands

$[(EtO)_2P(O)]_2C(H)[CH_2C(O)NEt_2]$ (1)

The methylene diphosphonate, $[(EtO)_2P(O)]_2CH_2$, was prepared as described in the literature [5] from $(EtO)_3P$ and CH_2Br_2. A sample of the diphosphonate (0.1 mol, 28.8 g) was loaded into a 100 ml Schlenk flask under nitrogen flow, and that flask was connected to a 250 ml Schlenk flask containing NaH (2.9 g, 0.12 mol) in 100 ml of dry THF held at 0 °C. The diphosphonate was added over 1 h to the stirred THF mixture, and a slow nitrogen flow over the reaction swept the hydrogen from the container. The reaction mixture was warmed slowly to room temperature, filtered under dry nitrogen, and the filtrate containing $Na^+\{[(EtO)_2P(O)]_2CH^-\}$ was used immediately without isolation. NMR analysis (anion displays a single ^{31}P resonance: δ 43.0 (THF)) and Toepler pump measurements of the evolved H_2 for reactions performed on smaller scales indicate that the deprotonation reaction is complete.

The THF solution of $Na^+\{[EtO)_2P(O)]_2CH^-\}$ was cooled to 0 °C and connected to a dropping funnel containing freshly distilled *N*,*N*-diethylchloro acetamide, $ClCH_2C(O)NEt_2$ (0.1 mol, 14.9 g). The amide was added over 1 h to the vigorously stirred, cold solution and then warmed to room temperature overnight. The reaction mixture was centrifuged in stoppered vials without further protection from the atmosphere. The THF supernatant was decanted, and the product recovered from the THF solution by vacuum evaporation. The resulting colorless oil was better than 98% pure, as indicated by ^{31}P NMR and GC/MS analysis, and it can be further purified by distillation through a short path distillation column: 105–115 °C (25 mtorr). *Anal.* Calc. for $C_{15}H_{33}NO_7P_2$: C, 44.89; H, 8.29; N, 3.49. Found: C, 44.97; H, 8.33; N, 3.77%.

$[(i\text{-}PrO)_2P(O)]_2C(H)[CH_2C(O)NEt_2]$ (2)

This compound was prepared exactly as described for **1**. The intermediate anion was characterized by a singlet, δ 41.8, in the $^{31}P\{^1H\}$ NMR spectrum obtained from a THF solution. The final product was obtained as a colorless oil after distillation: 120–135 °C (15 mtorr). Yield 98%. *Anal.* Calc. for $C_{19}H_{41}NO_7P_2$: C, 49.89; H, 8.97; N, 3.06. Found: C, 49.60; H, 9.01; N, 3.13%.

$[(i\text{-}PrO)_2P(O)][C(O)NEt_2]C(H)[(CH_2)_2P(O)(O\text{-}i\text{-}Pr)_2]$ (4)

Bromoethyl diisopropylphosphonate (**3**) was prepared in a manner similar to a method described in the literature [19]. Triisopropyl phosphite (100 g, 0.48 mol) was slowly added over 1 h to refluxing 1,2-dibromoethane (270.7 g, 1.44 mol). The reaction apparatus consisted of a 1 l reaction vessel outfitted with a dropping funnel and reflux condenser maintained with water at 70 °C. Nitrogen gas was passed through the reaction vessel in order to sweep out i-propyl bromide. The large excess of 1,2-dibromoethane was employed in order to suppress formation of the diphosphonate $(i\text{-}PrO)_2P(O)CH_2CH_2P(O)(O\text{-}iPr)_2$. After addition was complete, the reaction mixture was refluxed for an additional hour, and excess $BrCH_2CH_2Br$ was removed by vacuum evaporation. The residue was distilled (80–85 °C, 1 mtorr), leaving a colorless oil, $(i\text{-}PrO)_2P(O)CH_2CH_2Br$ (**3**). Yield 85%. *Anal.* Calc. for $C_8H_{18}O_3PBr$: C, 35.18; H, 6.64. Found: C, 35.16; H, 6.63%.

A sample of $Na^+\{(i\text{-}PrO)_2P(O)CHC(O)NEt_2^-$ (36 mmol) in THF solution was prepared as described in the literature [14] and cooled to −12 °C. A solution containing $(i\text{-}PrO)_2P(O)CH_2CH_2Br$ (10.8 g, 39.6 mmol) in 100 ml THF was added slowly with stirring over 1 h and then stirred for an additional hour. The resulting mixture was centrifuged, decanted, and the THF was removed by vacuum evaporation. The residue was distilled between 150–175 °C at 10 mtorr and a light yellow oil (**4**) was obtained. Yield 24%. *Anal.* Calc. for $C_{20}H_{43}NO_7P_2$: C, 50.95; H, 9.19; N, 2.97. Found: C, 50.86; H, 9.10; N, 3.31%.

$[(i\text{-}PrO)_2P(O)][C(O)NEt_2]C(H)[(CH_2)_3P(O)(O\text{-}iPr)_2]$ (6)

Bromopropyl diisopropylphosphonate (**5**) was prepared as described for **3**. It was purified by distillation (85–110 °C, 10 mtorr) and obtained as a colorless oil. Yield 68%. *Anal.* Calc. for $C_9H_{20}O_3PBr$: C, 37.65; H, 7.02. Found: C, 37.78; H, 7.20%.

