Bifunctional Phosphoric Acid–Phosphine Oxide Extractants: Synthesis and Complexes with Uranium-(IV) and -(VI) and Iron(III)

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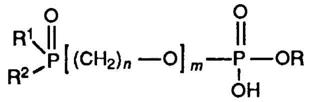
A bifunctional extractant (HL) carrying phosphine oxide and phosphoric acid complexing centres has been synthesized by the cyclic enediol phosphate method, using a two-step reaction with dihexyl(hydroxymethyl)phosphine oxide and 2-ethylhexanol. The bifunctional complexant complexes both U^{IV} and U^{VI}. The complexation process, as shown by ^{31}P n.m.r. spectroscopy, involves both the $R_3P=O$ and $(R'O)_2PO_2H$ centres ($R=C_6H_{13}$, $R'=C_8H_{17}$). The compound HL exists as hydrogen-bonded associates in the organic (hexane) phase. Involvement of anions in the complex structures is evident for U^{VI} (NO_3^-), U^{IV}(Cl^-, NO_3^-, or HPO_4^{2-}), and Fe(Cl^- or SCN^-).

Complexing ligands of high affinity for metal ions can be either solvating or chelating donors.[1] Both classes are subject to strong competition from inorganic ligands. As a consequence of this competition, only chelating ligands that form stable ring systems are generally strong complexing ligands.

The admixture of high concentrations of complexing agents in the appropriate solvents and in the right ratios provides, in some cases, an alternative to the careful design of bifunctional ligands. So-called 'synergistic' extractants show enhanced extraction power when mixed together, in comparison to the individual extractants in separate solutions.[2–4]

Synergistic extraction is a well known phenomenon in the extraction of uranium ions from phosphoric acid solutions.[5–7] The pair of extractants is composed of phosphoric acid esters, *i.e.* di(2-ethylhexyl)phosphate and trioctylphosphine oxide. This system has its limitations, under the following conditions: (1) either the extractant or metal-ion concentration is low; (2) extractants are diluted in a solid matrix, such as a polymeric carrier or membrane; and (3) in the presence of strong competing ions, such as a high concentration of phosphate ions.

A bifunctional extractant composed of a molecule with two centres, a phosphine oxide and alkyl ester of phosphoric acid, linked through a spacer group, is proposed as a single molecular entity combining the overall properties of the synergistic single components. The synthesis of such bifunctional complexing ligands and of their uranium and iron complexes is described in this paper. The application of such bifunctional extractants in the extraction of uranium is described elsewhere.[8]

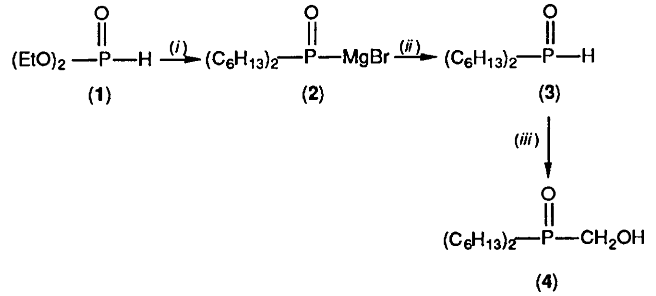


$R^1R^2P(=O)[(CH_2)_n-O]_m-P(=O)(OH)-OR$

Results

The synthesis of dihexyl(hydroxymethyl)phosphine oxide (4) is described in Scheme 1. Diethyl phosphonate (1) (prepared from phosphorus trichloride and three equivalents of butanol[5]) was treated with a Grignard reagent. Dihexylphosphoryl magnesium bromide (2) was hydrolyzed to dihexylphosphine oxide (3) and treated with formaldehyde to yield (4).

The synthetic strategy for the preparation of bifunctional extractants combining trialkylphosphine oxide and phosphoric acid ester involves non-symmetrical phosphoric acid triesters which have a phosphine oxide group as one of their ester groups, an hydrophobic group for good solubility in organic solvents as a second ester group, and a third ester group which can easily be removed to get to a diester phosphoric acid.



Scheme 1. Synthesis of dihexyl(hydroxymethyl)phosphine oxide. (*i*) $Mg(C_6H_{13})Br$; (*ii*) H^+, water; (*iii*) $(CH_2O)_n$

The cyclic enediol phosphate method of Ramirez *et al.*[9] using the reagent cyclic enediol phosphorochloridate suits the proposed strategy best. Compound (7) was synthesized from the cyclic phosphorochloridate (5) by reaction with 1 mol equivalent of 2-ethylhexanol, followed by 4 mol equivalents of the alcohol (4) (Scheme 2). The product (7) was purified by flash chromatography, hydrolyzed with pyridine and then neutralized to give the bifunctional reagent (8).

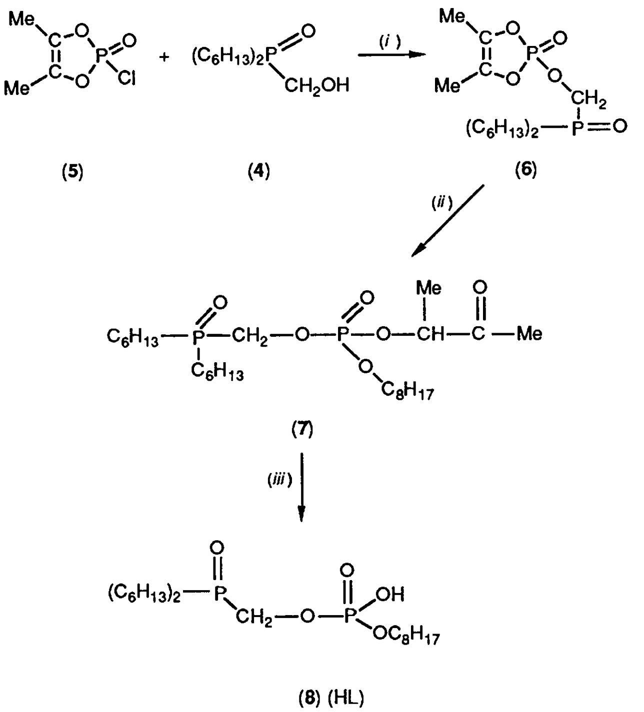
Uranium-(IV) *and -*(VI) *and Iron*(III) *Complexes of Dihexylphosphorylmethyl 2-Ethylhexyl Phosphate* (**8**).—Controlled extraction experiments (see Experimental section) of U^{IV}, U^{VI}, and Fe^{III} from solutions containing Cl^-, $H_2PO_4^-$, NO_3^-, and SCN^- anions provided oily products in the organic phase. Table 1 shows the extraction conditions and the solubility properties of the complexes: (**A**), (**B**), and (**C**) are complexes of U^{VI} obtained from chloride, phosphate, and nitrate solutions, respectively; (**D**) and (**E**) are complexes of U^{IV} respectively of chloride and phosphate; (**F**) and (**G**) refer to the products of extraction of Fe^{III} from chloride and thiocyanate, respectively. The numbers **1**—**3** relate to variation in concentrations of the anion. All the complexes of U^{VI} are insoluble in hexane or in dodecane, and all the complexes of U^{IV} are soluble in those solvents. The extraction of Fe^{III} from chloride gave two complexes (discernible by t.l.c.), (**F1**) only sparingly soluble in CCl_4 and (**F2**) very soluble in CCl_4.

