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Synthesis and coordination chemistry of arene soluble 4-alkyl-2,6-bis[(diphenylphosphino)methyl]pyridine *N*,*P*,*P*′-trioxide ligands†

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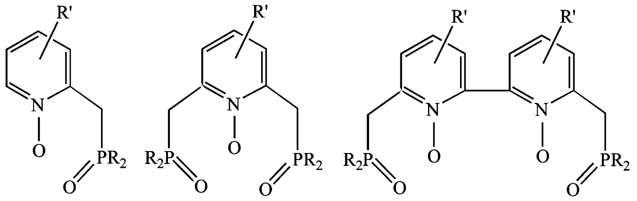
The trifunctional ligand 2,6-[$(C_6H_5)_2P(O)CH_2]_2C_5H_3NO$ forms stable complexes with trivalent and tetravalent f-element cations and it acts as an effective liquid–liquid extraction reagent when it is dissolved in $CHCl_3$. In a search for more hydrocarbon solvent soluble extraction reagents, derivative ligands having alkyl substituents in the 4-pyridyl ring position, 4-R′-2,6-[$(C_6H_5)_2P(O)CH_2]_2C_5H_2NO$ (R′ = Et, Oct), have been prepared and characterized. A single crystal X-ray diffraction analysis for the Et derivative shows that the ligand molecular structure is closely related to the parent ligand, 2,6-[$(C_6H_5)_2P(O)CH_2]_2C_5H_3NO$. The coordination chemistry of the ligands with $Nd(NO_3)_3$ has been examined, and the molecular structures of two complexes obtained with 1 : 1 and 2 : 1 ligand : metal reactant ratios are reported.

Liquid–liquid extraction (LLE) remains the method of choice for analytical and bulk scale separation and processing of nuclear materials solutions containing f-block element ions.[1–6] The key component of a successful LLE separation is the extractant reagent and the process is largely controlled by the intimate molecular features of the extractant (ligand)–metal interactions. Typically, the complexation chemistry occurs from a strongly acidic aqueous solution since these highly charged ions undergo ready hydrolysis in near-neutral solutions. For practical systems, the extraction process must occur with rapid ligation kinetics, without formation of an intractible third phase, and the metal–ligand binding process must be rapidly reversible under easily achieved conditions.

Historically, a number of simple monodentate ligands have been employed as f-block element LLE reagents;[1–6] however, all display various shortcomings. Due to the continuing need for more efficient f-block element separations, there is interest in the development of new, more selective extractant ligands. Two classes of bifunctional ligands have attracted the most attention: a) carbamoylmethylphosphonates (CMP) and carbamoylmethylphosphine oxides (CMPO)[6–10] and b) diamides and picolinamides.[11–15] Both families of ligands have significant benefits over the previously employed monofunctional extractants and considerable effort has been given to discovery of the fundamental coordination characteristics that convey favorable LLE performance. Stimulated by these studies, several groups have sought to design other new bifunctional and trifunctional extractants through logically crafted ligand design approaches.[16–18] Recently, we have described the synthesis, coordination chemistry and extraction performance of phosphinopyridine *N*-oxides of the general types **I–III**.[19–29] Briefly, ligand **I** (R = Ph) forms strong bidentate complexes with the lanthanide ions, Ln(III), and in the case where excess **I** is present, square antiprismatic $[ML_4]^{3+}$ complexes form.[19]

Unfortunately, ligand **I**, with R = Ph; R′ = H, does not display good organic phase compatability; therefore, new derivatives must be sought in order to assess its practical LLE performance. Ligand **II** (R = Ph; R′ = H) forms stable 1 : 1 and 2 : 1 ligand–Ln(III) and ligand–actinide, An(III) and An(IV), complexes.[19–28] In addition, the derivative with R = Ph displays good extraction performance. For example, Ln(III) and Am(III) ions in HNO_3[23] or in HCl[24] (1–6 M) are extracted into $CHCl_3$ solutions of **II** (R = Ph; R′ = H) (0.05M). Ligand type **III** (R = Ph; R′ = H) also forms very stable complexes with Ln(III) ions,[22] but with R = Ph the ligand is only soluble in chlorocarbon diluents which reduces the practicality of **III**.



The interesting chelation and extraction chemistry displayed by **II** (R = Aryl, R′ = H) encouraged us to develop syntheses for related organophosphine oxides (R = C_nH_{2n+1}, n = 2–8, R′ = H) that would have greater solubility in the hydrocarbon diluents preferred for practical separations. Initial LLE screening of several new R varied derivatives show potentially useful performance.[30] In the present contribution, we describe the synthesis of new derivatives of **II** that have an aliphatic substituent in the 4-position of the pyridyl ring (R = Ph, R′ = Et (**6-Et**) and R = Ph, R′ = Oct (**6-Oct**)). These substitutions should provide favorable hydrocarbon solvent solubility. The coordination chemistry of the ligands with $Nd(NO_3)_3$ was also surveyed, and it is found that the R′ substituents do not significantly alter the chelation properties of **II** although a new 2 : 1 complex structure type is found.

Results and discussion

As indicated above, the objectives of this study were to a) develop a general synthesis scheme for the preparation of derivatives of the chelating ligand type **II** substituted with an aliphatic group R′ (C_nH_{2n+1}) in the 4-position of the pyridyl ring, b) determine the organic solvent compatibility of the ligands and c) examine the coordination chemistry of the ligands with Ln(III) ions in order to determine what influence R′ substitution has on the chelation mode.

The five-step synthesis developed for 4-alkyl-2,6-bis[(diphenylphosphino)methyl]pyridine *N*,*P*,*P*′-trioxides (R′ = Et, Oct) is summarized below.

