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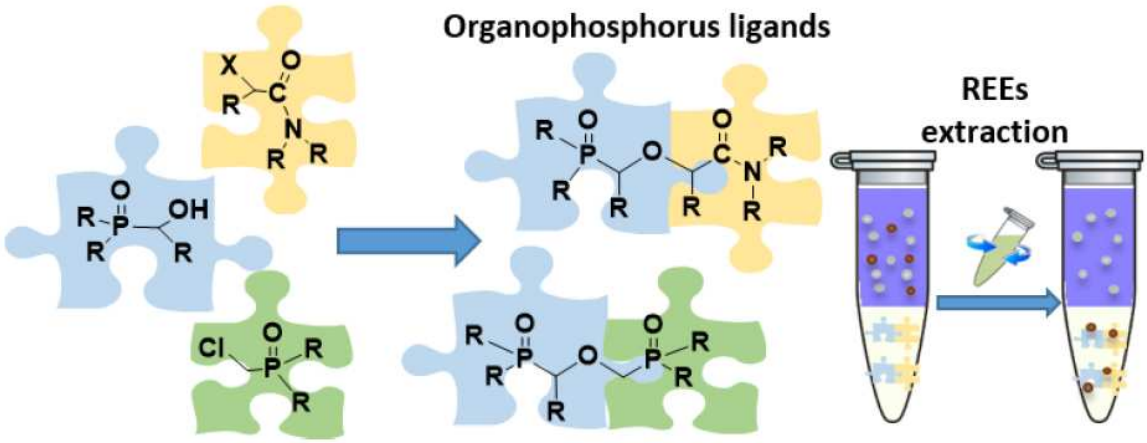

Synthesis of organophosphorus ligands with a central oxygen atom and their applications in solvent extraction

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Abstract

Various structurally related glycolamide compounds were synthesised and evaluated by solvent extraction experiments for the separation of rare earth elements (REEs) from aqueous acid solutions using dodecane as the diluent. We describe herein the full synthesis of a family of bifunctional ligands with a central oxygen and focus our investigation on the effects of structural modification on the extraction efficiencies. The combination of an amide, a P=O donor site, and a central oxygen in such a glycolamide ligand showed interesting extraction properties for heavy rare earth elements from phosphoric acid solutions.

Keywords

Organophosphorus ligands; REEs; Solvent extraction; Phosphoric acid.

1. Introduction

Rare earth elements (REEs) have an essential role in high-value technologies, many of which are in the green energy sector, including magnets, optics, electronics, and ceramics, among others.[1,2]
With increasing demand for REEs in the international marketplace, the separation and purification of these elements has gained considerable importance. Alternative methods that can be used to reduce the stress on the rare earth supply include the use of substitutes, recycling, extracting tailings from conventional mining, or the exploration of unconventional resources.[3]
The development of projects for the recovery of REEs from unconventional resources has gained considerable importance. Phosphate rocks, which contain REEs as a minor component, are considered a secondary source for REEs.[4] Because of the amount of phosphate rock processed annually for the production of phosphoric acid, this resource is a suitable alternative source of REEs. Indeed, the large volumes available offset the relatively low concentrations of rare earth elements present in the ores and waste products created by the phosphoric acid industry. Also, rare earth elements are often just by-products.[5,6] Therefore, these issues have encouraged researchers to innovate and propose efficient methodologies for recovering these metals from phosphate rocks.[7]
Several methods have been investigated to remove uranium from wet-process phosphoric acid (WPA);[8,9] the possibility to recover rare earth elements and uranium from these phosphoric acid leaching solutions has been performed in recent years based on solvent extraction or ion-exchange.[10]
Less attention has been given to the individual recovery of REEs from phosphoric acid. Different techniques have been proposed to recover the rare earth elements from crude phosphoric acid.[11-15]
As a function of the phosphoric acid concentration, Reddy et al. showed that organophosphorus solvents can manage the selectivity between light and heavy rare earth elements. Light rare earth elements (LREEs) are preferentially recovered at low phosphoric acid concentrations, while higher

phosphoric acid concentrations are more suitable for the extraction of heavy rare earth elements (HREEs.)[16,17]

The development of procedures as well as new processes to increase the purity and quality of the final product is encouraged. The design of new ligands can contribute to solving bottlenecks.

Within the context of nuclear waste management, different types of ligands have been developed for the separation of lanthanides and actinides.[18]

Several research groups have investigated the extraction of lanthanides(III) and actinides with diglycolamides, which have an ether oxygen between two amide groups, in nitric acid solutions.[19-21] The extractability of Ln(III) by these ligands follows the sequence diglycolamide > diamide, suggesting that the introduction of an ether oxygen is effective for the intragroup separation of Ln(III) cations.[22] Recently, it has been reported that the extraction efficiency of f-block elements with two diastereomers of dimethyl tetraoctyl diglycolamide (Me2-TODGA) is strongly affected by the stereochemical orientation of the methyl group. [23]

Organophosphorus compounds are also employed for the extraction of REEs from different media.[24] For example, 2-ethylhexyl 2-ethylhexylphosphoric acid (PC-88),[25] di-(2-ethylhexyl)phosphoric acid (HDEHP),[26] or cyanex compounds,[27] either alone or in a synergistic combination with another organic ligand,[28,29] are well-known systems for the solvent extraction of lanthanides.

The development of multifunctional molecules has also been proposed, and studies on the solvent extraction of uranium using multifunctional organophosphorus compounds from phosphoric acid have reported that these compounds have high selectivity.[30,31]

Consequently, it would be interesting to develop such multifunctional molecules for the selective extraction of REEs from phosphoric acid. Based on the abovementioned performances of diglycolamide and organophosphorus compounds, our objective was to synthesise multifunctional molecules that combine a structural backbone containing a combination of an amide and a P=O donor group separated by a central oxygen or a combination of two P=O groups separated by a central oxygen. Previously, these hybrid ligands were proposed by Iqbal *et al.* for the complexation of Am(III)/Eu(III) from nitric acid media.[32]

In the present paper, different combinations are explored, and the synthesis and characterization of seven multifunctional organophosphorus ligands is reported. We investigate the extraction behaviour and separation of REEs in phosphoric acid, the dependence of the extraction distribution ratio on the structure of the ligands, and the effects of the ligand and H_3PO_4 concentration.