No crystalline products could be obtained for any uranium complex. Vacuum evaporation of diethyl ether or acetone solutions yielded amorphous solids. Slow evaporation at room

Table 1. Complexes formed by extraction with 0.1 mol dm^{-3} HL^a under various conditions (0.02 mol dm^{-3} U^{IV} or U^{VI}, 0.05 mol dm^{-3} Fe^{III}; 0.02 mol dm^{-3} NH_4^+)

Designation	Aqueous phase^b (mol dm^{-3}) Cl$^-$	$H_2PO_4^-$	NO_3^-	Na$^+$	Phase ratio (v/v), organic : aqueous	Yield/ %	Formula
(A1)	0.11	—	—	—	1:2.5	98	UO_2L_2
(A2)	0.21	—	—	0.1	1:2.5	91	UO_2L_2
(A3)	0.41	—	—	0.3	1:2.5	96	UO_2L_2
(B1)	—	0.11	—	—	1:2.5	92	UO_2L_2·HL
(B2)	—	0.21	—	0.1	1:2.5	98	UO_2L_2·HL
(B3)	—	0.41	—	0.3	1:2.5	99	UO_2L_2·HL
(C1)	—	—	0.11	—	1:2.5	98	UO_2L_2·HL·HNO_3
(C2)	—	—	0.21	0.1	1:2.5	96	UO_2L_2·HL·HNO_3
(C3)	—	—	0.41	0.3	1:2.5	96	$(UO_2)_2L_4$·HL·3HNO_3
(D1)	0.11	—	—	—	1:25	94	$ULCl_3$·5HL
(D2)	0.21	—	—	0.1	1:25	93	$ULCl_3$·5HL
(D3)	0.41	—	—	0.3	1:25	98	$ULCl_3$·5HL
(E1)	—	0.11	—	—	1:25	86	UL_3·H_2PO_4
(E2)	—	0.21	—	0.1	1:25	88	UL_3·H_2PO_4
(E3)	—	0.41	—	0.3	1:25	86	UL_3·H_2PO_4
(F1)	0.4	—	—	0.2	1:20	52	$FeCl_3$·HL
(F2)	0.4	—	—	0.2	1:20	46	$FeLCl_2$
(G)	0.4^c	—	—	0.4	1:20	100	$FeL_2(HL)_2(SCN)$

^{a} Initial amount of HL is 176 mg (4 cm^3). ^{b} In addition to U^{IV}, U^{VI}, or Fe^{III} and 0.05 mol dm^{-3} H$^+$ (to pH 1.3). ^{c} 0.2 mol dm^{-3} SCN$^-$.



Scheme 2. Synthesis of bifunctional phosphoric acid diesters using cyclic enediol phosphorochloridate. (*i*) NEt_3; (*ii*) $C_8H_{17}OH$, NEt_3; (*iii*) (*a*) pyridine, (*b*) acid

temperature (several weeks) of a moist methanol solution yielded crystalline powders of $FeCl_3$·HL and $FeL_2(HL)_2(SCN)$, which gave *X*-ray powder diffraction patterns of poor quality. Better crystals have not yet been obtained.

Discussion

Previous solvent-extraction studies[8] from dilute UO_2^{2+} solutions with compound (**8**) (HL) in dodecane, using a large excess of extractant *vs.* uranium, have shown a linear dependence of the distribution ratio on the concentration of extractant HL. On the other hand, experiments with higher uranium concentrations show the metal ion to be associated with at least two extractant molecules. This is understood if the extractant is assumed to be polymeric, *i.e.* associated through hydrogen bonding in solution. The occurrence of hydrogen bonding is also shown by the i.r. spectrum of HL, with typical POH bands[10] at 2 900 and 2 350 cm^{-1}.

Both these absorption bands also appear in the i.r. spectra of the uranium complexes. This suggests that part of the hydrogen is present in the HL polymers, so that hydrogen-bonded associates exist in the metal complexes as well. This might reflect on the difficulty of crystallizing the complexes.

The slight shift in the band of 1 260 cm^{-1} (ref. 10) of the uranium complexes, as compared to pure HL, indicates a minor participation of the phosphate-phosphoryl oxygen in the complex formation. On the other hand, the band at 1 170 cm^{-1} (carbon-bonded phosphoryl C–P=O[4]) shows a pronounced shift towards lower frequencies and hence a strong complexation of the metal ion by the phosphine oxide oxygen.

The band at 930 cm^{-1}, found for all uranium complexes but not the extractant HL, should be attributed to the anionic phosphate group where the hydrogen has been replaced by a metal ion. The weakness of this band for the iron(III) complexes suggests that complexation of iron occurs mostly through the phosphoryl groups; more specifically, the C-bonded phosphoryl oxygen. This is borne out by the increase in absorption of the shifted band at 1 130 cm^{-1}, as compared to the uranium complexes.