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† Electronic supplementary information (ESI) available: synthesis details. See http://www.rsc.org/suppdata/dt/b2/b206782j/

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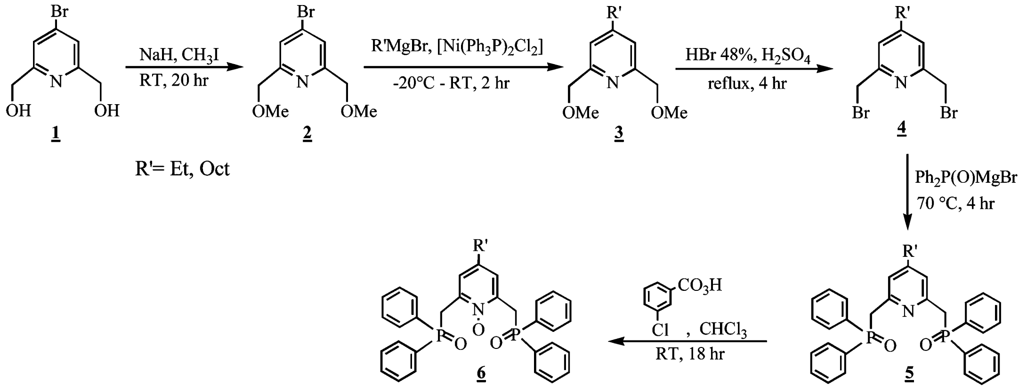

R = Et, **6-Et**
R′ = Oct, **6-Oct**

The route is generally applicable to derivatives with other primary and secondary aliphatic groups in the pyridyl 4-position.[31] It also can be incorporated into a reaction scheme recently developed[29,31] to introduce other R group substituents bonded to the phosphoryl moieties. The starting material **1** is not generally available from a commercial supplier although it can be obtained from another five-step reaction scheme (see ESI), starting with diethyl oxalate by using individual reactions reported previously in the literature.[32–35] The yield of **1** from this sequence is about 55%. The five-step conversions of **1** to **6-Et** or **6-Oct** proceed with overall yields of 44% and 38%, respectively. Both compounds are obtained as crystalline white solids. Each displays a parent ion in its high resolution mass spectrum, and the agreement with the calculated exact mass is excellent. Interestingly, the most intense ion can be assigned to $(M + 1^+)$ which corresponds to the protonated form of the free ligand. Similar observations have been made with previously reported examples of ligand types **I–III**.[19,20,22,25,29] The infrared spectra for **6-Et** and **6-Oct** are similar, both showing strong absorptions that may be tentatively assigned to ν_{NO} 1238–1236 cm^{-1} and ν_{PO} 1197–1194 cm^{-1}. These band positions are comparable to those reported for other examples of ligand types **I–III**.[19,20,25,29] The pyridine compounds **5-Et** and **5-Oct** show ν_{PO} bands at 1192 cm^{-1} and 1195 cm^{-1} and no adsorptions in the region 1250–1200 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectra display a single resonance, δ 31.8 (**6-Et**) and 31.6 (**6-Oct**). These chemical shifts compare favorably with the previously reported shifts for examples of ligand types **I–III**, and they are slightly downfield from the shift for **5-Et** and **5-Oct**, δ 30.9. Finally, the ^1H and $^{13}C\{^1H\}$ NMR spectra are in full agreement with the proposed structures of **6-Et** and **6-Oct**.

The molecular structure of **6-Et**·H_2O was confirmed by single crystal X-ray diffraction analysis. A view of the molecule is shown in Fig. 1 and selected bond lengths are summarized in Table 1. The P=O distances, 1.481 (2)Å and 1.483(2)Å, and N–O distance, 1.318(3)Å, are identical to the values reported for the parent ligand, $[Ph_2P(O)CH_2]_2C_5H_3NO$, P=O 1.480(3)Å and N–O 1.315(6)Å.[20] As in the parent ligand, the two $Ph_2P(O)CH_2$ "arms" in **6-Et**·H_2O rotate so that the P=O bond vectors point away from the N–O bond vector. However, in the case of **6-Et**·H_2O, the unit cell also contains four water molecules (one per ligand). Each water molecule hydrogen bonds to a N–O oxygen atom in one ligand unit and to a P=O oxygen atom in a second ligand forming chains along the *a* axis. A view of this arrangement is shown in Fig. 2. This H-bonding structure is distinct from the H-bonding interactions found for the related *sym*-octahydroacridine *N*,*P*,*P*′-trioxide ligand that uses only its P=O donor centers to hydrogen-bond with $CHCl_3$ and MeOH.[25]

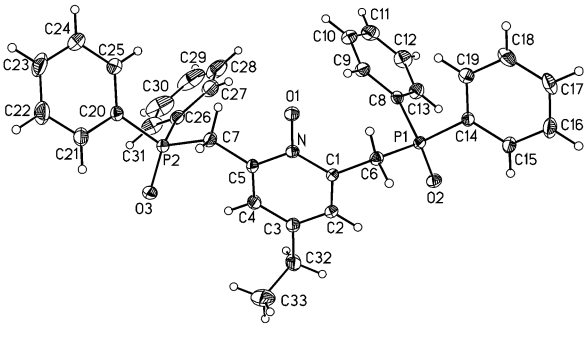

Fig. 1 Molecular structure and atom labeling scheme for **6-Et**·H_2O.

Since the parent ligand, $[Ph_2P(O)CH_2]_2C_5H_3NO$, is only soluble to a useful extent in $CHCl_3$, one of the present study objectives was to obtain derivatives with greater solubility in aliphatic and aromatic hydrocarbon solvents. Solubility tests for **6-Et** reveal only modest improvements. For example, **6-Et** is highly soluble in $CHCl_3$ and CH_2Cl_2, but it is soluble only to about 1×10^{-3}M in C_6H_6. It is insoluble in the more desirable solvents toluene, *o*-xylene, diisopropylbenzene and aliphatic hydrocarbons. The longer chain derivative, **6-Oct**, shows improved behavior as indicated by the following solubilities: C_6H_6 (3×10^{-1}M), toluene (1×10^{-1}M), *o*-xylene (5×10^{-2}M) and decane (3×10^{-4}M). These observations and data reported previously[29] provide guidance for further ligand modifications that should show further enhanced solubility in both aromatic and aliphatic solvents.