2. Results and discussion

2.1. Synthesis

2.1.1. Synthesis of phosphonates and phosphine oxides with a central oxygen atom (I and II)

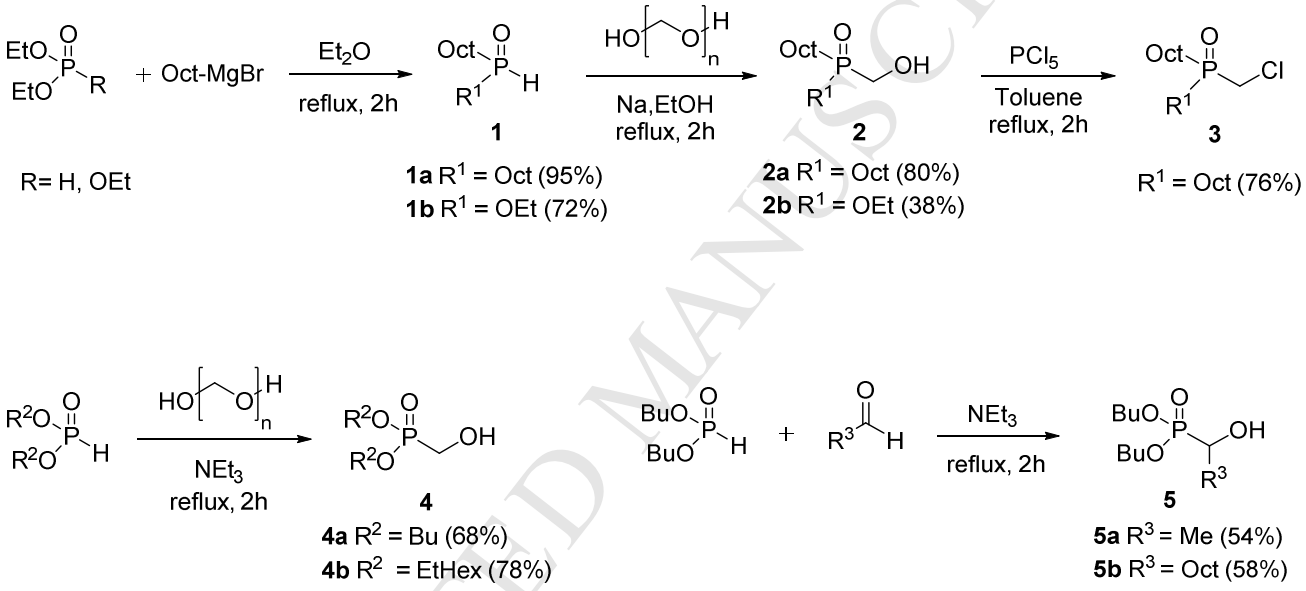
The first objective was to synthesise a phosphorous analogue with the well-known diglycolamide TODGA (tetraoctyldiglycolamide) structure[20] by replacing the two amide groups with two P=O donor groups. The synthesis of multifunctional molecules which combine two P=O donor groups separated by a central oxygen was guided by a disconnection approach through a retrosynthetic analysis which proposes a chloromethyl- and a hydroxymethyl- phosphonate or -phosphine oxides as synthons.

For this purpose, various phosphoryl precursors have been synthesised (Scheme 1). The synthesis of dioctylphosphine oxide **1a** was adapted from a method found in the literature,[33] where di-*n*-butylphosphite was reacted with *n*-octylmagnesium bromide in diethylether. A similar procedure was

used for the synthesis of octyl ethoxy phosphinate (**1b**). The reaction of compound **1a** or **1b** with paraformaldehyde using sodium as a base in ethanol gave the corresponding hydroxymethyl-phosphine oxide (**2a** or **2b**) in high yield. A similar approach was used for the synthesis of various hydroxymethyl-phosphonates (**4**) using triethylamine as a base instead of sodium leading to phosphonates **4a** and **4b** respectively with a butyl (Bu) or an ethylhexyl (EtHex) group.

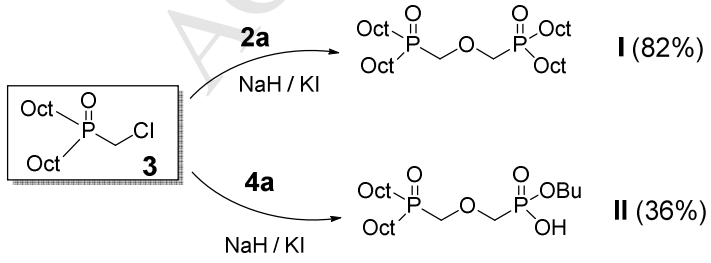
To investigate the effect of the steric hindrance of the methyl or octyl groups introduced on the methylene bridge, we synthesised two molecules: compound **5a**, which contains a methyl group substituent, and **5b**, which has an octyl group substituent; these were synthesised from dibutyl phosphonate with methanal or octanal, respectively, following the procedure described for compound **4**.

The alcohol group of dioctyl (hydroxymethyl)-phosphine oxide (**2a**) was then chlorinated with PCl_5, yielding the desired dioctyl (chloromethyl)-phosphine oxide, **3**.



Scheme 1. Synthesis of organophosphorus building blocks

Finally, both **2a** and **4a** were reacted with dioctyl chloromethyl-phosphine oxide (**3**) in the presence of NaH to yield the desired phosphine oxides and phosphonates with central oxygen **I** and **II** ligands in 82% and 36% yields, respectively (Scheme 2). The treatment in basic conditions can lead to the monosaponification and/or saponification of the phosphonate.[30,31] After purification, the mono-phosphonate **II** was isolated.



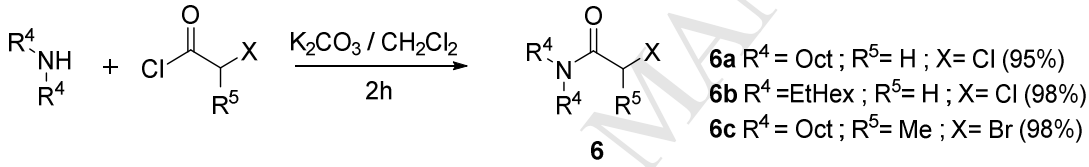
Scheme 2. Synthesis of organophosphorus ligands with a central oxygen atom combining phosphine oxides or phosphine oxide phosphonate functional groups.