The band at 2 100 cm^{-1} in the spectrum of $FeL_2(HL)_2(SCN)$ obviously belongs to the SCN$^-$ group and confirms that the complexation of iron with HL (also when SCN$^-$ is absent and replaced by Cl$^-$) is not very different from that with monofunctional phosphoryl extractants, *e.g.* tributyl phosphate, where the aqueous counter ions play an important part.[11]

The ^{31}P n.m.r. spectra (H_3PO_4 as external standard) are very interesting. When compared with di(2-ethylhexyl)phosphate [δ 1.46 p.p.m. for the $O{=}P(OR)_2OH$ group] and trioctylphosphine oxide (δ 49.30 p.p.m. for the R_3PO group), the

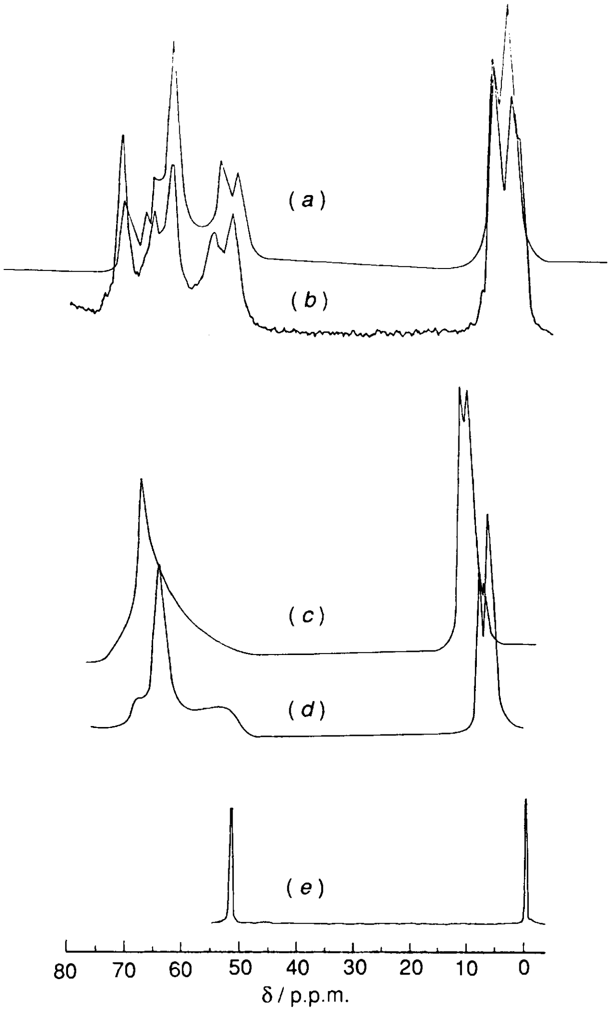


Figure 1. ^{31}P N.m.r. spectra of uranium(VI) complexes: (*a*) (**C3**), (*b*) (**C1**), (*c*) (**B3**), (*d*) (**B1**), and (*e*) HL

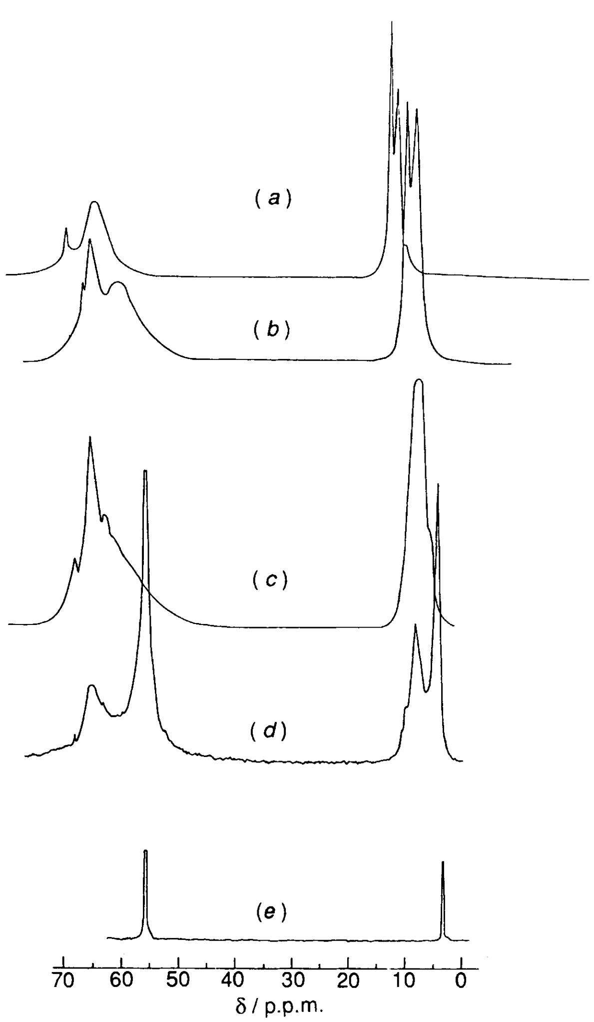


Figure 2. ^{31}P N.m.r. spectra of uranium(IV) complexes: (*a*) (**E3**), (*b*) (**E1**), (*c*) (**D3**), (*d*) (**D1**), and (*e*) HL

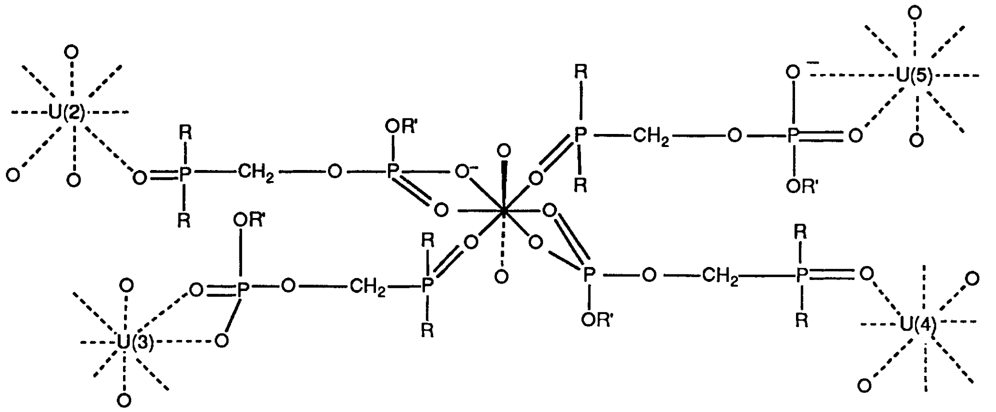


Figure 3. Proposed structure of UO_2L_2; $R = C_6H_{13}$, $R' = C_8H_{17}$

bifunctional complexing agent shows both bands as doublets ($J = 10$ Hz) with δ -1.53 [$O{=}P(OR)_2OH$] and 51.61 p.p.m. (R_3PO). In the complexation experiments described in Table 1, the anion concentration varied from 0.1 (1) to 0.2 (2), to 0.4 mol dm^{-3} (3), *i.e.* 5-, 10-, and 20-fold excesses over the initial uranium-ion concentration. Generally, in the extraction of U^{IV} the disappearance of absorptions due to free HL and the appearance of an upfield shift of the signals due to both $O{=}P(OR)_2OH$ and R_3PO was noted with all complexes. From Figure 1 [showing uranium(VI) complexes] it is clear that both phosphorus ligands participate in the complexation and there is no free HL. It seems from n.m.r. spectroscopy (no free PO_4^{3-}) and from elemental analysis that the complex obtained from U^{VI} in H_3PO_4 contains no phosphate. A similar conclusion is reached for the complex of U^{VI} extracted from HCl. However, there is a drastic change in the case of extraction from nitrate.