It is also important to determine if the new 4-substituted derivatives of **II** chelate in the same or different fashions than reported previously for $[Ph_2P(O)CH_2]_2C_5H_3NO$.[19–22] Therefore, the coordination chemistry of **6-Et** and **6-Oct** with Nd(III) was surveyed using 1 : 1 and 2 : 1 L : Nd(III) ratios. Appropriate mixtures of **6-Et** and **6-Oct** with $Nd(NO_3)_3 \cdot 6H_2O$ in MeOH–EtOH each give purple colored solutions. Following slow solvent evaporation, these solutions deposit blue/purple crystals. Analytical (CHN) data are consistent with the formation of 2 : 1 complexes from the 2 : 1 L : Nd(III) combinations; however, the analytical results for complexes formed from 1 : 1 combinations fit poorly with calculated values for 1 : 1 complexes. In the past, CHN analyses for some 1 : 1 complexes formed by ligand types **I–III** have been found to be unreliable due in part to loss of outer sphere solvent molecules during sample handling. However, as will be described below, this is not the culprit with these complexes. The infrared spectra of all of the complexes in KBr pellets are similar to those of the free ligands except that the ν_{NO} and ν_{PO} bands are shifted to significantly lower frequencies: ν_{NO} 1155–1153 cm^{-1} and ν_{PO} 1128–1121 cm^{-1}, respectively. This observation is similar to that reported for complexes formed by $[Ph_2P(O)CH_2]_2C_5H_3NO$[19] and the shifts are consistent with Nd(III) binding to both the N–O and P=O donor groups in the solid complexes. The data, on the other hand, do not unambiguously reveal the ligand denticity.

Table 1 Selected bond lengths (Å) for **6-Et**·H_2O, [Nd(**6-Et**)$_2$(NO_3)](NO_3)$_2$·4EtOH and [Nd(**6-Et**)$_2$(NO_3)]$_2$[Nd(NO_3)$_5$](NO_3)$_2$·1.5H_2O

6-Et·H_2O			[Nd(**6-Et**)$_2$(NO_3)](NO_3)$_2$·4EtOH		[Nd(**6-Et**)$_2$(NO_3)]$_2$[Nd(NO_3)$_5$](NO_3)$_2$·1.5H_2O	
		M–O(N)$_{pyr}$	Nd–O(1)	2.451(3)	Nd(1)–O(1)	2.454(9)
			Nd–O(4)	2.474(3)	Nd(1)–O(4)	2.447(9)
					Nd(2)–O(10)	2.432(9)
					Nd(2)–O(13)	2.438(9)
		M–O(P)	Nd–O(2)	2.377(3)	Nd(1)–O(2)	2.377(9)
			Nd–O(3)	2.385(3)	Nd(1)–O(3)	2.357(8)
			Nd–O(6)	2.367(3)	Nd(1)–O(5)	2.380(8)
			Nd–O(5)	2.365(3)	Nd(1)–O(6)	2.400(9)
					Nd(2)–O(11)	2.375(8)
					Nd(2)–O(12)	2.406(9)
					Nd(2)–O(14)	2.382(9)
					Nd(2)–O(15)	2.382(9)
		M–O(N)$_{nitrate}$	Nd–O(7)	2.556(4)	Nd(1)–O(7)	2.551(9)
			Nd–O(8)	2.535(4)	Nd(1)–O(9)	2.538(9)
					Nd(2)–O(16)	2.560(9)
					Nd(2)–O(17)	2.522(9)
P(1)–O(2)	1.483(2)		P(1)–O(2)	1.497(3)	P(1)–O(2)	1.500(10)
P(2)–O(3)	1.481(2)		P(2)–O(3)	1.498(3)	P(2)–O(3)	1.508(9)
P(1)–C(6)	1.808(3)		P(3)–O(6)	1.510(3)	P(3)–O(5)	1.500(9)
P(2)–C(7)	1.805(3)		P(4)–O(5)	1.500(3)	P(4)–O(6)	1.489(10)
N–O(1)	1.318(3)		N(1)–O(1)	1.333(5)	P(5)–O(11)	1.507(9)
			N(2)–O(4)	1.343(5)	P(6)–O(12)	1.477(9)
					P(7)–O(14)	1.498(9)
					P(8)–O(15)	1.507(10)
					N(1)–O(1)	1.336(14)
					N(2)–O(4)	1.322(14)
					N(4)–O(10)	1.328(14)
					N(5)–O(13)	1.348(14)

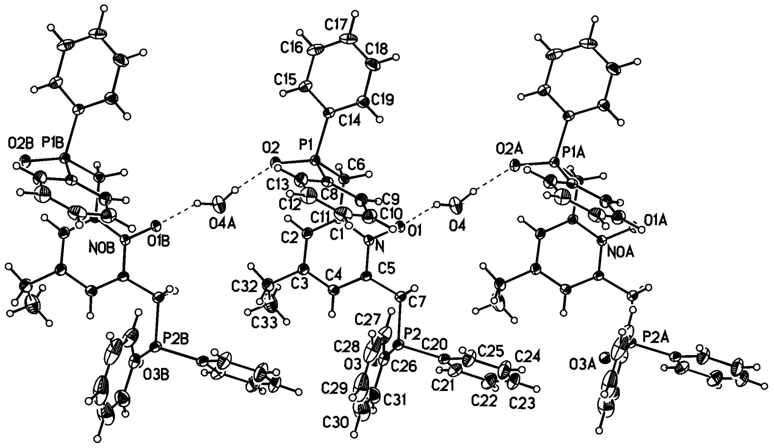

Fig. 2 H-bonded chain network formed by **6-Et**·H_2O.