Compound **6** was prepared exactly as described for **4**. The residue was distilled at 155–180 °C (10 mtorr) and isolated as a pale yellow oil. Yield 42%. *Anal.* Calc. for $C_{21}H_{45}NO_7P_2$: C, 51.95; H, 9.34; N, 2.88. Found: C, 51.43; H, 9.46; N, 2.79%.

TABLE 1. Characterization data for ligands

Compound	Mass spectrum M^+ (*m*/*e*)	IR (cm^{-1}) $\nu(CO)/\nu(PO)$	NMR $^{31}P\{^1H\}^a$	$^{13}C\{^1H\}^{a,b}$		$^1H^{a,b}$
$[(EtO)_2P(O)]_2C(H)[CH_2C(O)NEt_2]$ (**1**)	401 402 ($M^+ + 1$)	1647/1252	23.5	$167.1(C_3, J_{PC}=7.1)$ $61.7(C_8, J_{PC}=5.9)$ $61.3(C_{10}, J_{PC}=5.9)$ $41.0(C_4)$ $39.8(C_6)$	$31.4(C_1, J_{PC}=134.3)$ $28.2(C_2)$ $15.4(C_9, J_{PC}=5.4)$ $13.4(C_5)$ $12.3(C_7)$	$4.12(HC_{10}, J_{HH}=6.6)$ $4.11(HC_9, J_{HH}=7.0)$ $3.51(HC_1, J_{PH}=30.0, J_{HH}=5.1)$ $3.35(HC_4, J_{HH}=3.9, HC_6)$ $2.75(HC_2, J_{PH}=18.0, J_{HH}=5.4)$
$[(i\text{-}PrO)_2P(O)]_2C(H)[CH_2C(O)NEt_2]$ (**2**)	458 ($M^+ + 1$)	1648/1251	21.7	$167.2(C_3, J_{PC}=7.0)$ $70.0(C_8, J_{PC}=6.0)$ $69.4(C_{10}, J_{PC}=6.0)$ $41.0(C_4)$ $40.1(C_6)$	$32.9(C_1, J_{PC}=135.8)$ $28.5(C_2)$ $23.2(C_9)$ $13.5(C_5)$ $12.4(C_7)$	$4.73(HC_8, J_{HH}=6.0)$ $4.72(HC_{10}, J_{HH}=6.0)$ $3.46(HC_1, J_{PH}=24.0, J_{HH}=4.9)$ $3.33(HC_4, J_{PH}=6.7)$ $3.28(HC_6, J_{HH}=6.8)$
$(i\text{-}PrO)_2P(O)(CH_2)_2Br$ (**3**)	273	–/1244	22.9	$70.1(C_2, J_{PC}=6.3)$ $32.4(C_3, J_{PC}=134.3)$ $25.2(C_4)$ $24.1(C_1, J_{PC}=4.4)$		$4.54(HC_2)$ $3.44(HC_4)$ $2.20(HC_3)$
$[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_2P(O)(O\text{-}i\text{-}Pr)_2]$ (**4**)	471	1639/1247	28.0 $J_{PP}=4.5$ 21.0	$166.8(C_8, J_{PC}=4.0)$ $71.5(C_2, J_{PC}=6.7)$ $70.4(C_{2'}, J_{PC}=6.7)$	$41.0(C_6)$ $25.4(C_{10}, J_{PC}=141.2, 14.8)$ $24.1(C_1, C_{12})$	$4.61(HC_2, HC_{11})$ $3.51(HC_6)$ $3.31(HC_{10})$
$(i\text{-}PrO)_2P(O)(CH)_2)_3Br$ (**5**)	287			$69.7(C_{11}, J_{PC}=6.7)$ $69.7(C_{11'}, J_{PC}=5.4)$ $42.7(C_4)$	$22.2(C_9, J_{PC}=4.0)$ $14.6(C_5)$ $13.1(C_7)$	$3.05(HC_4, J_{HH}=6.9)$ $2.54(HC_3)$ $2.17(HC_9)$
$[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_3P(O)(O\text{-}i\text{-}Pr)_2]$ (**6**)	485	–/1225	27.0	$70.8(C_2, J_{PC}=6.4)$ $35.2(C_5, J_{PC}=18.3)$ $28.1(C_4, J_{PC}=4.2)$	$25.3(C_1, J_{PC}=4.3)$ $23.6(C_3, J_{PC}=143.0)$	$4.54(HC_2)$ $3.33(HC_5)$ $1.94(HC_3)$
$(EtO)_2P(O)(CH_2)_4Br$ (**7**)	273	1642/1249	28.0 21.2	$167.0(C_8, J_{PC}=4.4)$ $71.1(C_2, J_{PC}=7.3)$ $70.1(C_{2'}, J_{PC}=7.4)$ $69.2(C_{12}, J_{PC}=4.4)$	$29.5(C_9, J_{PC}=16.8, 5.2)$ $27.1(C_{11}, J_{PC}=142.3)$ $24.1(C_1)$ $21.0(C_{10}, J_{PC}=16.2, 4.4)$	$4.56(HC_2, HC_{12})$ $3.42(HC_4, J_{HH}=7.3)$ $3.28(HC_6, J_{HH}=6.6)$ $3.08(HC_{11})$
$[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_4P(O)(O\text{-}Et)_2]$ (**8**)	499			$42.7(C_3, J_{PC}=132.0)$ $42.6(C_4)$ $41.0(C_6)$	$14.7(C_5)$ $13.1(C_7)$	$2.20(HC_3)$ $1.80(HC_9)$
		–/1249	29.9	$61.3(C_2, J_{PC}=6.7)$ $33.7(C_6)$ $33.4(C_5, J_{PC}=14.8)$	$24.7(C_3, J_{PC}=141.2)$ $21.5(C_4, J_{PC}=5.3)$ $16.6(C_1, J_{PC}=5.4)$	$3.90(HC_2, J_{HH}=7.5)$ $3.25(HC_6, J_{HH}=6.6)$ $1.73(HC_3)$
		1641/1246	30.2 21.4	$162.0(C_8, J_{PC}=4.4)$ $70.9(C_2, J_{PC}=5.8)$ $70.0(C_{2'}, J_{PC}=7.3)$ $61.0(C_{13}, J_{PC}=5.8)$ $42.5(C_3, J_{PC}=132.1)$ $42.5(C_4)$ $40.9(C_6)$ $29.2(C_{10}, J_{PC}=16.2)$	$27.9(C_9, J_{PC}=4.4)$ $25.5(C_{12}, J_{PC}=140.9)$ $24.1(C_1)$ $22.7(C_{11}, J_{PC}=5.8)$ $16.6(C_{14}, J_{PC}=5.9)$ $14.7(C_5)$ $13.0(C_7)$	$4.53(HC_2)$ $3.88(HC_{13})$ $3.48(HC_4, J_{HH}=6.6)$ $3.35(HC_6, J_{HH}=6.6)$ $3.09(HC_{12})$ $2.01(HC_3)$ $1.62(HC_9)$