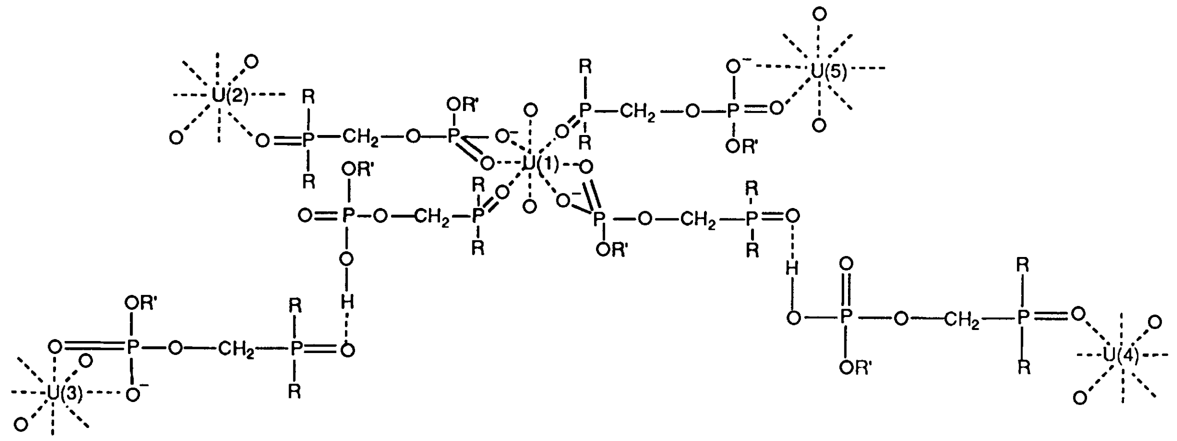


Figure 4. Proposed structure of $UO_2L_2{\cdot}HL$

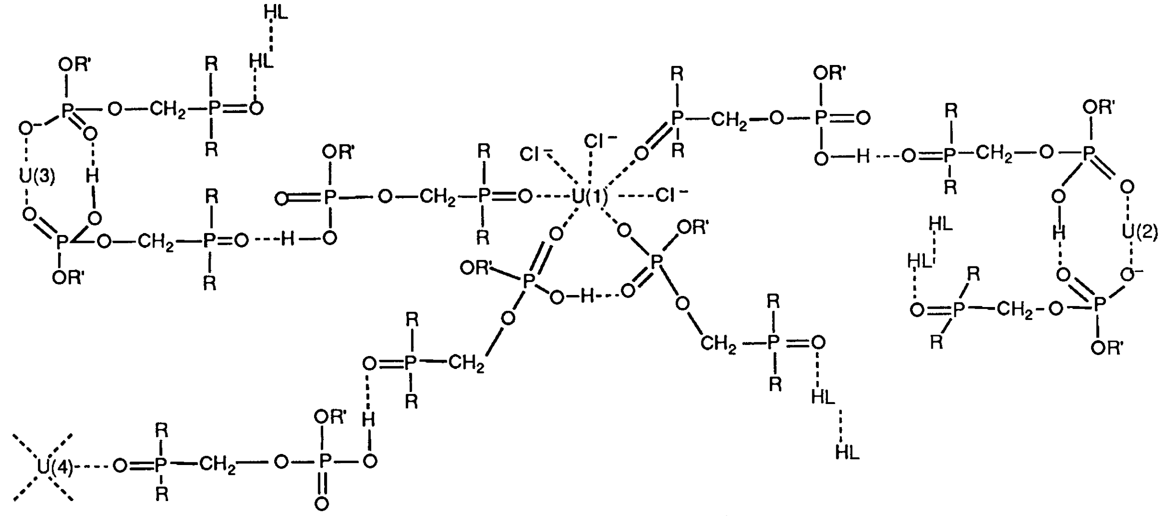


Figure 5. Proposed structure of $ULCl_3{\cdot}5HL$

Both n.m.r. spectroscopy and elemental analysis indicate a strong involvement of nitrate anions. The formulae proposed in Table 1 were calculated in view of the i.r. and n.m.r. observations, yet they may be only approximations and further careful measurements will be needed for absolute certainty.

A different situation exists for the uranium(IV) complexes. N.m.r. spectroscopy (Figure 2) shows a large band of the free ligand in the spectrum of the complex extracted from 0.1 mol dm^{-3} Cl^-. On increasing the chloride concentration the band due to free HL disappeared. These differences in behaviour of the uranium complexes agree with previous observations on synergistic extraction systems. Participation of neither chloride[12] nor phosphate[2] was found for uranium(VI) complexes extracted with mixtures of di(2-ethylhexyl)phosphate and trioctylphosphine oxide. On the other hand, extraction of Th^{IV}, the chemical properties of which are very similar to those of U^{IV}, by a similar synergistic mixture from a chloride solution yielded[13] a complex containing chloride. As to nitrate, the only crystalline compound of U^{IV} containing both alkyl phosphate and phosphine oxide groups ever reported[14] contained nitrate anions as well.

With the analytical and spectroscopic data available at this stage the following conclusions relating to the structures of the complexes can be drawn.

(*i*) Both chelate structures and intermolecular complexes are possible. Thus, the structure of the complex obtained from U^{VI} in HCl is calculated to be UO_2L_2 which corresponds to a six-co-ordinated octahedral chelate, similar to that found by Burns[14] for $UO_2(BuPO_4)_2$, or to the eight-co-ordinated oligomeric complex described in Figure 3. As mentioned, dimeric complexes of dibutylphosphoric acid and tributylphosphine oxide were isolated by solvent extraction of UO_2^{2+} ions and their crystal and molecular structure determined. In the case of the bifunctional ligand HL, the bifunctionality allows for oligomeric structures.