Crystal structure determinations for the complexes formed with 2 : 1 reagent combinations between Nd(III) and **6-Et** and **6-Oct** were undertaken in order to examine the ligand binding mode. They reveal the compositions [Nd(**6-Et**)$_2$(NO_3)](NO_3)$_2$·4EtOH and [Nd(**6-Oct**)$_2$ (NO_3)](NO_3)$_2$·H_2O thereby confirming the 2 : 1 L : M stoichiometry. The methods of preparation/crystallization are slightly different (EtOAc was employed instead of EtOH in the formation of the **6-Oct** complex), hence the outer sphere solvent environments are different. Nonetheless, the inner sphere structures are virtually identical except that an octyl substituent on one of the bound ligands in [Nd(**6-Oct**)$_2$(NO_3)](NO_3)$_2$·H_2O is severely disordered resulting in a poor overall refinement: ($R1$ = 0.106; $wR2$ (all data) = 0.35). As a result, the discussion of structural details is limited to the complex containing **6-Et**. A view of the complex is shown in Fig. 3 and selected bond lengths are summarized in Table 1. The central Nd(III) ion is bonded to six oxygen atoms provided by two neutral, tridentate **6-Et** ligands and two oxygen atoms from one bidentate NO_3^- ion. The oxygen atoms form a distorted square antiprismatic inner sphere coordination polyhedron (CN = 8).[36] The remaining two nitrate ions required for charge neutralization and four ethanol molecules reside in the

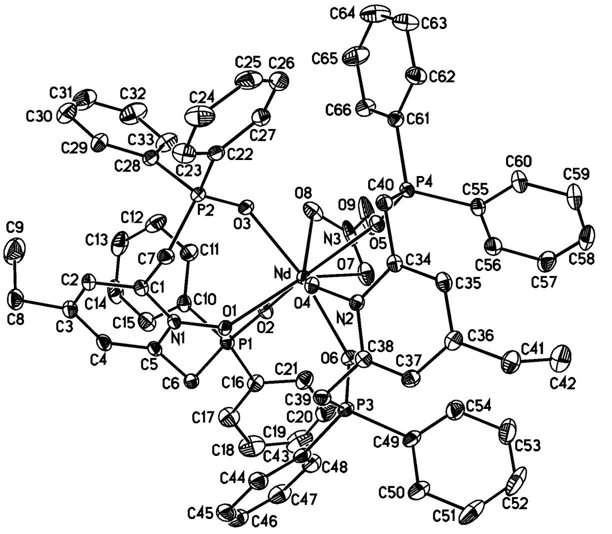

Fig. 3 Molecular structure and atom labeling scheme for [Nd(**6-Et**)$_2$(NO_3)](NO_3)$_2$·4EtOH.

outer sphere. This inner sphere structure type is identical to that found for Yb{$[(Ph_2P(O)CH_2)_2C_5H_3NO]_2(NO_3)\}(NO_3)_2\cdot 2H_2O\cdot 2(CH_3CN)$. It is interesting to compare the new structure against the structure observed for Nd{$[(Tol_2P(O)CH_2)_2C_5H_3NO]_2(H_2O)_2\}(NO_3)_3$ **7**[29]. In the latter case, the central Nd(III) ion is bonded in the inner coordination sphere (CN = 8) to the oxygen atoms from two neutral tridentate ligands (**II**, R = tolyl, R′ = H) and two water molecules. All three nitrate ions appear in the outer sphere along with a water molecule and 2.5 CH_3CN molecules. The two Nd–O(N)$_{pyr}$ distances in [Nd(**6-Et**)$_2(NO_3)](NO_3)_2\cdot$4EtOH, 2.451(3) Å and 2.474(3) Å are shorter than the average distance in **7**, 2.506 (6) Å. This suggests that the *N*-oxide donor groups are more tightly bound to Nd(III) in [Nd(**6-Et**)$_2(NO_3)](NO_3)_2\cdot$4EtOH probably in response to the absence of water in the inner coordination sphere. This conclusion is also supported by the N–O bond lengthening upon coordination of **6-Et**: 1.318(3)Å in the free ligand, 1.333(5) Å and 1.343(5) Å in the complex. The average M–O(P) distance in [Nd(**6-Et**)$_2(NO_3)](NO_3)_2\cdot$4EtOH, 2.374(9) Å, is identical to the average value in **7**, 2.375(6) Å. The P=O bonds are also lengthened upon coordination: free ligand (P=O)$_{avg}$ 1.482(2) Å; [Nd-(**6-Et**)$_2(NO_3)](NO_3)_2\cdot$4EtOH (P=O)$_{avg}$ 1.501(6) Å. The inner sphere NO_3^- anion is bonded to Nd(III) in a slightly asymmetric manner as indicated by the distances Nd–O(7) 2.556(4)Å and Nd–O(8) 2.535(4) Å.

Our prior studies have shown that trifunctional ligands of type **II**, when combined in a 1 : 1 ratio with Ln(III) ions form nine-coordinate complexes containing one tridentate ligand and three bidentate nitrate anions in the inner coordination sphere.[19] However, the crystal structure determination for the complex formed from the 1 : 1 combination of **6-Et** and $Nd(NO_3)_3$ reveals the formation of a significantly different complex: [Nd(**6-Et**)$_2(NO_3)]_2[Nd(NO_3)_5](NO_3)_2\cdot 1.5H_2O$. A view of the molecular structure is shown in Fig. 4 and selected bond lengths are listed in Table 1. The structure contains two independent [Nd(**6-Et**)$_2(NO_3)]^{2+}$ cations that are identical to the cation unit formed in the 2 : 1 complex. That is, the Nd(III) ion in each cation is bonded to *two* tridentate **6-Et** ligands and one asymmetric bidentate NO_3^- ion. The average Nd–O(N)$_{pyr}$ bond length is 2.44(1) Å, the average Nd–O(P) bond length is 2.38(2) Å and the average Nd–O(N)$_{nitrate}$ bond lengths are 2.556(6) Å (long) and 2.53(1) Å (short). These distances are comparable to those found in the 2 : 1 complex [Nd(**6-Et**)$_2(NO_3)](NO_3)_2\cdot$4EtOH. The coordination polyhedron formed by this cation is a distorted square antiprism.