[a] Spectra recorded from C_6D_6 solutions. Coupling constants listed in Hz. [b] The atom numbering scheme is given in the footnote on p. 16.

TABLE 2. Analytical and IR spectroscopic data for coordination complexes

Complex	Elemental analysis[a]			IR spectrum	
	C	H	N	C=O	P=O
$La(NO_3)_3 \cdot$ **4**	30.16	5.44	7.03	1616	1192
	31.14	5.74	6.73		
$Gd(NO_3)_3 \cdot$ **4**	29.48	5.32	6.88	1610	1178
	29.64	5.47	6.93		1196
$Er(NO_3)_3 \cdot$ **4**	29.13	5.25	6.79	1612	1179
	28.02	5.52	6.83		1200
$UO_2(NO_3)_2 \cdot$ **4**	28.21	5.09	4.93	1605	1162
	28.11	5.15	4.81		1178
$Th(NO_3)_4 \cdot$ **4**	25.24	4.55	7.36	1605	1160
	26.47	4.99	6.99		
$La(NO_3)_3 \cdot$ **6**				1605	1190
$Gd(NO_3)_3 \cdot$ **6**	30.43	5.47	6.76	1604	1186
	30.47	5.60	6.56		
$Er(NO_3)_3 \cdot$ **6**	30.58	5.50	6.79	1603	1190
	30.94	5.59	6.71		
				[b]	1180
$UO_2(NO_3)_2 \cdot$ **6**	28.68	5.16	4.78		
	28.10	5.43	4.48	1609	1201
$Th(NO_3)_4 \cdot$ **6**	25.19	4.76	7.34		
	25.14	5.07	6.89	1611	1180
$La(NO_3)_3 \cdot$ **8**	30.16	5.44	7.03		
	29.61	5.86	6.59	1604	1178
$Gd(NO_3)_3 \cdot$ **8**				1605	1206
					1182
$Er(NO_3)_3 \cdot$ **8**	29.63	5.35	6.91		
	29.76	5.44	7.03	1599	1160
				1603	[b]
$UO_2(NO_3)_2 \cdot$ **8**	28.21	5.09	4.93		
	28.07	5.12	4.81		

[a] Calculated values are listed on top and observed values below. [b] Bands were not clearly separated from neighboring absorptions.

$[(i\text{-}PrO)_2P(O)][C(O)NEt_2]C(H)[(CH_2)_4P(O)(OEt)_2]$ (8)

Bromobutyl diethylphosphonate (**7**) was prepared as described for **3**, except triethylphosphite was used. The product was purified by distillation (90–112 °C, 10 mtorr) and obtained as a colorless oil. Yield 65%. *Anal.* Calc. for $C_8H_{18}O_3PBr$: C, 35.18; H, 6.64. Found: C, 35.71; H, 6.91%.

Compound **8** was prepared as described for **4**. The residue was distilled at 165–193 °C (10 mtorr) and isolated as a pale yellow oil. Yield 55%. *Anal.* Calc. for $C_{20}H_{43}NO_7P_2$: C, 50.95; H, 9.19; N, 2.97. Found: C, 50.44; H, 9.24; N, 3.01%.