2.1.2. Synthesis of combined amides and phosphonates or phosphine oxides with a central oxygen (III–IX)

Further modifications were investigated involving the replacement of only one of TODGA amide group with P=O donors to give various phosphonate-O-acetamide and phosphinoxide-O-acetamide ligands. This approach was proposed by Iqbal *et al.* using sodium hydride for the coupling of an hydroxyl phosphorous derivative with an halogenated compound.[32] For this purpose, 2-chloro or 2-bromo-*N*,*N*-dialkylacetamide derivatives (**6**) were synthesised, following the procedure illustrated in Scheme 3.[30,31]

The extraction efficiency of the diglycolamides is related to the steric hindrance around the binding site and from electro-inductive effects. The presence of branched alkyl groups or long, linear alkyl groups on the amide of DGA act as electron donating groups, thus providing a more basic character.

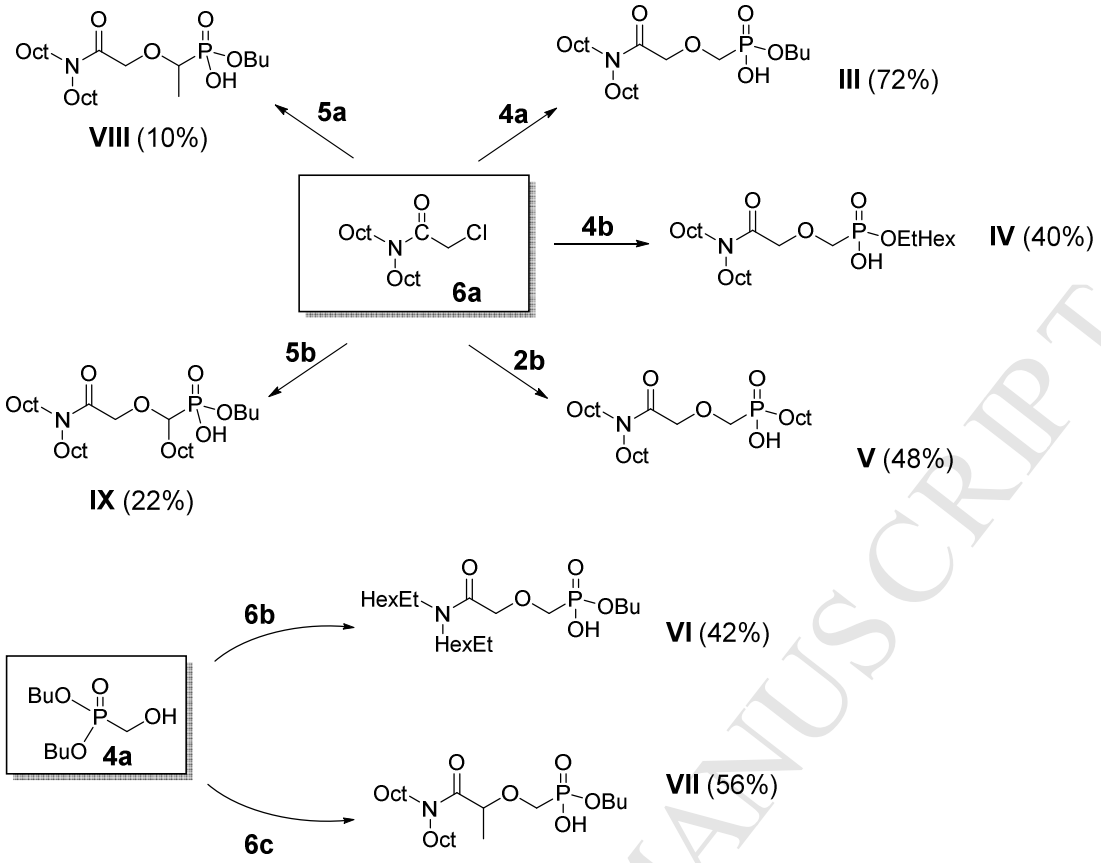
Based on this and to improve the selectivity, solubility, extraction efficiency, and the behaviour of the molecule during the extraction process, the substituent on the amide group has been chosen to be an ethylhexyl (EtHex) or an octyl group (Oct).



Scheme 3. Synthesis of amido building blocks

Then, the hydroxymethyl phosphine oxide or hydroxymethyl phosphonate were combined with the 2-chloro or 2-bromo-*N*,*N*-dialkylacetamide (**6**) in the presence of a mixture of NaH and KI to give seven ligands (Scheme 4), each containing one amide and one P=O donor group separated by a central oxygen. Interestingly, in comparison to previous studies[32] no dialkylphosphonate-*O*-acetamides were obtained after the treatment. In fact, monosaponification occurred systematically during the reaction, resulting in monoalkylphosphonate-*O*-acetamides, which are isolated after the purification step.

It appears that the methyl or octyl groups introduced on the methylene bridge of the phosphorous compounds (respectively **5a** and **5b**) significantly decreased the reactivity of the compound and therefore the yield of the obtained corresponding products (**VIII** and **IX**).



Scheme 4. Synthesis of organophosphorus ligands with a central oxygen atom combining amido, phosphine oxide or phosphonate functional groups.

2.2. Solvent extraction results

In preliminary solvent extraction experiments, the extraction of a mixture of three heavy rare earth elements (HREEs), such as gadolinium, dysprosium, and ytterbium, and a mixture of two light rare earth elements (LREEs), such as lanthanum and neodymium, from phosphoric acid solutions was investigated. Iron(III) was also studied as a competitive metallic cation. The aim of these experiments was to investigate the extraction behaviour and separation possibilities for HREEs and LREEs and the separation of HREEs as a group from LREEs in the aqueous acid phase. In addition, we hoped to evaluate possible relationships between the structures of the ligands and their extraction efficiency.

The suitability of the ligand is associated with the distribution ratio, D_M ($D_M = [M]_{org}/[M]_{aq}$) and the percentage extraction of metal E(%), where $E(\%) = ([M]_{org}/[M]_{aq\ ini}) \times 100$). The separation factor $SF_{M1/M2}$, which is the ratio of the distribution ratio D_{M1} and D_{M2} ($SF_{M1/M2} = D_{M1}/D_{M2}$) describes the selectivity for one metal (M1) over another (M2). The parameters studied include the concentrations of phosphoric acid and the ligand.

Figure 1 illustrates the extraction efficiency of REEs by ligands **I** and **II**. Ligand **II** differs from ligand **I** by the presence of a phosphonic acid group instead of a phosphine oxide group; this has the effect of improving the *D* values.