The unit cell also contains a $[Nd(NO_3)_5]^{2-}$ complex anion as well as two "free" nitrate anions and 1.5 H_2O molecules. Lanthanide cations, in the presence of excess nitrate, typically form $M_2[Ln(NO_3)_5]$ complex salts especially with monovalent cations Li^+, Na^+, K^+, and NH_4^+.[37] Therefore, it is not a complete surprise that a $[Nd(NO_3)_5]^{2-}$ anion appears in the 1 : 1 **6-Et** : $Nd(NO_3)_3$ system. The complex anion contains five NO_3^- anions coordinated in a bidentate manner to the central Nd(III). One chelate interaction is symmetric [Nd(3)–O(19) 2.52 (1)Å, Nd(3)–O(20) 2.52(1) Å] while the other four chelate interactions are asymmetric [Nd(3)–O(22) 2.48(1) Å, Nd(3)–O(23) 2.52(1) Å, Nd(3)–O(25) 2.48(2) Å, Nd(3)–O(26) 2.47(2) Å, Nd(3)–O(28) 2.55(2) Å, Nd(3)–O(29) 2.50(2) Å, Nd(3)–O(31) 2.51(4) Å, Nd(3)–O(33) 2.55(2) Å; average 2.51 Å]. The resulting ten vertex oxygen atom coordination polyhedron is a bicapped square antiprism with O(23) and O(26) serving as the capping atoms. This structure contrasts, however, with the structure typically encountered with $M_2[Ln(NO_3)_5]$ complexes which often contain two water molecules coordinated in the Nd(III) inner coordination sphere. Therefore, the complexes $M_2[Nd(NO_3)_5(H_2O)_2]$ (M = Li, Na, K, NH_4^+) are twelve-coordinate, distorted icosahedral.[38] As expected for a higher coordination number complex, the average Nd–O (nitrate) distance is 2.62 Å. It is worth noting that the structure of the $[Nd(NO_3)_5]^{2-}$ anion in the 1 : 1 complex is identical to the complex ion structure reported for $Li_3[Er(NO_3)_6]$ that forms when $Er(NO_3)_3$ is added to a $LiNO_3$ melt.[39]

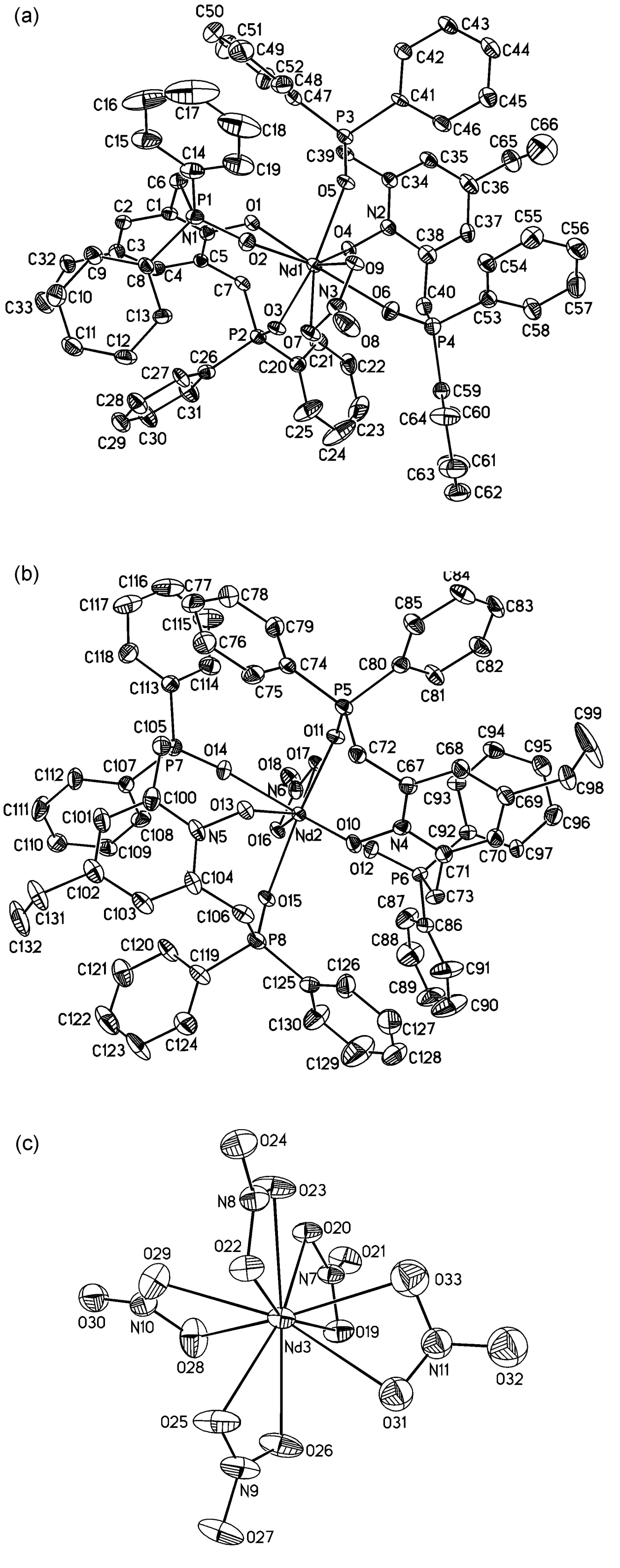

Fig. 4 Molecular structure and atom labeling scheme for [Nd(**6-Et**)$_2(NO_3)]_2[Nd(NO_3)_5](NO_3)_2\cdot 1.5H_2O$: (a) cation 1, (b) cation 2, (c) $[Nd(NO_3)_5]^{2-}$.