Preparation of the complexes

Ligands **1** and **2** were combined with $UO_2(NO_3)_2 \cdot 6H_2O$ and $Ln(NO_3)_3 \cdot xH_2O$ in 1:1 and 2:1 ratios in ethanol, and the mixtures stirred for 1 h. The solvent was evaporated, leaving oily residues. Numerous attempts were made to recrystallize these complexes; however, no solid materials were obtained. Elemental analyses gave a range of results that could not be interpreted in terms of a single reasonable composition. Infrared spectra suggest that the complexes are variously solvated with water, ethanol, or other donor solvents used in recrystallization efforts.

Ligands **4**, **6** and **8** were combined in a 1:1 ratio with $UO_2(NO_3)_2 \cdot 6H_2O$, $Ln(NO_3)_3 \cdot xH_2O$ (Ln = La, Ce, Gd, Er) and $Th(NO_3)_4 \cdot 4H_2O$ in ethanol and the mixtures stirred for 1 h. The ethanol was allowed to evaporate slowly, and the resulting solids were collected by filtration and recrystallized from CH_2Cl_2/hexane. The crystals were washed with Et_2O and dried *in vacuo*. Elemental analysis data and IR data are provided in Table 2.

X-ray diffraction analysis

Single crystals of $Gd(NO_3)_3 \cdot$ **6** were grown by slow evaporation of a CH_2Cl_2/hexane solution of the complex. A pale pink plate (0.23 × 0.35 × 0.46 mm) was glued to a fiber, and data were collected in the ω 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

TABLE 3. X-ray data for $Gd(NO_3)_3 \cdot$ **6**

Crystal parameters (293 K)	
Crystal system	monoclinic
Chemical formula	$C_{21}H_{45}N_4O_{16}P_2Gd$
Space group	$P2_1/c$
Formula weight	828.8
a (Å)	10.156(2)
b (Å)	18.009(4)
c (Å)	19.690(4)
β (°)	96.65(1)
V (Å^3)	3577(1)
Z	4
λ (Å)	0.71073
ρ_{calc} (g cm^{-3})	1.539
μ (mm^{-1})	2.015
$F(000)$	1684
Data collection	
Diffractometer	Nicolet R3m/V
Radiation	Mo Kα (λ = 0.71073 Å)
2θ Range (°)	2.0–50.0
Scan type	ω
Scan speed (min^{-1})	variable; 6–30° in ω
Reflections collected	13748
Independent reflections	6297
Observed reflections	5102 ($F > 3\sigma(F)$)
Min./max. transmission	0.7392/0.9538
R_F (%)	5.34
R_{wF} (%)	4.57

$\omega^{-1} = \sigma^2(F) + |g|F^2$; $g = 0.0003$.

summarized in Table 3. A small correction for absorption was made by using Ψ scans*.

Redundant 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 to the observed data with full matrix least-squares methods by 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 [20a]. (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 made. A general description of the least-squares algebra is found in ref. 21.) 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 set to be in the range of 0.08 to 0.33. All $U_{iso}(H) = 0.08$ or equal to U_{eq} of the parent atom, whichever was greater. Final refinements converged at $R_F = 5.34\%$ and $R_{wF} = 4.57\%$ on 5102 independent reflections with $F > 3\sigma(F)$. A listing of non-hydrogen atomic positional parameters and thermal factors is provided in Table 4. See also 'Supplementary material'.

TABLE 4. Atomic coordinates ($\times 10^4$) for $Gd(NO_3)_3\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_3P(O)(O\text{-}i\text{-}Pr)_2]\}$

	x	*y*	*z*
Gd	2112(1)	2166(1)	1814(1)
P(1)	4618(2)	2295(1)	3245(1)
O(1)	4021(4)	2002(2)	2578(2)
O(2)	5578(5)	2959(3)	3213(3)
O(3)	5420(4)	1701(3)	3686(2)
P(2)	−170(2)	1940(1)	5411(1)
O(4)	660(4)	2159(2)	6047(2)
O(5)	−1011(4)	1237(2)	5525(2)
O(6)	−1153(4)	2532(3)	5096(2)
C(1)	3395(6)	2673(3)	3743(3)
C(2)	2584(6)	2063(3)	4035(3)
C(3)	1526(6)	2360(3)	4451(3)
C(4)	755(7)	1727(4)	4720(3)
C(5)	2527(6)	3206(3)	3294(3)
O(7)	1832(4)	2944(2)	2774(2)
C(6)	1587(8)	4415(4)	3010(4)
C(7)	257(9)	4497(5)	3214(6)
C(8)	3085(9)	4263(5)	4081(5)
C(9)	4362(11)	4605(6)	3991(7)
C(10)	6731(9)	2929(7)	2825(5)
C(11)	7919(10)	2830(7)	3297(7)
C(12)	6715(11)	3633(11)	2466(8)
C(13)	5250(8)	888(4)	3622(4)
C(14)	5983(10)	597(5)	3076(5)
C(15)	5726(11)	595(5)	4319(5)
C(16)	−750(7)	725(4)	6099(3)
C(17)	−1970(8)	250(4)	6092(4)
C(18)	489(8)	288(4)	6045(4)
C(19)	−2063(7)	2940(4)	5499(4)
C(20)	−2037(12)	3705(6)	5310(9)
C(21)	−3374(10)	2653(7)	5329(8)
N	2434(6)	3912(3)	3462(3)
N(1)	3708(7)	3180(4)	1114(4)
O(8)	3271(5)	3365(3)	1661(3)
O(9)	3543(5)	2510(4)	948(3)
O(10)	4255(7)	3612(4)	771(4)
N(2)	82(7)	1420(4)	2490(4)
O(11)	1296(6)	1207(3)	2571(3)
O(12)	−184(5)	1945(3)	2084(3)
O(13)	−736(7)	1131(4)	2798(4)
N(3)	2317(8)	825(4)	1044(4)
O(15)	3178(6)	993(3)	1525(3)
O(14)	1363(6)	1267(3)	917(3)
O(16)	2385(8)	247(3)	718(4)