The difference in performance can be attributed to the fact that in the case of ligand **I**, the functional groups are only phosphine oxide, considered as neutral / solvating agents. Ligand **II** presents a phosphonic acid group at the same time, which can act as a cationic exchanger, and a phosphine oxide moiety that can be considered donor-solvating.

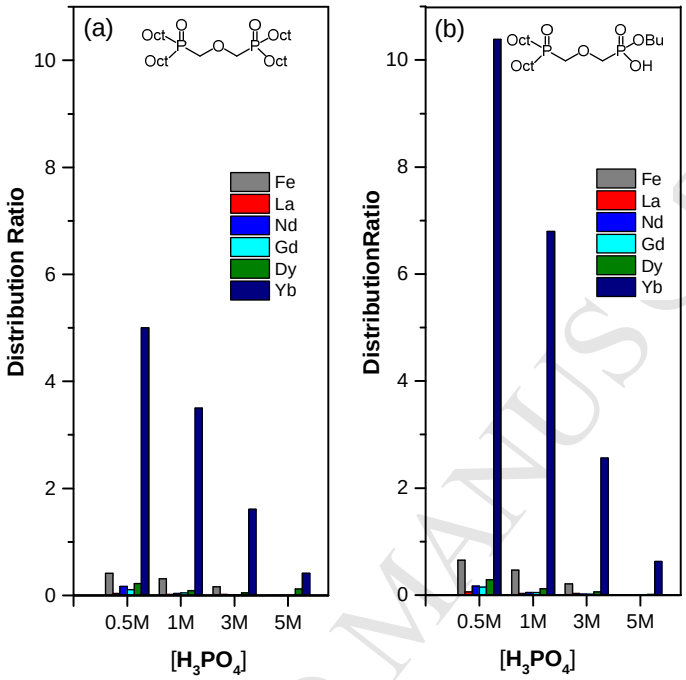


Figure 1. Distribution ratio for a series of five lanthanides (1 mmol/L) and iron(III) (50 mmol/L) at constant total ligand concentration (10 mmol/L) in dodecane after contact with H_3PO_4 (0.5 - 5 M): a) ligand **I** and b) ligand **II**.

The distribution ratio and extraction of REEs decreases with increasing phosphoric acid concentration which is in accordance with the results obtained by Krea using the DOPPA.[34] Therefore, relatively low concentrations of phosphoric acid are required for efficient REE extraction. This behaviour suggests that the mechanism of metal transfer to the organic phase follows an ion exchange type mechanism.

Further, the results suggest large differences in extraction efficiencies of some metals over others at certain acidities, thereby showing separation possibilities. A selectivity / affinity towards Yb over light rare earth elements and iron has been observed with $SF_{Yb/M} > 10$ (Figure SI-1 see supporting information). However, these values have to be taken with caution, given that the distribution ratio values are very low, and the associated uncertainty is high.

The extraction from 0.5 M H_3PO_4 is suitable for the selective separation of Yb from the other metals, the extraction of Fe(III) was also observed but was low compared to that of Yb(III). These properties indicate that such a ligand is effective for Yb extraction, despite the lower efficiency observed in concentrated acidic solutions.

Surprisingly, the corresponding monoalkylphosphonate-*O*-acetamides differ from the above-studied ligands. In particular, for ligand **III**, the extraction performance was high at all acidity values of the aqueous phase (Figure 2). This behaviour has been observed for neutral extractants such as TODGA

for the extraction of REEs from acidic media such as nitric or sulfuric acid.[35,36] Additionally, it is possible to carry out mutual extraction of HREEs from highly concentrated H_3PO_4. The extractability of Nd was quite low compared to Yb, Dy, and Gd; furthermore, La was not extracted, and Fe(III) was poorly extracted, which resulted in high separation factors for HREEs over Fe at high phosphoric acid concentrations (Figure SI-2). The mutual separation of REEs over Fe with a pronounced affinity for HREEs such as Yb and Dy can be achieved when the concentration of the ligand is increased.

From the strong D_M dependence on the H_3PO_4 concentration, it is assumed that the ligands act as solvating ligands. To study the influence of ligand concentration on the REE distribution ratio, experiments were performed at a constant acidity (5 M H_3PO_4) with several ligand **III** concentrations from 10 to 50 mM in dodecane. The log D values are plotted as a function of the log of free extractant concentration (Figure 2b). A linear relationship with a slope of ~1.5 obtained by regression reflects that the extraction mechanism involves a mixture of 1:1 and 1:2 ratios of complex:REE. It is also important to note that the linear nature of Figure 2b indicates that there is no change in the extraction mechanism over the concentration range studied (from 10 to 50 mM).

The extraction efficiency of the ligands is related to the steric hindrance around the binding site. Indeed, the presence of branched alkyl groups (ethylhexyl - EtHex for ligand **VI**) instead of linear alkyl groups (octyl – Oct for ligand **III**) on the amide part led to a decrease in extraction performance (see supporting information Figure SI-3).