(*ii*) The structure of the complex obtained by extraction from H_3PO_4 involves one extra HL unit, probably through hydrogen bonding (Figure 4).

(*iii*) The structure of the uranium(IV) complexes involves direct participation of inorganic ligands ($ULCl_3{\cdot}5HL$, Figure 5, $UL_3{\cdot}H_2PO_4$, Figure 6) in the oligomeric complexes. The HL ligands serve as monodentate (for each U^{IV}) bifunctional bridging ligands. The anions serve for charge neutralization. In the case of phosphate, hydrogen bonding allows stabilization of the oligomeric structure. Halide complexes of uranium are well known.[15–19] The structure of the uranium nitrate complexes is more complex[20,21] and will not be discussed.

As for the iron(III) complexes, both octahedral, chelate-type complexes, $FeCl_3{\cdot}HL$ and $FeL_2(HL)_2(SCN)$, and tetrahedral complexes, $FeLCl_2$ (Figure 7), are suggested. Again, the bifunctional nature of the molecules results in oligomeric structures.

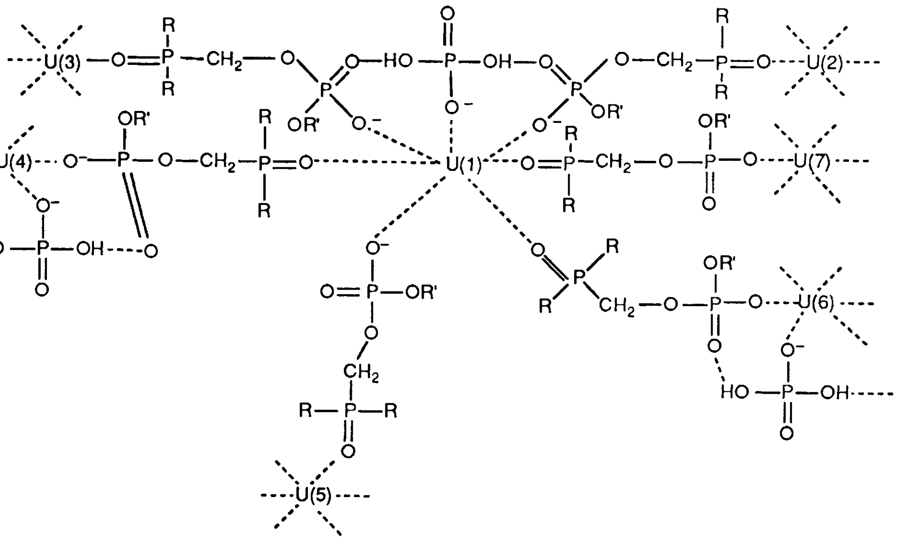


Figure 6. Proposed structure of $UL_3{\cdot}H_2PO_4$

Conclusion

The synthesis of a novel bifunctional chelator for heavy metals, incorporating phosphine oxide and phosphate ester ligand centres, was accomplished using cyclic enediol phosphate chemistry. Complexes of U^{IV}, U^{VI}, and Fe^{III} were prepared and studied.

Both Fourier-transform i.r. and n.m.r. spectroscopy indicate a significant degree of polymerization of HL in its metal-complexed form. Phosphorus-31 n.m.r. spectroscopy of uranium complexes shows clearly that both ligating centres participate in the complexation process. This is seen in the upfield shift of both $O{=}P(OR)_2OH$- and R_3PO-type signals for the complexed form. The broadening of the signal indicates a dynamic equilibrium within the n.m.r. time-scale. The nature of the complexation process and the structure of the complexes is strongly dependent on the anion in aqueous solution. Chloride and phosphate anions participate in the structure of the complexes of U^{IV} but not in those of U^{VI}, yet nitrate anions participate in the structure of uranium(VI) complexes. It is important to note that this bifunctional chelator is able to extract both U^{IV} and U^{VI}, unmatched for monofunctional complexes.

The structure of the iron complexes also involves the anion, in a manner similar to that for U^{IV}. It is highly plausible that other heavy transition-metal ions and lanthanides will also form complexes.

Experimental

T.l.c. was performed on Merck Kieselgel 60F 254 plates with the eluants ethyl acetate and 95% chloroform–5% methanol. The developing agents were a basic aqueous 1% $KMnO_4$ solution and ethanolic 0.2% ninhydrin solution. Flash chromatography was carried out on 40—63 μm silica gel (Merck no. 9385 and ethyl acetate or $CHCl_3$–1% MeOH as eluant. Clearing points were determined on a Gallenkamp apparatus and are not corrected. I.r. spectra in dry $CHCL_3$ were obtained on a Mattson CYGNUS 25 FTIR spectrophotometer, ^1H n.m.r. spectra on a 270 Bruker in $CDCl_3$ with $SiMe_4$ as internal standard, and ^{31}P n.m.r. spectra in $CDCl_3$ on a Bruker AC-200 with 85% H_3PO_4 as external standard; signal frequency 81.0 MHz.

The products obtained were tested by t.l.c. to demonstrate the absence of free HL. Solvent systems were CH_2Cl_2–MeOH–$MeCO_2H$ and PrOH–Bu^tOH–NH_4OH–water. Detection was by u.v. spectroscopy and by use of phosphomolybdic acid. High-performance liquid chromatography was performed on a Waters model 6000A instrument with a model 480 u.v.–visible spectrophotometric detector (230 nm), RP-C18 column, Δp = 1000 lbf in^{-2} (*ca.* 7 × 10^6 Pa), flow-rate 1 cm^3 min^{-1}, and tetrahydrofuran as eluant.

Iron(III) solutions were obtained by dissolving anhydrous $FeCl_3$ in HCl, with or without addition of NaSCN. Uranium(VI) solutions were prepared by dissolving analytically pure $[NH_4]_2$-$[U_2O_7]$ in the appropriate (analytical grade) acid; solutions of U^{IV} (green) were prepared by reduction of those of U^{VI} (yellow) with hydrazine chloride.