Results and discussion

Syntheses and spectroscopic data

It is well known that the bifunctional ligands, $(RO)_2P(O)CH_2C(O)NEt_2$ and $(RO)_2P(O)CH_2P(O)(OR)_2$ act as bidentate chelating ligands toward hard, oxophilic f-element ions and as effective extractants for these metals [9, 22]. The extraction complexes are sufficiently strong to facilitate aqueous to organic phase transfer of the metal ions, yet they are weak enough to release the metal ions by pH variation during back-extraction. Structural studies for several complexes indicate that the bifunctional ligands in some cases do not fully displace water from the inner coordination sphere of lanthanide ions. From a ligand design perspective, we have reasoned that trifunctional ligands, constructed by attachment of a third oxide donor site on a pendant chain at the bridging methyl group of the parent bidentate ligands, might act as tridentate ligands which could fully displace inner sphere water molecules. This in turn should provide additional thermodynamic stability to extraction complexes. In fact, the bis-carbamoyl-phosphono ethane $[(RO)_2P(O)][C(O)NEt_2]CH[CH_2C(O)NEt_2]$ does form a series of lanthanide complexes with the following compositions [22]: $Ln(NO_3)_3\{[(RO)_2P(O)][C(O)NEt_2]CH[CH_2C(O)NEt_2]\}_2$ (Ln = La–Nd) and $Ln(NO_3)_3\{[(RO)_2P(O)][C(O)NEt_2]CH[CH_2C(O)NEt_2]\}_2 \cdot H_2O$ (Ln = Gd–Yb). Single crystal X-ray diffraction analyses for complexes with Ln = Gd and Er confirmed the latter composition and established that the ligand surprisingly favors a monodentate phosphoryl binding mode. The short arm amide carbonyl is hydrogen bonded to a water molecule bonded to the central metal atom, and

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

the long arm amide group remains uncoordinated. Apparently, the amide fragments either are not sufficiently basic or are not able to adopt favorable conformations under the conditions employed to provide bidentate or tridentate chelation. In addition, the amide groups must be sterically congested or too weakly basic to act as a bridging group by binding to another $Ln(NO_3)_3L_2$ fragment. That this might be a potential coordination mode for a bis-carbamoyl-phosphono alkane ligand is demonstrated by the molecular structure adopted in the complex $Er(NO_3)_3\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[CH_2CH_2C(O)NEt_2]$ [18] in which the pendant amide arm is extended by one CH_2 group. It is noted as well that $[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[CH_2C(O)NEt_2]$ forms a tridentate chelate complex with $Er(NO_3)_3$ when $(EtO)_3PO$ is present in the synthesis mixture, and it is thought that the $(EtO)_3PO$ assists in the dehydration of the hydrated Er(III) ion [17]. Lastly, it is worth noting that liquid–liquid extraction data for $[(HxO)_2P(O)][C(O)NEt_2]CH[CH_2C(O)NEt_2]$ indicate that this ligand displays similar distribution coefficients, *D*, at low acid concentrations as the bifunctional CMP ligand, $(HxO)_2P(O)CH_2C(O)NEt_2$, but smaller *D*s at high acid concentrations [23].

Based on these results, it was concluded that replacement of an amide group either on the short or long pendant arms of the trifunctional bis-carbamoyl-phosphono alkanes with a more basic phosphonate group might provide for tridentate chelation. As noted above, Quimby *et al.* [6] reported a metathetical synthesis of $[(i\text{-}PrO)_2P(O)]_2CH[C(O)(O\text{-}i\text{-}Pr)]$ from $Na^+\{[(i\text{-}PrO)_2P(O)]_2CH^-\}$ and isopropyl formate, but this ligand was found to be unstable toward acid hydrolysis and decomposition to $[(HO)_2P(O)]_2CH_2$. However, when ethyl chloroacetate was used, a stable carbon ester $[(i\text{-}PrO)_2P(O)]_2CH[CH_2C(O)Et]$ was obtained in good yield. A CPK model suggests that this compound may be able to adopt a tridentate binding mode, and replacement of the carbon ester with a more basic amide should amplify this bonding mode.

$$[(RO)_2P(O)]_2CH_2 + NaH \xrightarrow{THF} Na^+\{[(RO)_2P(O))]_2CH^-\} \xrightarrow{ClCH_2C(O)NEt_2} [(RO)_2P(O)]_2CHCH_2C(O)NEt_2 \qquad (1)$$