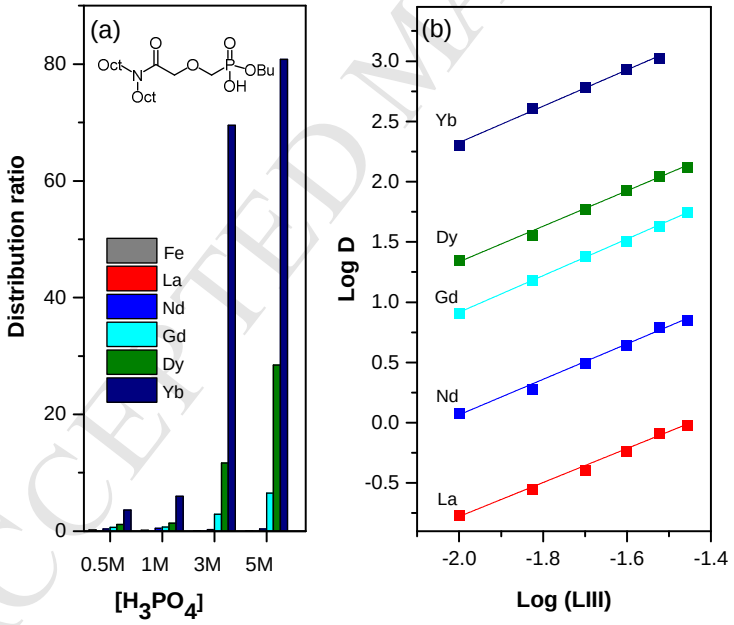


Figure 2. a) Distribution ratio for a series of five lanthanides (1 mmol/L) and iron(III) (50 mmol/L) at constant total ligand **III** concentration (10 mmol/L) in dodecane after contact with H_3PO_4 (0.5 - 5 M); b) distribution ratio versus ligand **III** concentration. log(D La) = f(log[ligand III]): y = 1.411(±0.057)x + 2.032(±0.097), R^2 = 0.993; log(D Nd) = f(log[ligand III]): y = 1.471(±0.061)x + 2.998(±0.103), R^2 = 0.993; log(D Gd) = f(log[ligand III]): y = 1.521(±0.023)x + 3.950(±0.039), R^2 = 0.999; log(D Dy) = f(log[ligand III]): y = 1.473(±0.045)x + 4.273(±0.076), R^2 = 0.996; log(D Yb) = f(log[ligand III]): y = 1.509(±0.048)x + 5.336(±0.084), R^2 = 0.997.

In addition, the extraction of the REEs is affected by the branching of an alkyl group on the methylene close to the central oxygen (Figure 3). Indeed, with the introduction of an alkyl group between the phosphorous and the central oxygen in compounds **VIII** and **IX**, the extraction performance decreased for most of the REEs, except for Yd. In comparison, when an alkyl group was introduced between the amide and the central oxygen (compound **VII**), the extractability of REEs decreased significantly. The efficiency is also affected by acidity. The mechanism of metal transfer to the organic phase seems to follow an ion exchange type mechanism, as the efficiency of the extraction decreased as the acid concentration increased. Generally, acid and neutral organo-phosphorus extractants were used with formula of $(RO)_3PO$ or R_3PO and the extraction efficiency of acid organo-phosphorus extractants decreased with the RO branched chain.[11]

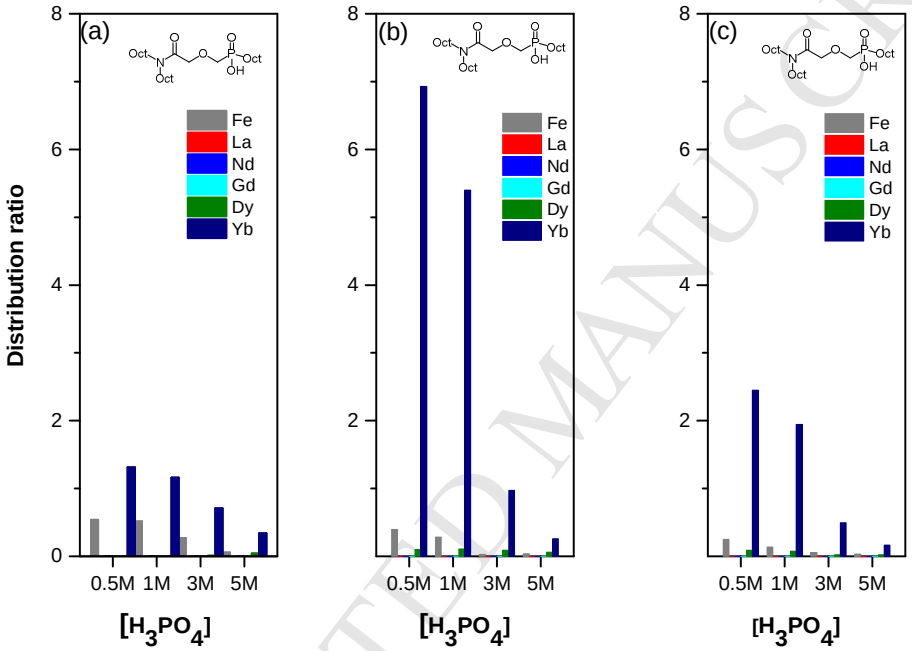


Figure 3. Distribution ratios for a series of five lanthanides (1 mmol/L) and iron(III) (50 mmol/L) at constant total ligand concentration (10 mmol/L) in dodecane after contact with H_3PO_4 (0.5 - 5 M): a) ligand **VII**; b) ligand **VIII**; c) ligand **IX**.

Therefore, from these results, it appears that the separation of individual/groups of REEs from others and from iron(III) and the separation of HREEs from LREEs is made possible by using a specific organophosphorus. Furthermore, the presence of a branching alkyl group on the methylene closest to the central oxygen does not affect the separation efficiency but impacts the performance with lower D values. The steric hindrance on the methylene has a strong impact on the extraction efficiency.

Additionally, the extraction performance was affected by modifying the alkyl substituent of the phosphonate moiety. Although the trend was similar for compounds **III** and **IV**, a decrease in efficiency was observed when a branching group, such as ethylhexyl chain (ligand **IV**), was used instead of a linear butyl chain (ligand **III**). Additionally, the amount of iron extracted is higher when an ethylhexyl chain is introduced on the phosphonate group. This outcome was even more pronounced when the phosphonate was changed for a phosphine oxide group (**V**) (see supporting information Figure SI-4).

In most of the systems studied, the order of the extractability is as follows: Yb > Dy > Gd > Nd >> La. Yb(III) is therefore selectively extracted over the other REEs. The tendency of the prepared ligands to preferentially extract Yb can be linked to lanthanide contraction. The observed differences in the extraction efficiency are due to their ionic radii. The percentage extraction decreases with increasing ionic radii. The results are in good agreement with reported literature.[11] According to the hard-soft acid-base (HSAB) theory, lanthanides are hard acids while the abovementioned *O* donor ligands are hard bases. With increasing atomic number, the hardness of the lanthanides also increases, resulting in an increase in extraction abilities. Cations with higher positive charge densities are strongly bound, resulting in the heavier Ln(III)-ligand complexes being more stable than the lighter Ln(III) ones. In contrast, the Ln(III) ions bind readily to water molecules and the energy required to dehydrate the Ln(III) ions is enhanced with increasing atomic number/decreasing ionic radius.

The extraction efficiency for Yb is greater than that for LREEs, suggesting that, in all systems, the coordination ability of the ligand to Ln(III) is greater than the dehydration energy of Ln(III). The extractability of Fe(III) is quite low compared to Yb; this can also be connected to the hard acid properties of Fe(III), which are lower than those of REE(III). In addition to these factors, we show that the geometry of the coordination site in the ligand also has an effect on the extraction efficiency and the selective separation of Yb (HREEs) and LREEs or separation of Yb (HREEs) from LREEs.