Dihexylphosphine Oxide (**3**)—The Grignard reagent (**2**) was prepared by adding n-hexyl bromide (119.88 g, 0.762 mol) in diethyl ether (70 cm^3) to a suspension of magnesium turnings (16.72 g, 0.687 mol) in ether containing several iodine crystals. The hexyl bromide was added at a rate that kept the ether at gentle reflux. After the addition was complete the mixture was cooled to room temperature and diethyl phosphite (37 g, 0.268 mol) in ether (150 cm^3) was slowly added at a rate that kept the temperature below 15 °C. The mixture which contained a grey precipitate was left to stir overnight. After cooling to 0 °C H_2SO_4 (25%, 150 cm^3) was added and the layers were separated. The ether layer was washed with water (50 cm^3), K_2CO_3 (15%) solution (200 cm^3), water, and saturated NaCl solution. After drying (Na_2SO_4), the ether was removed. The white residue was crystallized from hexane (77% yield, m.p. 72—75 °C). ^1H N.m.r. ($CDCl_3$): δ 9.66, 4.05 [2 wide singlets, 2 wings of a doublet, *J* (PH) = 450 Hz, 1H], and 2.04—0.82 (m, 26 H, C_6H_{13}) (Found: C, 65.85; H, 12.15; P, 13.95. $C_{12}H_{27}OP$ requires C, 66.05; H, 12.45; P, 14.10%).

Dihexyl(hydroxymethyl)phosphine oxide (**4**).—Dihexyl phosphine oxide (**3**) (43.28 g, 0.198 mol) was dissolved in ethanol (500 cm^3). Formaldehyde (57.5 cm^3 of a 37% solution in water, 0.71 mol) was added together with $NaHCO_3$ (8.1 g, 0.095 mol) and K_2CO_3 (1.15 g, 0.007 mol) and the mixture was refluxed for 8 h. After cooling to room temperature, the solvent was removed and the residue dissolved in CH_2Cl_2 (250 cm^3). The solution was washed with water (3 × 100 cm^3), dried (Na_2SO_4), and the solvent removed. The residue was an oil (43.3 g, 88% yield). ^1H N.m.r. ($CDCl_3$): δ 3.86 (wide singlet, 2 H, CH_2OH) and 1.73—0.82 (m, 27 H, C_6H_{13} + OH); on addition of D_2O a doublet appeared at δ 3.87 and 3.85 (Found: C, 63.30; H, 12.00; P, 12.05. $C_{13}H_{29}O_2P$ requires C, 62.90; H, 11.75; P, 12.45%).

Compound (**7**).—The cyclic phosphorochloridate (**5**) (17.0 g, 0.1 mol) in dry CH_2Cl_2 (75 cm^3) was placed in a flask (250 cm^3)

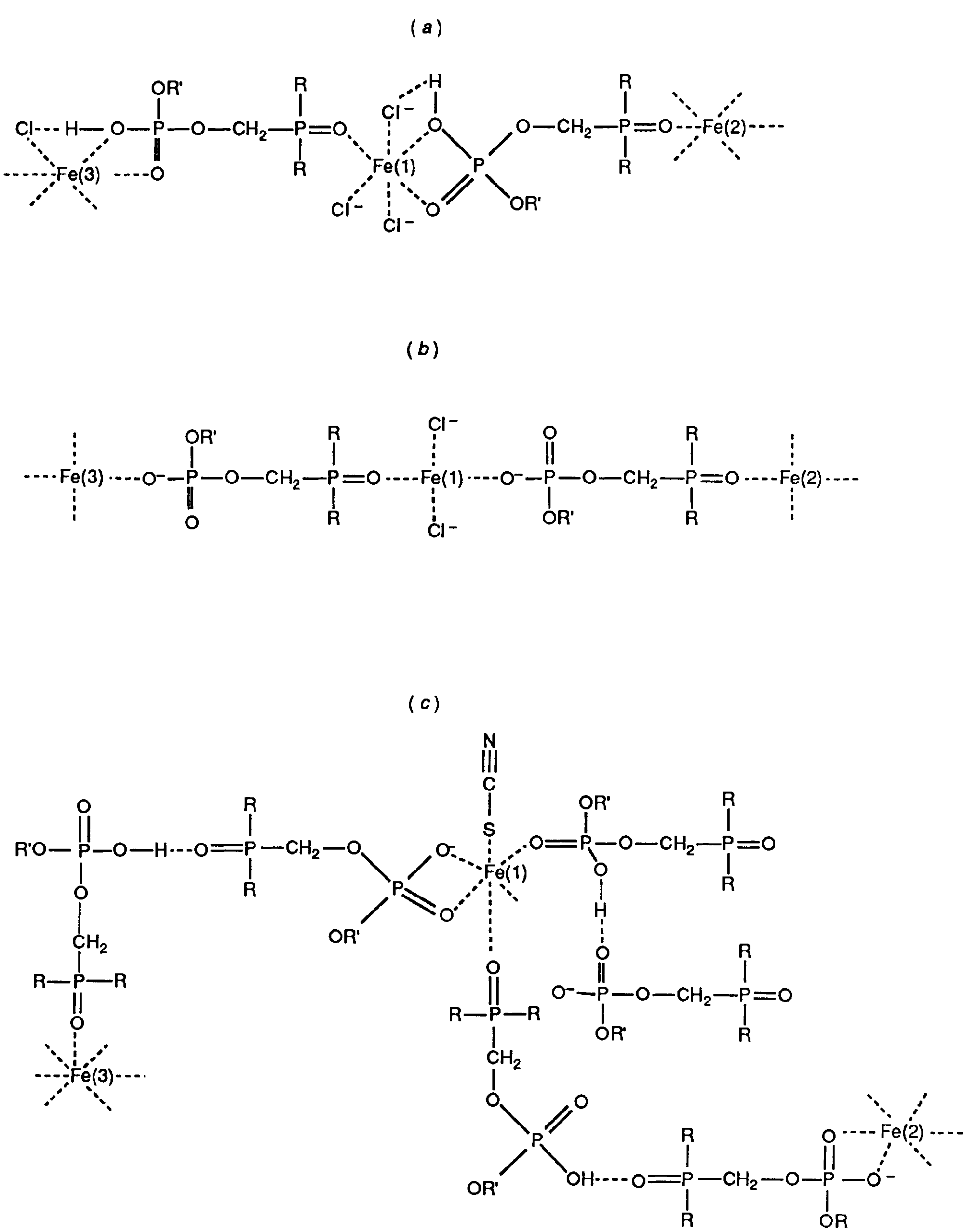


Figure 7. Proposed structures of (*a*) $FeCl_3 \cdot HL$, (*b*) $FeLCl_2$, and (*c*) $FeL_2(HL)_2(SCN)$