Based upon these structural results, it can be concluded that the neutral tridentate ligand **6-Et** successfully competes against NO_3^-, MeOH, EtOH and residual water for inner sphere coordination positions around Nd(III) even when **6-Et** is present in less than the ideal 2 : 1 L : M ratio. Indeed, some of the inner sphere NO_3^- ions are ejected to the outer sphere even in the condition where the L : M ratio is 1 : 1. This is a unique behavior relative to other type **II** ligands.

The multistep syntheses described here for **6-Et** and **6-Oct** provide a useful pathway to 4-pyridyl substituted derivatives of ligand type **II**. The **6-Oct** derivative has good solubility in aromatic hydrocarbons and modest solubility in aliphatic hydrocarbons. Hence, it is feasible to study the LLE properties of a family of ligands against $[Ph_2P(O)CH_2]_2C_5H_3NO$ when **6** is present in 2 : 1 L : M ratios or higher. The structural studies suggest that the 4-substitution will not drastically affect extractant binding. Liquid–liquid extraction and ligand binding thermodynamic studies are planned in the near future in support of these studies.

Experimental

The organic reagents employed in the synthetic schemes were purchased from Aldrich Chemical Co. and used as received unless noted otherwise. Organic solvents were obtained from VWR, and they were dried by standard procedures. The lanthanide nitrate salts were purchased from Ventron. Infrared spectra were recorded on a Mattson 2020 FTIR and NMR spectra were obtained from Bruker FX-250 and JEOL GSX-400 spectrometers using Me_4Si (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P) as external shift standards. All downfield shifts from the reference are designated as + δ. The mass spectra were obtained at the Midwest Center for Mass Spectrometry, University of Nebraska. Elemental analyses were acquired from Galbraith Laboratories.

Ligand synthesis

The ligands **6-Et** and **6-Oct** were prepared in a similar fashion and full details are provided for **6-Et**. Variances for **6-Oct** are summarized in the ESI along with the five step synthesis for compound **1** starting with diethyl oxalate.

Sodium hydride (60% in mineral oil, 19.2 g, 0.48 mol) was washed under a dry nitrogen atmosphere with diethyl ether (3 × 40 ml), vacuum dried and then added to dimethylformamide (DMF) (800 ml). To this suspension, CH_3I (82 g, 0.58 mol) and **1** (16.2 g, 0.074 mol) were added with stirring at 0 °C. The mixture was then stirred at 23 °C (20 h). Water (30 ml) was added to quench unreacted NaH, and DMF and excess CH_3I were removed by vacuum distillation at 40 °C. Water (130 ml) and saturated $NaHCO_3$ solution (40 ml) were added to the residue and the mixture extracted with Et_2O (3 × 100 ml). The Et_2O layers were combined, dried with anhydrous Na_2SO_4 and the Et_2O removed by vacuum evaporation leaving 4-bromo-2,6-bis(methoxymethyl)pyridine **2** as a light orange oil (17.4 g, 95%); ^1H NMR ($CDCl_3$): δ 3.48, 4.54, 7.52; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 58.8, 74.7 123.0 134.2 159.4.

Ethyl magnesium bromide (14.0 ml, 3.0 M in Et_2O, 42 mmol) was added dropwise (30 min) with stirring to a mixture of **2** (9.5 g, 38.6 mmol) and dichlorobis(triphenylphosphine)-nickel(II) (340 mg, 0.52 mmol) in tetrahydrofuran (THF) (160 ml) at −20 °C. The mixture was warmed to 25 °C and maintained below 30 °C (2 h). The resulting red-brown mixture was quenched with aqueous HCl (40 ml, 2 M) and the volatiles removed by vacuum evaporation at 25 °C. The residue was treated with water (100 ml) and the mixture washed with Et_2O (2 × 70 ml). The aqueous phase was then treated with saturated aqueous $NaHCO_3$ solution (150 ml) and this solution (pH 7–8) was extracted with Et_2O (3 × 120 ml). The combined Et_2O solution was washed with dilute aqueous $NaHCO_3$ (50 ml) and the ether fraction dried over Na_2SO_4. The Et_2O was then vacuum evaporated leaving 4-ethyl-2,6-bis (methoxymethyl)pyridine **3** as an orange oil (6.3 g, 84%); ^1H NMR ($CDCl_3$): δ 1.25 (t, J = 7.6 Hz), 2.66 (q, J = 7.6 Hz), 3.47 4.55, 7.18; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.1, 28.1, 58.5, 75.3, 119.3, 154.2, 157.4.

A mixture of **3** (3.7 g, 19 mmol) in HBr (15 ml, 48%) and concentrated H_2SO_4 (2.4 ml) was refluxed (4 h) at 130 °C. The mixture was cooled, slowly neutralized with KOH solution (0–5 °C, pH = 7–7.5), filtered and the solid recovered was washed with Et_2O (4 × 20 ml). The aqueous filtrate was also extracted with Et_2O (4 × 30 ml) and the combined Et_2O solution was dried over Na_2SO_4. The dried solution was vacuum evaporated leaving 4-ethyl-2,6-bis(bromomethyl)-pyridine **4** as an orange oil (4.5 g, 81%); ^1H NMR ($CDCl_3$): δ 1.24 (t, J = 7.6 Hz), 2.64 (q, J = 7.6 Hz), 4.50, 7.21; $^{13}C\{^1H\}$NMR ($CDCl_3$): J 13.8, 27.7, 33.4, 122.2, 155.1, 156.2.