The literature review on solvent extraction and separation of rare earth elements shows that many systems have been investigated for mineral acid media but not many from phosphoric acid media. [11,15,16] Separation possibilities among REEs from phosphoric acid using organo-phosphorus reagents has been reported using TOPS 99, an equivalent to di-2-ethylhexyl phosphoric acid. [37]

The researchers show that the separation of a mixture of REEs was suitable from acid and extractant effects.

Comparable performances were reported for different organo-phosphorus reagents under reasonably similar conditions with the increase of extraction efficiency following ionic radii.

For example, Wang *et al.* showed that with 0.5 M of di-2-ethylhexyl phosphoric acid (HDHEP), less than 20% of LREEs were extracted (D < 0.25) from a 10% P_2O_5 solution (2 M H_3PO_4) containing 1 g/L of rare earth oxides while efficiencies higher than 70% were obtained for HREEs (D ≥ 2).[11] The extraction efficiencies can be managed by changing the HDEHP concentration. In a similar way, the use of 0.7 M of TOPS 99 allowed preferential extraction of HREEs (extraction ≥ 90%; D ≥ 8) in comparison to LREEs (40% <extraction > 75%; 0.7 < D > 3) from an 1 M H_3PO_4 with 25 ppm of elements.[37]

Therefore, compared to the literature, this work obtained competitive extraction efficiencies. The structure of the ligand can be adapted depending on the objective: selective or mutual extraction as a function of the acidity of the medium. Considering efficiencies are related to acidity, it is possible to consider the stripping of the REEs from the loaded organic phases by adjusting the acidity of the stripping solution.

3. Conclusion

The synthesis of multifunctional molecules that combine two P=O donor groups or one P=O donor group and one amide group separated by a central oxygen was performed. The extraction efficiency of ligands towards REEs from H_3PO_4 medium was investigated. Depending on the target, the structure of the ligand can be adapted. The possibility of the separation of one or groups of metals from HREEs and LREEs has been highlighted. The mutual separation of REEs can be achieved with a pronounced affinity for Yb when using monoalkylphosphonate-*O*-acetamide without alkyl groups on

the methylene close to the central oxygen. However, the selective separation of Yb from the other metals is effective with a mono-phosphonate-*O*-phosphine oxide ligand or with the introduction of an alkyl group on the central methylene of the alkylphosphonate-*O*-acetamide.

4. Experimental

4.1. Synthetic chemistry

4.1.1. Chemicals and identification techniques.

Chemicals (analytically pure >99%) were purchased from Sigma Aldrich or Alfa Aesar and were used without further purification. Anhydrous solvents were purchased from Acros (AcroSeal®). Reactions were monitored by Thin Layer Chromatography (Merck TLC Silica Gel 60 F254) using different revelatory systems: phosphomolybdic acid (25 g/500 mL ethanol), sulfuric acid (10% in ethanol), or ninhydrin (1% in ethanol) following by heating and potassium permanganate (10 g K_2CO_3, 1.5 g $KMnO_4$, 150 mL H_2O, 1.5 mL NaOH 10%). Flash chromatography purifications were performed on a Combiflash Agilent Intelliflash 971-FP. NMR analyses were performed on Bruker 400 Ultrashield VS spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 162 MHz for ^{31}P). Displacements are reported in parts per million (ppm). Considering the presence of similar alkyl chains in the ligand structures, some overlapping of carbon signals can be observed. The purity of the various compounds has been determined thanks to the NMR analysis and be assumed to be ≥95%. HRMS were realized using a Synapt G2-S (Waters) spectrometer.

4.1.2. Procedure and characterizations of compounds

4.1.2.1. Phosphoryl precursors

- Compound **1a** : dioctylphosphine oxide. The synthesis was adapted from a literature method.[33,38]

- Compound **1b** : ethyl-octylphosphinate.

To a mixture of octyl magnesium bromide (2 M, 20 mL) in dry Et_2O was added dropwise triethyl phosphite (10 ml, 57.5 mmol) under argon over 1 h at 0°C. Subsequently, HCL 1 M (10 mL) was added until complete dissolution of the precipitated salts (addition of Et_2O may be required). The resulting mixture was stirred at room temperature and then heated at reflux for 4 h. After cooling to room temperature, the mixture was extracted with Et_2O (100 mL). The combined organic layers were washed with HCl 1 M (100 mL), water (100 mL), brine (100 mL), then dried over $MgSO_4$ and evaporated to dryness. After flash chromatography on silica gel (Cyclohexane-ethyl acetate 50-50), the ethyl-octylphosphinate **1b** (72 %) was obtained as a colorless oil.

^{31}P NMR ($CDCl_3$, 162 MHz) δ(ppm): 39
^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 7.04 (d, J_{P-H} = 728 Hz, 1H, P-*H*), 4.22 - 4.05 (m, 2H, O-C*H*$_2$-CH_3), 1.81-1.73 (m, 2H, P-C*H*$_2$), 1.65 – 1.54 (m, 2H, P-CH_2-C*H*$_2$), 1.42-1.24 (m, 13H, -C*H*$_2$- & O-CH_2-C*H*$_3$), 0.89 (t, *J* = 6.8 Hz, 3H, CH_2-CH_2-C*H*$_3$)
^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 62.5 (P-O-*C*H_2-CH_3), 31.9, 30.7, 30.5, 29.4, 29.2, 28.5, 22.8, 20.9 (CH_2), 16.5, 14.2 (CH_3)
HRMS-ESI [M+H]+ Calc. for $C_{10}H_{24}O_2P$: 205.1514; found: 205.1510

- Compound **2a** : dioctyl-hydroxylmethyl-phosphine oxide. The synthesis was adapted from a literature method.[39]

- Compound **2b** : ethyl-(hydroxymethyl)(octyl)phosphinate.

The title compound (38%) was prepared following the same procedure used for the synthesis of compound **2a**.