and kept under N_2. The solution was cooled to 0 °C and 2-ethylhexanol (15.6 cm^3, 13.0 g, 0.1 mol) and triethylamine (13.9 cm^3, 0.1 mol) in CH_2Cl_2 (50 cm^3) were slowly added (15 min). The ice-bath was removed and the solution stirred for 1 h. A solution of dihexyl(hydroxymethyl)phosphine oxide (**4**) (24.9 g, 0.1 mol) and triethylamine (13.88 cm^3, 10.1 g, 0.1 mol) in CH_2Cl_2 (50 cm^3) was slowly added and left to stir overnight. The precipitate ($NHEt_3Cl^-$) was filtered off and washed with CH_2Cl_2. The filtrate, combined with the CH_2Cl_2 washings, was dried. (over Na_2SO_4) and concentrated and more crystals were filtered off. The solution was washed with HCl (5%, 2 × 150 cm^3) and water (2 × 150 cm^3), dried (Na_2SO_4), treated with activated charcoal, and the solvent was removed. The residue (50.15 g) which contained, besides the product, dihexyl(hydroxymethyl)phosphine oxide and di(2-ethylhexyl) 1-methylacetonyl phosphate, was purified by flash column chromatography. First fractions were eluted with 20% hexane in ethyl acetate and were found to contain di(2-ethylhexyl) 1-methylacetonyl phosphate. ^1H N.m.r. ($CDCl_3$): δ 4.82 (m, 1 H, POC*H*Me), 4.03 (m, 4 H, OCH_2CH), 2.25 (s, Me, 3 H), and 1.80—0.8 (m, 33 H, aliphatic H).

The next fractions, eluted with 10% hexane in ethyl acetate, were found to contain compound (**7**). ^1H N.m.r. ($CDCl_3$): δ 4.81 [dd, J_1 = 6.4, J_2 = 1.6, 1 H, POC*H*Me), 4.31 (q, d of d, J_1 = 10.4, J_2 = 4.8, 2 H, $O=PCH_2O$), 4.03 (q, d of d, J_1 = 10.4, J_2 = 4.8 Hz, 2 H, OCH_2CHEt), 2.23 (s, 3 H, CHMe), and 2.03—0.81 (m, 44 H, aliphatic H). Mass spectrum: *m*/*z* 510.336 (M^+); 453.2735, 423.2756, 397.211, 383.176, and 311.153 (typical fragments of the various ester groups).

The last fractions were eluted with 5% MeOH in ethyl acetate and found to contain dihexyl(hydroxymethyl)phosphine oxide.

Dihexylphosphorylmethyl 2-Ethylhexyl Phosphate (**8**).—*Method* (*A*). The triester (**7**) (200 mg) was dissolved in acetonitrile–water (2:1). Sodium carbonate (200 mg) was added and the solution warmed to 60 °C for 8 h, then cooled to room

Table 2. Characterization data for the complexes

	Complex	Yield/%	Clearing point/°C	Analysis[a]/% C	H	P	I.r./cm^{-1}
(A)	UO_2L_2	91—98	90—92	43.80 (43.90)	7.90 (7.90)	10.85 (10.80)	2 950—2 900, 2 350, 1 240—1 200, 1 120, 1 050, 930
(B)	UO_2L_2·HL	92—98	90—92	47.60 (47.10)	8.55 (8.35)	11.70 (11.25)	2 950—2 900, 2 350, 1 230—1 200, 1 110, 1 050, 930
(C1)	UO_2L_2·HL·HNO_3[b]	98	73—77	45.45 (45.80)	8.35 (8.35)	10.50 (11.30)	2 950—2 900, 2 350, 1 240—1 220, 1 100—1 070, 930
(C2)	UO_2L_2·HL·HNO_3[b]	96		45.95 (45.80)	8.40 (8.35)	10.55 (11.30)	
(C3)	$(UO_2)_2L_4$·HL·3HNO_3[c]	96		43.15 (43.05)	7.95 (7.90)	9.75 (10.10)	
(D)	$ULCl_3$·5HL[d]	93—98	69—72	51.15 (50.70)	9.40 (9.30)	11.65 (12.45)	2 950—2 900, 2 350, 1 240—1 220, 1 160—1 050, 930
(E)	UL_3·H_2PO_4	86—88	68—70	45.25 (45.75)	8.55 (8.35)	12.25 (13.10)	2 950—2 900, 2 350, 1 230—1 200, 1 130—1 050, 930
(F1)	$FeCl_3$·HL	52	143—146	41.90 (41.85)	7.70 (7.70)	10.30 (10.30)	
(F2)	$FeLCl_2$	46	127—132	44.50 (44.55)	7.65 (8.00)	10.85 (10.95)	2 950—2 900, 1 230—1 210, 1 120, 1 040
(G)	$FeL_2(HL)_2(SCN)$[e]	98	120—124	53.95 (54.50)	9.40 (9.80)	13.10 (13.20)	2 950—2 900, 2 100, 1 250—1 210, 1 120, 1 040

[a] Calculated values are given in parentheses. [b] N 0.60 (0.85%). [c] N 1.15 (1.45%). [d] Cl 3.60 (3.55%). [e] N 0.80 (0.75), S 1.70 (1.70%).

Table 3. ^{31}P N.m.r. in $CDCl_3$ (85% H_3PO_4 as external standard)[a]