A solution of Ph(EtO)(H)P(O) (3.54 g, 20.8 mmol) in an Et_2O (8 ml)–C_6H_6 (15 ml) mixture was added dropwise to PhMgBr (14.0 ml, 3 M solution in Et_2O, 42.0 mmol). The temperature of the mixture rose and the rate of addition was adjusted in order to control the reflux. When the addition was complete, THF (20 ml) was added and the mixture was refluxed (65 °C, 1.5 h). The mixture was cooled and **4** (3.0 g, 10.2 mmol) in THF (20 ml) was added. This mixture was refluxed (65 °C, 4 h) and then allowed to stand at 20 °C (12 h). A saturated aqueous solution of NH_4Cl (30 ml) and CH_2Cl_2 (40 ml) was added to the reaction mixture. This combination was agitated in a separatory funnel, and the phases were separated. The aqueous phase (pH = 7–8) was washed with CH_2Cl_2 (2 × 30 ml) and the combined organic phases dried over Na_2SO_4. The solvent was removed by vacuum evaporation and the residue was purified by column chromotography (silica, $CHCl_3$–MeOH 100 : 2.5). The product, 4-ethyl-2,6-bis[(diphenylphosphino)methyl]-pyridine *P,P′*-dioxide **5-Et** was isolated as a white solid (4.1 g, 75%), mp 72–74 °C. IR (KBr, cm^{-1}) ν_{PO} 1192; ^{31}P NMR ($CDCl_3$): δ 30.9; ^1H NMR ($CDCl_3$): δ 0.91 (t, J_{PH} = 7.6 Hz, 3H), 2.32 (q, J = 7.6 Hz, 2H), 3.71 (d, J_{PH} = 14.6 Hz, 4H), 6.84 (1H), 7.33–7.42 (12H), 7.61–7.69 (8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.9, 27.2, 40.4 (d, J_{PC} = 65.0 Hz), 122.6, 128.3 (d, J_{CP} = 12.0 Hz), 131.1 (d, J_{CP} = 9.6 Hz) 131.6, 132.5 (d, J_{CP} = 100.4 Hz), 151.8 (d, J_{CP} = 7.0 Hz), 153.7.

A sample of **5-Et** (2.8 g, 5.2 mmol) in $CHCl_3$ (25 ml) was combined with 3-chloroperoxybenzoic acid (1.3 g, 57–86%) and the mixture stirred at 20 °C (18 h). The mixture was then extracted with saturated aqueous $NaHCO_3$ solution (50 ml), the aqueous phase was separated (pH = 7–8), extracted with CH_2Cl_2 (2 × 30 ml) and the combined organic phases dried over Na_2SO_4. The solvent was then vacuum evaporated at 25 °C and the residue was washed with Et_2O (3 × 15 ml). The product, **6-Et**, was obtained as a white solid (2.6 g, 90%) mp 180–181 °C. (Found: C, 69.38; H, 6.09; N, 2.32%. $C_{33}H_{31}NO_3P_2$ requires C, 71.76; H, 5.80; N, 2.54%. MS: *m/z* 551.1779 (M^+); $C_{33}H_{31}NO_3P$ requires 551.1761. IR(KBr) ν_{NO} 1238 cm^{-1}, ν_{PO} 1194 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 31.8. ^1H NMR ($CDCl_3$): δ 0.99 (t, J = 7.6 Hz, 3H), 2.38 (q, J = 7.6 Hz, 2H), 4.10 (d, J_{PH} = 13.9 Hz, 4H), 7.32–7.43 (12H), 7.71–7.80 (8H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.0, 27.2, 31.5 (J_{PC} = 67.0 Hz), 125.3, 128.5 (d, J_{CP} = 12.2 Hz), 130.8 (d, J_{CP} = 9.8 Hz), 131.9 (d, J_{CP} = 2.2 Hz, 132.2 (d, J_{CP} = 101.7 Hz), 141.8, 142.9 (d, J_{CP} = 4.9 Hz). Solubility: soluble in $CHCl_3$, CH_2Cl_2, C_6H_6 (4 × 10^{-3}M); insoluble in toluene, *o*-xylene, petroleum ether (bp 60–80 °C).

Synthesis of complexes

A sample of $Nd(NO_3)_3{\cdot}6H_2O$ (44 mg, 0.1 mmol) was dissolved in methanol (MeOH) (10 ml) and a sample of **6-Et** (55 mg, 0.1 mmol) was added. The mixture was stirred (5 min) and then ethyl acetate (10 ml) was added. The resulting solution was filtered and the filtrate was allowed to evaporate slowly (7 d). The complex was isolated as light blue crystals [Nd(**6-Et**)$_2$-$(NO_3)]_2[Nd(NO_3)_5](NO_3)_2{\cdot}1.5\ H_2O$ that were suitable for crystallographic analysis. (Found: C, 49.15; H, 3.90; N 6.18%). $C_{132}H_{127}N_{13}Nd_3O_{40.5}P_8$ requires C, 49.18; H, 3.97: N 5.65%; IR (KBr, cm^{-1}): ν_{NO} 1155, ν_{PO} 1126.

Table 2 Crystal and data collection parameters for **6-Et**·H$_2$O, [Nd(**6-Et**)$_2$(NO$_3$)](NO$_3$)$_2$·4EtOH, [Nd(**6-Et**)$_2$(NO$_3$)]$_2$[Nd(NO$_3$)$_5$](NO$_3$)$_2$·1.5H$_2$O and [Nd(**6-Oct**)$_2$(NO$_3$)](NO$_3$)$_2$·H$_2$O