^{31}P NMR ($CDCl_3$, 162 MHz) δ(ppm): 25.8
^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 4.98 (s, 1H, -O*H*), 4.41-4.08 (m, 2H, C*H*$_2$-O), 3.88-3.84 (m, 2H, P-C*H*$_2$-OH), 1.84-1.77 (m, 4H, C*H*$_2$-P), 1.64-1.56 (m, 2H, C*H*$_2$-CH_2-P), 1.40-1.27 (m, 13H, -C*H*$_2$- *&* O-CH_2-C*H*$_3$), 0.88 (t, *J* = 6.8 Hz, 3H, CH_2-C*H*$_3$)
^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 62.8 (P-O-*C*H_2-CH_3), 60.1 (d, J_{C-P}= 75.4 Hz, P-CH_2-OH), 31.9, 30.9, 30.5, 29.4, 29.2, 28.5, 22.8, 20.9 (CH_2), 16.3, 14.1 (CH_3)
HRMS-ESI [M+H]+ Calc. for $C_{11}H_{26}O_3P$: 237.1620; found: 237.1608

- Compound **3** : dioctyl-chloromethyl-phosphine oxide. The synthesis was adapted from a literature method.[39]

- Compound **4a** : dibutyl-(hydroxymethyl)-phosphonate. The synthesis was adapted from a literature method.[40]

- Compound **4b** : diethylhexyl-(hydroxymethyl)-phosphonate

The title compound (78%) was prepared following the same procedure used for the synthesis of compound **4a**.

^{31}P NMR ($CDCl_3$, 162 MHz) δ(ppm): 24.2

^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 4.04-3.98 (m, 4H, C*H*$_2$-O), 3.92 (d, 2H, P-C*H*$_2$-OH), 1.60-1.54 (m, 2H, -C*H*-), 1.44-1.28 (m, 16H, C*H*$_2$-), 0.94 – 0.83 (m, 12H, C*H*$_3$)
^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 67.7, 67.0 (P-O-*C*H_2-), 60.0 (d, J_{C-P}= 75.4 Hz, P-CH_2-OH), 40.6 (P-O-CH_2-*C*H), 31.0, 30.4, 28.5, 27.2, 22.9 (CH_2), 14.3, 14.1, 10.5, 10.4 (CH_3)
HRMS-ESI [M+H]+ Calc. for $C_{17}H_{38}O_4P$: 337.2508; found: 337.2514

- Compound **5a** : dibutyl-1-(hydroxyethyl)-phosphonate

The title compound (54%) was prepared following the same procedure used for the synthesis of compound **4a** starting from acetaldehyde instead of paraformaldehyde.

^{31}P NMR ($CDCl_3$, 162 MHz) δ(ppm): 25.8
^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 4.87 (s, 1H, OH), 4.07-3.95 (m, 5H, C*H* & C*H*$_2$-O), 1.62-1.54 (m, 4H, -C*H*$_2$- CH_2-O), 1.38-1.28 (m, 7H, -C*H*$_2$- & CH-C*H*$_3$), 0.86 (t, *J* = 6.8 Hz, 6H, C*H*$_3$)
^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 69.0 (d, JC-P= 77.3 Hz, P-*C*H(CH_3)-OH), 65.8 (P-O-*C*H_2-CH_2), 60.1 (d, J_{C-P}= 75.4 Hz, P-CH_2-OH), 31.8, 20.6 (CH_2), 13.9, 13.4 (CH_3)
HRMS-ESI [M+H]+ Calc. for $C_{10}H_{24}O_4P$: 239.1412; found: 239.1410

- Compound **5b** : dibutyl-1-(hydroxynonyl)-phosphonate

The title compound (58%) was prepared following the same procedure used for the synthesis of compound **5a** starting from nonanal.

^{31}P NMR ($CDCl_3$, 162 MHz) δ(ppm): 25.4

^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 4.13-4.04 (m, 4H, C*H*$_2$-O), 3.85-3.80 (m, 1H, C*H*), 1.82-1.59 (m, 6H, -C*H*$_2$-), 1.42-1.24 (m, 16H, -C*H*$_2$-), 0.93-0.84 (m, 9H, C*H*$_3$)

^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 69.0 (d, J_{C-P}= 77.3 Hz, P-*C*H(Oct)-OH), 65.8 (P-O-*C*H_2-CH_2), 60.1 (d, J_{C-P}= 75.4 Hz, P-CH_2-OH), 31.8, 31.5, 30.8, 29.7, 29.5, 29.3, 26.6, 22.5, 20.8 (CH_2), 14.2, 13.8 (CH_3)
HRMS-ESI [M+H]+ Calc. for $C_{17}H_{38}O_4P$: 337.2508; found: 337.2510

4.1.2.2. Amide precursors

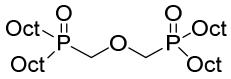
- Compound **6a** : 2-chloro-*N,N*-dioctylacetamide, compound **6b** : 2-chloro-*N,N*-bis(2-ethylhexyl)acetamide and compound **6c**: 2-bromo-*N,N*-bis(2-octyl)propanamide were synthesized from a literature method.[30]

4.1.2.3. Multifunctional organophosphorous ligands

General procedure for ligands synthesis

To a solution of alcohol derivative (2 or 4) (5 mmol) in THF (10 mL) was added NaH (60% in oil) (0.8 g, 20.0 mmol) and KI (5 mmol) at 0°C. The mixture was stirred at 0°C for 1 h, then a solution of halogenated compound (3 or 6) (6 mmol) in THF (10 mL) was added dropwise at this temperature. The resulting mixture was stirred at room temperature at least for 6 hour. The resulting mixture was then carefully acidified at 0°C with 3M HCl or NH_4Cl saturated aqueous solution. Once the effervescence had stopped, the solvent was evaporated. The residue was dissolved in ethyl acetate washed twice with NH_4Cl aqueous solution and water. The organic layer was dried over sodium sulfate, filtered and concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (Ethyl acetate-methanol 100-0 / 80-20)

- Compound **I** : (Oxybis(methylene))bis(di-octylphosphine oxide)



The title compound (82%) was prepared following the general procedure starting from **2a** and **3**. The product was recrystallized from ethyl acetate to give the compound **I** as a white powder (m.p : 48±0.5°C).

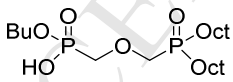
^{31}P NMR ($CDCl_3$, 162 MHz) δ (ppm): 46.1

^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 3.90 (m, 4H, C*H*$_2$-O), 1.78-1.57 (m, 16H, -C*H*$_2$-), 1.44-1.18 (m, 40H, -C*H*$_2$-), 0.98-0.84 (m, 12H, C*H*$_3$)

^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 69.8 (P-CH_2-O), 32.9, 32.0, 31.4, 31.3, 29.4, 22.8, 22.0 (CH_2), 14.3 (CH_3)

HRMS-ESI [M] Calc. for $C_{34}H_{72}O_3P_2$: 590.4957; found: 590.4955

- Compound **II** : Butyl-((di-octanoylphosphoryl)-2-oxoethoxy)methyl)-phosphonate



The title compound (36%) was prepared following the general procedure starting from **4a** and **3**. The product was purified by flash chromatography on silica gel (Ethyl acetate-methanol 100-0 / 80-20) to give the compound **II** as an oil.