Compound	δ/p.p.m. (*J* in Hz)
(8)	1.31 (d) (J = 10) (PO_3H), 51.61 (d) (J = 10) (R_3PO)
(A1)	3.39, 4.09 (64),[b] 5.47 (36) ($PO_3H·UO_2$), 50.1 (br) (23.8), 61.60 (62.9), 65.0 (br) (13.3) ($R_3PO·UO_2$)
(A2)	3.40, 5.71 ($PO_3H·UO_2$), 62.20 ($R_3PO·UO_2$)
(A3)	5.57 ($PO_3H·UO_2$), 62.25 ($R_3PO·UO_2$)
(B1)	3.82 (72.3), 5.41 (27.7) ($PO_3H·UO_2$), 52.5 (br), (28.2), 61.69 (57.2), 66.0 (br) (14.5) ($R_3PO·UO_2$)
(B2)	4.27 (61.5), 5.62 (38.5) ($PO_3H·UO_2$), 57.0 (br) (46.6), 62.17 (53.4) ($R_3PO·UO_2$)
(B3)	4.37 (61.1), 5.66 (38.9), 56.0, 62.3 ($R_3PO·UO_2$)
(C1)	3.13 (68.0), 5.90 (32.0) ($PO_3H·UO_2$), 54.32 (40.6), 62.18 (42.3), 66.5 (br) (13.5), 71.2 (br) (9.0) ($R_3PO·UO_2$)
(C2)	3.19 (59.0), 5.45 (41.0), 51.2 (br) (35.0), 62.03 (42.3), 64.7 (65.0) ($R_3PO·UO_2$)
(C3)	2.97 (56.0), 6.13 (44.0) ($PO_3H·UO_2$), 51.89, 55.28 (34.6), 62.58, 65.72 (40.0), 71.38 (25.4) ($R_3PO·UO_2$)
(D1)	0.30 (51.0), 3.51 (49.0) ($PO_3H·UO_2$), 51.30 (66.8), 60.70 (33.2) ($R_3PO·UO_2$)
(D2)	3.68 (62.5), 6.0 (27.5), 56.72, 59.49 (51.8), 62.50 (41.2) ($R_3PO·UO_2$)
(D3)	4.27 ($PO_3H·UO_2$), 62.31 ($R_3PO·UO_2$)
(E1)	3.94 (59.0), 5.80 (41.0) ($PO_3H·UO_2$), 57.17 (53.0), 61.74 (47.0) ($R_3PO·UO_2$)
(E2)	3.83 (63.0), 5.16 (37.0) ($PO_3H·UO_2$), 61.86 (18.0) ($R_3PO·UO_2$)

[a] δ 49.30 for trioctylphosphine oxide, 1.46 p.p.m. for di(2-ethylhexyl)phosphate. [b] Percentage of the total integration of the functional group signal. When peaks cannot be resolved, the integration percentage for both of them is given; br = broad. Such signals indicate a dynamic exchange process.

temperature and left to stir overnight. The solution was filtered, the solvents removed, and the residue found to be the diester. Recrystallization from hexane. M.p. 204—206 °C, 100% yield. ^{1}H N.m.r. ($CDCl_3$): δ 4.13—3.97 (m, 2 H, PCH_2O), 3.77—3.58 (m, 2 H, RCH_2), and 1.70—0.76 (m, 41 H). I.r. (KBr): 1 600—1 700 (br, HO–P=O), 1 160, 1 150, and 1 110 cm^{-1}.

Method (*B*). The triester (**7**) (200 mg) was dissolved in pyridine–water (1:1, 50 cm^3), and triethylamine (0.8 cm^3, 6 mmol) was added. The mixture was stirred for 92 h at room temperature (15 °C). The solvents were stripped out (oil pump). The residue was found to be the triethylammonium salt of the acid (100% yield). ^{1}H N.m.r. ($CDCl_3$): δ 4.16 (t, 2 H, J = 6.8, $OCH_2P{=}O$), 3.84 (d of d, J_1 = 3.9, J_2 = 4.4, 2 H, $CHCH_2OP$), 3.11—2.91 (br t, J_1 = 6.8, J_2 = 4.9 Hz, 6 H, NCH_2), and 1.81—0.8 (m, 50 H, aliphatic H).

The triethylammonium salt was converted into the acid by dissolving the salt in CH_2Cl_2 and washing the solution with 0.5 mol dm^{-3} HCl solution. H.p.l.c. on RP-C18 column, in thf: R_f = 2.96 (thf), 3.52 min (**8**) (Found: C, 57.45; H, 10.70; P, 14.00. $C_{21}H_{46}O_5P_2$ requires C, 57.25; H, 10.50; P, 14.05%). I.r.: 2 950—2 900, 2 350, 1 250—1 210, 1 170, and 1 050 cm^{-1}. ^{13}P N.m.r.: δ 1.31 (PO_3H) and 51.61 p.p.m. (R_3PO).

Preparation of the Complexes.—The complexes were prepared by solvent extraction from aqueous solutions of UO_2^{2+}, U^{4+}, and Fe^{3+}, using 0.1 mol dm^{-3} HL in hexane or dodecane. The aqueous phase contained, in addition to the extracted metal ion and 0.05 mol dm^{-3} H^+, the following anions: Cl^-, $H_2PO_4^-$, or NO_3^- (in experiments involving UO_2^{2+}), Cl^- and $H_2PO_4^-$ (in experiments with U^{4+}), and Cl^- or SCN^- (in experiments with Fe^{3+}). For both hexa- and tetra-valent uranium (0.20 mol dm^{-3}), three sets of extraction experiments were carried out, with aqueous solutions containing 0.1, 0.2, and 0.4 mol dm^{-3} anion (Cl^-, $H_2PO_4^-$, or NO_3^-) respectively. The extraction experiments were carried out at room temperature (20—25 °C); equilibration time 1 min.

Preliminary extraction experiments with UO_2^{2+} in aqueous chloride showed that the uranium was quantitatively concentrated in a third phase, insoluble in either water or aliphatic solvent (hexane or dodecane) and that the molar ratio U/HL in this phase was approximately 1:2. All further UO_2^{2+} experiments were, therefore, devised so that the aqueous phase contained an amount of uranium equal (in mols) to half the HL content of the organic phase. The third phase was purified by several washings with hexane and with water to eliminate any unreacted HL or residual salt. The solubility of the complexes of U^{4+} and Fe^{3+} in hydrocarbon solvents (hexane, dodecane) was not appreciably different from that of pure HL. Extraction experiments on U^{4+} and Fe^{3+} were, therefore, carried out with a large excess of metal ion over HL (molar ratio M/HL = 5:1 and 10:1, respectively), on the assumption that the amount of unreacted HL in the organic phase would be negligible.

After high-vacuum solvent evaporation at room temperature, all complexes were obtained in viscous liquid form. They are designated as in Table 1. Attempts were made to crystallize the complexes obtained from acetone, chloroform, carbon tetrachloride, dioxane, ethyl acetate, diethyl ether, and methanol, using either rapid (vacuum) evaporation of the solvent at room temperature or 70 °C, or slow evaporation at room temperature, both in the absence or presence of water. Characterization data are given in Table 2, ^{31}P n.m.r. data in Table 3.

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