1: R = Et
2: R = i-PrO

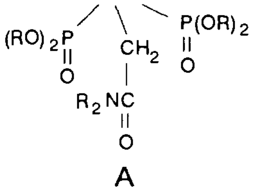
$$(RO)_3P + Br(CH_2)_nBr \longrightarrow (RO)_2P(O)(CH_2)_nBr \qquad (2)$$

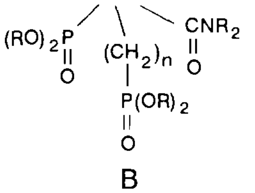
n	R = Et	i-Pr
2	–	**3**
3	–	**5**
4	**7**	–

$$Na^+\{(R'O)_2P(O)CHC(O)NEt_2^-\} + (RO)_2P(O)(CH_2)_nBr \longrightarrow [(R'O)_2P(O)][C(O)NEt_2]C(H)[(CH_2)_nP(O)(OR)_2] \qquad (3)$$

4: R′ = i-Pr, R = i-Pr, *n* = 2
6: R′ = i-Pr, R = i-Pr, *n* = 3
8: R′ = i-Pr, R = Et, *n* = 4

In the present study, synthetic routes to carbamoyl-bis-phosphono alkanes of the types shown as **A** (**1** and **2**) and **B** (**4**, **6**, **8**) were developed. The ligands were obtained as stable, distillable oils in good yields, as described in eqns. (1)–(3) and their formulations are consistent with analytical data and mass, IR and NMR spectroscopic data summarized in Table 1*.


A


B

IR spectra for **1**, **2**, **4**, **6** and **8** show a single carbonyl stretching frequency in the range 1648–1639 cm^{-1} and a single phosphoryl stretching frequency in the range 1252–1246 cm^{-1}. Ligands **1** and **2** show a single ^{31}P NMR resonance consistent with equivalent phosphorus environments and a single carbonyl resonance in the $^{13}C\{^1H\}$ NMR spectrum. Ligands **4**, **6** and **8** show a single carbonyl resonance, but two ^{31}P resonances consistent with the structural differences in the molecules. The phosphoryl group on the long pendant arm is assigned to the lower field resonance (δ 28–30); *J*(PP) coupling was resolved only in **4**. The remaining features in the $^{13}C\{^1H\}$ spectra and the ^1H spectra were assigned by using chemical shift and coupling constant trends established in our previous studies [22].

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*The numbering system used in the assignment of NMR spectra is as follows:
1 $[(C^9H_3C^8H_2O)(C^9H_3C^{10}H_2O)P(O)]_2C^1(H)[C^2H_2C^3(O)N\text{-}(C^4H_2C^5H_3)(C^6H_2C^7H_3$
2 $\{[(C^9H_3)_2C^8H_2O)(C^9H_3)_2C^{10}HO]P(O)_2C^1(H)[C^2H_2C^3(O)N\text{-}(C^4H_2C^5H_3)(C^6H_2C^7H_3)]\}$
3 $[(C^1H_3)_2C^2HO][(C^{1'}H_3)_2C^{2'}HO]P(O)C^3H_2C^4H_2Br$
4 $\{[(C^1H_3)_2C^2HO][(C^{1'}H_3)_2C^{2'}HO]P(O)\}\{C^8(O)N(C^4H_2C^5H_3)\text{-}(C^6H_2C^7H_3)\}C^3H\{C^9H_2C^{10}H_2P(O)[OC^{11}HC^{12}H_3]_2\}$
5 $[(C^1H_3)_2C^2HO][(C^{1'}H_3)_2C^{2'}HO]P(O)C^3H_2C^4H_2C^5H_2Br$
6 $\{[(C^1H_3)_2C^2HO][(C^{1'}H_3)_2C^{2'}HO]P(O)\}\{C^8(O)N(C^4H_2C^5H_3)\text{-}(C^6H_2C^7H_3)\}C^3H\{C^9H_2C^{10}H_2C^{11}H_2P(O)[OC^{12}HC^{13}H_3]_2\}$
7 $[(C^1H_3)_2C^2HO][(C^{1'}H_3)_2C^{2'}HO]P(O)C^3H_2C^4H_2C^5H_2C^6H_2Br$
8 $\{[(C^1H_3)_2C^2HO][(C^{1'}H_3)_2C^{2'}HO]P(O)\}\{C^8(O)N(CH_2C^5H_3)\text{-}(C^6H_2C^7H_3)\}C^3H\{C^9H_2C^{10}H_2C^{11}H_2C^{12}H_2P(O)[OC^{13}HC^{14}H_3]_2\}$

Attempts to prepare discrete crystalline coordination complexes of ligands **1** and **2** with $UO_2(NO_3)_2$, $Th(NO_3)_4$ and $Ln(NO_3)_3$ in 1:1 and 2:1 ratios were surprisingly unsuccessful. In each case, oily products with variable compositions, as indicated by elemental analyses, were obtained. As a result, no unambiguous conclusions can be drawn regarding the favored stoichiometry of the complexes or the preferred denticity of the ligands. On the other hand, crystalline coordination complexes are obtained with ligands **4**, **6** and **8**, and each displays a 1:1 stoichiometry with general compositions $UO_2(NO_3)_2\cdot(L)$, $Th(NO_3)_4\cdot(L)$ and $Ln(NO_3)_3\cdot L$, as indicated by elemental analysis data. The compositions of two of the lanthanide complexes, $Gd(NO_3)_3\cdot$**6** and $Er(NO_3)_3\cdot$**6**, are confirmed by X-ray crystallographic analysis, and the results from the gadolinium structure determination are described*.