	6-Et·H$_2$O	[Nd(**6-Et**)$_2$(NO$_3$)](NO$_3$)$_2$·4EtOH	[Nd(**6-Et**)$_2$(NO$_3$)$_2$][(Nd(NO$_3$)$_5$](NO$_3$)·1.5H$_2$O	[Nd(**6-Oct**)$_2$(NO$_3$)](NO$_3$)$_2$·H$_2$O
Empirical formula	$C_{33}H_{33}NO_4P_2$	$C_{74}H_{86}N_5NdO_{19}P_4$	$C_{132}H_{127}N_{13}Nd_3O_{40.5}P_8$	$C_{78}H_{88}N_5NdO_{16}P_4$
Formula weight	569.54	1617.60	3223.95	1619.65
Crystal system	Monoclinic	Triclinic	Triclinic	Tridinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.977(1)	13.2909(8)	17.830(7)	16.905(3)
b/Å	15.249(2)	14.9667(9)	17.959(6)	18.322(3)
c/Å	21.718(4)	20.0288(11)	25.691(8)	31.301(5)
α/°	90	86.494(1)	79.42(2)	89.17(1)
β/°	95.67(1)	79.813(1)	79.79(3)	77.16(1)
γ/°	90	83.380(1)	71.69(3)	64.19(1)
V/Å^3	2958.4(7)	3891.8(4)	7547(5)	8472(2)
Z	4	2	2	4
μ/mm^{-1}	0.185	0.820	1.180	0.751
Reflections collected	9804	22883	55366	33010
Reflections unique (R_{int})	4654 (0.0442)	12021 (0.0276)	19135 (0.0677)	19037 (0.1125)
$R1$ [$I > 2\sigma(I)$]	0.0464	0.0457	0.0839	0.1060
$wR2$ (all data)	0.1169	0.1363	0.2579	0.3519

A sample of Nd(NO$_3$)$_3$·6H$_2$O (44 mg, 0.1 m mol) was combined with **6-Et** (110 mg, 0.2 m mol) in MeOH (10 ml) and stirred (5 min). Ethanol (10 ml) was added and the mixture filtered. The filtrate was allowed to slowly evaporate (10 d) and purple crystals [Nd(**6-**Et)$_2$(NO$_3$)](NO$_3$)$_2$·4EtOH formed that were suitable for crystallographic analysis (Found: C, 53.43; H, 4.75; N, 4.71%). $C_{74}H_{86}N_5NdO_{19}P_4$ requires C, 54.94; H, 5.36; N, 4.32%. IR (KBr, cm^{-1}): ν_{NO} 1153, ν_{PO} 1126. The complex with (**6-Oct**) was prepared in a similar fashion except that ethyl acetate was added to the ethanol solution.

Single crystal X-ray diffraction

The single crystals for **6-Et** (colorless prism 0.28 × 0.26 × 0.18 mm), [Nd(**6-Et**)$_2$(NO$_3$)]$_2$[Nb(NO$_3$)$_5$](NO$_3$)$_2$·1.5H$_2$O (pale blue prism 0.8 × 0.46 × 0.23 mm), and [Nd(**6-Et**)$_2$(NO$_3$)](NO$_3$)$_2$·4EtOH (pale blue plate 1.5 × 0.46 × 0.15 mm) and [Nd(**6-Oct**)$_2$(NO$_3$)](NO$_3$)$_2$·H$_2$O (pale blue prism 0.36 × 0.25 × 0.14 mm) were obtained from the preparative workups described above. The data sets for **6-Et**·H$_2$O, [Nd(**6-Et**)$_2$(NO$_3$)]$_2$[Nb(NO$_3$)$_5$](NO$_3$)$_2$·1.5H$_2$O and [Nd(**6-Oct**)$_2$(NO$_3$)](NO$_3$)$_2$·H$_2$O were collected on a Siemens R3m/V diffractometer equipped with a graphite monochromator and using Mo-K$_\alpha$ radiation. Data for [Nd(**6-Et**)$_2$(NO$_3$)](NO$_3$)$_2$·4EtOH were collected on a Siemens P4 instrument with a CCD area-detector and low temperature device. Mo-K$_\alpha$ radiation was employed with a graphite monochromator. Pertinent crystal and data collection information are provided in Table 2. Structures were solved by direct methods and refined by full-matrix least-squares techniques. Absorption corrections were applied using semi-empirical psi scans. The structure solution for **6-Et**·H$_2$O was well behaved and the final cycles of least-squares refinements varied all non-hydrogen atoms anisotropically. All H-atoms in **6-Et** were included in idealized positions using the riding model. The water H atoms were located in a difference map and they were allowed to vary in position. The structure solution for [Nd(**6-Et**)$_2$(NO$_3$)](NO$_3$)$_2$·4EtOH was well behaved although the four outer sphere EtOH molecules were disordered over two sites. The EtOH molecules were fixed in position with isotropic U's and occupancy set at 50%. The outer sphere nitrate groups have a wide range of N–O bond lengths and the oxygen atoms may be involved in H-bonding with EtOH molecules. The structure solution for [Nd(**6-Oct**)$_2$(NO$_3$)](NO$_3$)$_2$·H$_2$O was well behaved except that one octyl group was disordered. This led to a large $R1$ = 0.106. As a result, the bond distance and angle data are not discussed in the text. Nonetheless, the inner sphere coordination environment at the Nd(III) ion is identical to that found for the complex containing **6-Et**. The structure solution for [Nd(**6-Et**)$_2$(NO$_3$)]$_2$[Nd(NO$_3$)$_5$](NO$_3$)$_2$·1.5H$_2$O was well behaved except for disorder in C(66) (two sites, C(66)/C(66′) with occupancies fixed to 0.66/0.34) and two nitrate ions involving N(11) and N(13). One of these, N(11) O(31) O(32) O(33), is bonded to the Nd(III) in the [Nd(NO$_3$)$_5$]$^{2-}$ anion. It is disordered over two sites N(11) O(31) O(32) O(33) and N(11′) O(31′) O(32′) O(33′) refined with half occupancy. The second is a "free" nitrate ion, N(13) O(37) O(38) O(39) that is disordered over three sites, each set at 1/3 occupancy. The phenyl groups were constrained as regular hexagons. The atoms refined isotropically were O(2w), N(12), O(34), O(35), O(35), O(36). The atoms involved in disorder are C(66)/C(66′), N(11)/N(11′), O(31)/O(31′), O(32)/O(32′), N(13x), O(37x), O(38x), O(39x), (x = a,b,c).

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See http://www.rsc.org/suppdata/dt/b2/b206782j/ for crystallographic data in CIF or other electronic format.

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