Structural study of $Gd(NO_3)_3\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_3P(O)(O\text{-}i\text{-}Pr)]\}$

A view of the molecule is shown in Fig. 1, and a summary of selected bond distances and angles is provided in Table 5.

This complex displays a polymeric structure in which each Gd(III) ion is bonded to three bidentate nitrate ions and one trifunctional ligand **6**. The ligand is bonded to the Gd ion in a bidentate fashion through the phosphoryl oxygen atom and the short arm amide oxygen atom, as found in the structures of early lanthanide complexes with CMP ligands [24]. In addition, each Gd is bridge bonded to the oxygen atom in the long arm phosphoryl group from another molecular unit. This coordination environment provides a total Gd coordination number of nine. Interestingly, the trifunctional ligands **6**, through a combination of steric and base strength factors, is able to displace all of the water of hydration on the Gd(III) ion. This coordination condition is distinct from that found for the bis-carbamoyl-phosphono ethane ligand in $Gd(NO_3)_3\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[CH_2C(O)NEt_2]\}_2\cdot H_2O$ (**9**) mentioned above, wherein the ligand binds in a monodentate fashion to Gd [15, 22].

TABLE 5. Selected bond distances (Å) and bond angles (°) for $Gd(NO_3)_3\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_3P(O)(O\text{-}i\text{-}Pr)_2]\}$

Bond distances[a]			
Gd–O(1)	2.332(4)	P(1)–O(1)	1.479(4)
Gd–O(4′)	2.328(4)	P(1)–O(2)	1.548(5)
Gd–O(7)	2.396(4)	P(1)–O(3)	1.549(5)
Gd–O(8)	2.495(5)	P(1)–C(1)	1.802(7)
Gd–O(9)	2.445(6)	P(2)–O(4)	1.480(4)
Gd–O(11)	2.486(5)	P(2)–O(5)	1.558(4)
Gd–O(12)	2.483(5)	P(2)–O(6)	1.540(5)
Gd–O(14)	2.451(5)	C(5)–O(7)	1.265(7)
Gd–O(15)	2.470(6)		
Bond angles			
O(1)–Gd–O(7)	74.4(1)	O(2)–P(1)–C(1)	102.0(3)
O(4′)–Gd–O(7)	94.7(1)	O(3)–P(1)–C(1)	107.8(3)
O(1)–Gd–O(4)	154.4(1)	Gd′–O(4)–P(2)	160.7(3)
Gd–O(1)–P(1)	138.8(3)	P(1)–C(1)–C(2)	111.7(4)
Gd–O(7)–C(5)	138.6(4)	P(1)–C(1)–C(5)	108.2(4)
O(1)–P(1)–O(2)	115.8(3)	C(2)–C(1)–C(5)	111.9(5)
O(1)–P(1)–O(3)	112.7(3)		
O(1)–P(1)–C(1)	112.4(3)		

[a] O(4′) obtained by symmetry operation x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$ on position of O(4).

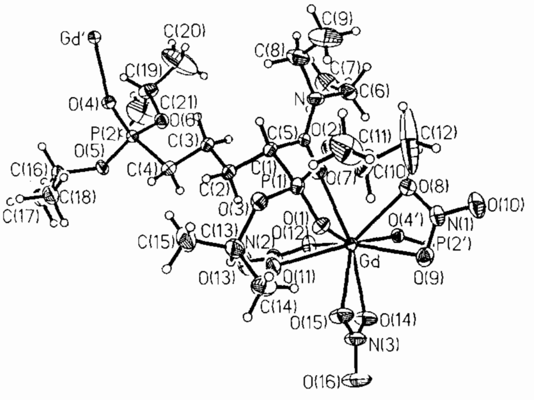

Fig. 1. Molecular geometry and atom labeling scheme for $Gd(NO_3)_3\{[(i\text{-}C_3H_7O)_2P(O)][C(O)NEt_2]CH[(CH_2)_3P(O)(O\text{-}i\text{-}Pr)_2]$ (20% thermal ellipsoids).

The Gd–O (phosphoryl) distances, Gd–O(1) 2.332(4) and Gd–O(4′) 2.328(4) Å, are identical, and they are comparable with the Gd–O(P) distance in **9**, 2.343(5) Å. The phosphoryl distances, P(1)–O(1) 1.479(4) and P(2)–O(4′) 1.480(4) Å, are slightly longer than the average bonded P=O distance in **9**, 1.468 Å. The Gd–O(carbonyl) distance, 2.396(4) Å, does not have a direct analog for comparison amongst gadolinium–CMP-like ligand structures; however, it is comparable to the Sm–O(carbonyl) distance, 2.433(2) Å, in $Sm(NO_3)_3[(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2]_2$ when corrections for the difference in ionic radii are made. Further, the carbonyl distance, C(5)–O(7) 1.265(7) Å, is relatively long and is consistent with carbonyl participation in bidentate chelation. The corresponding carbonyl distance in the bidentate samarium complex is 1.261(3) Å. The average Gd–O(nitrate) bond distance, 2.472 Å, is comparable to the average distance in **9**, 2.475 Å.

IR spectra for the La(III), Gd(III) and Er(III) complexes of **4**, **6** and **8** are similar to each other. The carbonyl stretching frequencies are assigned to a band appearing in a narrow region 1616–1599 cm^{-1}, and

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*The late lanthanide complex $Er(NO_3)_3\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)_3C(O)NEt_2]\}$ is isostructural with the Gd complex **9**. Some important metrical parameters include: Er–O(1) 2.280(4), Er–O(4′) 2.286(4), Er–O(7) 2.355(4), P(1)–O(1) 1.479(4), C(5)–O(7) 1.256(7) Å. See also ‘Supplementary material’.

these represent coordination shifts of ~35 cm^{-1}, which are typical of carbonyl shifts in lanthanide–CMP complexes [24, 25]. The phosphoryl stretching frequencies are assigned to bands appearing in the range 1206–1160 cm^{-1}. This band is 'split' in $Gd(NO_3)_3 \cdot$**4**, $Er(NO_3)_3 \cdot$**4** and $Er(NO_3)_3 \cdot$**8**. The origin of the splitting is not certain; however, it may result from resolution of the two distinct phosphoryl donor centers. It is also noteworthy that the $\Delta\nu$(CO) values for the Ln complexes of **4** are ~10 cm^{-1} smaller than the coordination shifts of the complexes of **6** and **8**, and this may reflect a more sterically crowded, hence weaker, coordination environment. Although not unambiguous, the IR data are consistent with the ligand coordination mode revealed in the crystallographic study.

IR spectra for the coordination complexes of **4**, **6** and **8** with $UO_2(NO_3)_2$ and $Th(NO_3)_4$ are similar. They clearly show carbonyl stretching frequencies in the range 1609–1603 cm^{-1} which correspond to coordination shifts of 30–40 cm^{-1}. (The ν(CO) band in $UO_2(NO_3)_2 \cdot$**6** was not unambiguously assigned.) As described above, the magnitude of these shifts suggests that the amide group is directly involved in metal ion binding. Further support for this conclusion is provided by the carbonyl coordination shifts found in $UO_2(NO_3)_2\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH[(CH_2)C(O)OEt]\}$: short arm $\Delta\nu(CO) = 35$ cm^{-1}, long arm $\Delta\nu(CO) = -1$ cm^{-1} [18].

Crystallographic analysis of this complex reveals that the short arm amide carbonyl is bonded to the UO_2^{2+} group, while the long arm ester carbonyl is not involved in coordination. The phosphoryl stretching frequencies range from 1180–1160 cm^{-1} (the ν(PO) band in $UO_2(NO_3)_2 \cdot$**8** was not unambiguously assigned), which correspond to coordination shifts of 69–87 cm^{-1}, clearly indicative of strong metal–phosphoryl interactions [22]. It might be expected that the thorium complexes could adopt a bidentate/bridged ligand structure comparable to that found in the Gd complex. The uranyl complexes, on the other hand, would not be expected to adopt the bridge bonded structure with the pendant arm phosphonate since this would require expansion of the coordination number for UO_2^{2+} to nine. It is surprising then that only one phosphoryl frequency is resolved in the IR spectra of these complexes. A crystal structure determination for one of the uranyl complexes would resolve the apparent structural anomaly; however, efforts to obtain suitable single crystals have not yet been fruitful.

Conclusions

The synthetic studies described here provide straightforward routes to two families of new trifunctional ligands with potential novel chelation and solvent extraction properties. The molecular structure determination for $Gd(NO_3)_3 \cdot$**6** reveals that the 1-carbamoyl-1,4-bis-phosphono butane ligand **6** acts both as a bidentate and as a bridging ligand in the formation of a 1:1 polymeric complex. This behavior is distinctly different from the coordination character displayed by the 1,3-carbamoyl-1-phosphono propane ligand found in complex **9**. It is likely that the greater basicity of the phosphoryl group on the long arm pendant chain favors the formation of the bridged structure, and a combination of steric and electronic features may be responsible for the favored bidentate chelation of the CMP-like fragment. Although the data may be interpreted in other ways, the IR spectra for the Th(IV), La(III) and Er(III) complexes suggest that all three functional groups in **4**, **6** and **8** are involved in metal binding. Analytical data in each case also suggest formation of 1:1 metal/ligand complexes; therefore, it is likely that each complex adopts a polymeric structure involving linkage of individual M · L units via the pendant phosphoryl donor group. Further attempts will be made to crystallize representative complexes in order to test this tentative conclusion. In addition, we intend to survey the extraction characteristics of **4**, **6** and **8** in order to determine if these ligands display selective solvent extraction characteristics compared to CMP ligands.

Supplementary material

Full listings of data collection information, bond distances, bond angles, hydrogen atom positional parameters, and structure factors for $Gd(NO_3)_3 \cdot$**6** are available from author R.T.P. A complete set of X-ray diffraction data for **9** is also available.

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