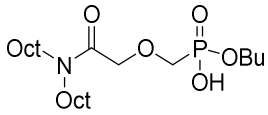
^{31}P NMR ($CDCl_3$, 162 MHz) δ (ppm): 51.9, 19.8

^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 10.9 (s, 1H, O*H*), 4.35 (s, 2H, CO-C*H*$_2$-O), 4.15-4.1 (m, 2H, O-C*H*$_2$-), 3.95 (m, 4H, O-C*H*$_2$-P), 3.32 (t, J = 7.5 Hz, 2H, C*H*$_2$-N), 3.13 (t, J = 7.5 Hz, 2H, C*H*$_2$-N), 1.72-1.63 (m, 2H, -C*H*$_2$-), 1.61-1.49 (m, 4H, -C*H*$_2$-), 1.49-1.37 (m, 2H, -C*H*$_2$-), 1.37-1.20 (m, 20H, -C*H*$_2$-), 0.94-0.86 (m, 9H, C*H*$_3$)

^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 69.9, 69.7 (P-CH_2-O), 67.3 (P-O-*C*H_2-CH_2), 32.9, 32.0, 31.4, 31.3, 29.4, 22.8, 22.0, 19.1 (CH_2), 14.3, 14.0 (CH_3)

HRMS-ESI [M+H]+ Calc. for $C_{22}H_{49}O_5P_2$: 455.3055; found: 455.3055

- Compound **III** : Butyl-((*N,N*-dioctylcarbamoyl)-2-oxoethoxy)methyl)-phosphonate



The title compound (72%) was prepared following the general procedure starting from **4a** and **6a**. The product was purified by flash chromatography (SiO_2, ethyl acetate – methanol (methanol 0 -20%) to give the compound **III** as an oil.

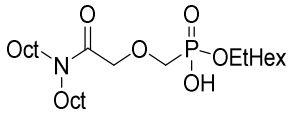
^{31}P NMR ($CDCl_3$, 162 MHz) δ(ppm): 21.5

^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 10.9 (s, 1H, O*H*), 4.35 (s, 2H, CO-C*H*$_2$-O), 4.15-4.1 (m, 2H, O-C*H*$_2$-), 3.95 (m, 4H, O-C*H*$_2$-P), 3.32 (t, J = 7.5 Hz, 2H, C*H*$_2$-N), 3.13 (t, J = 7.5 Hz, 2H, C*H*$_2$-N), 1.72-1.63 (m, 2H, -C*H*$_2$-), 1.61-1.49 (m, 4H, -C*H*$_2$-), 1.49-1.37 (m, 2H, -C*H*$_2$-), 1.37-1.20 (m, 20H, -C*H*$_2$-), 0.94-0.86 (m, 9H, C*H*$_3$)

^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 166.1 (C=O), 69.8 (P-CH_2-O), 67.2 (P-O-*C*H_2-CH_2), 65.6 (C(O)-*C*H_2-O), 48.3, 46.3 (CH_2-N), 31.8, 31.7, 29.4, 29.3, 29.2, 27.4, 26.8, 26.6, 22.9, 22.4, 22.0, (CH_2), 14.3, 14.1, 13.8 (CH_3)

HRMS-ESI [M+H]+ Calc. for $C_{23}H_{49}NO_5P$: 450.3348 ; found: 450.3348

- Compound **IV** : Ethylhexyl-((*N,N*-dioctylcarbamoyl)-2-oxoethoxy)methyl)-phosphonate



The title compound (40%) was prepared following the general procedure starting from **4b** and **6a**. The product was purified by flash chromatography (SiO_2, ethyl acetate – methanol (methanol 0 -20%) to give the compound **IV** as an oil.

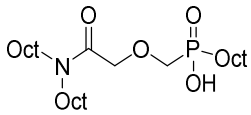
^{31}P NMR ($CDCl_3$, 162 MHz) δ(ppm): 21.2

^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 10.4 (s, 1H, O*H*), 4.37 (s, 2H, CO-C*H*$_2$-O), 4.20-4.04 (m, 2H, O-C*H*$_2$-), 3.96 (m, 2H, O-C*H*$_2$-P), 3.32 (m, 2H, C*H*$_2$-N), 3.13 (m, 2H, C*H*$_2$-N), 1.77-1.49 (m, 5H, -C*H*$_2$-CH_2-N & -C*H*-), 1.48-1.12 (m, 28H, -C*H*$_2$-), 0.98-0.80 (m, 12H, C*H*$_3$)

^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 166.0 (C=O), 69.7 (P-*C*H_2-O), 67.2 (P-O-CH_2-), 65.7 (C(O)-*C*H_2-O), 48.4, 46.2 (CH_2-N), 36.8, 38.5 (CH), 31.8, 31.6, 29.4, 29.3, 29.2, 29.1, 27.4, 26.9, 26.8, 22.8, 22.6, 22.0 (CH_2), 14.6, 14.3, 14.1, 10.9, 10.5, 10.4 (CH_3)

HRMS-ESI [M+H]+ Calc. for $C_{27}H_{57}NO_5P$: 506.3974; found: 506.3974

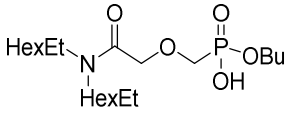
- Compound **V** : Octyl-((*N,N*-dioctylcarbamoyl)-2-oxoethoxy)methyl)-phosphinate



The title compound (48%) was prepared following the general procedure starting from **2b** and **6a**. The product was purified by flash chromatography (SiO_2, ethyl acetate – methanol (methanol 0 -20%) to give the compound **V** as an oil.

^{31}P NMR ($CDCl_3$, 162 MHz) δ(ppm): 48.6
^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 4.35 (s, 2H, CO-C*H*$_2$-O), 3.93 (m, 2H, O-C*H*$_2$-P), 3.29 (m, 2H, C*H*$_2$-N), 3.20 (t, 2H, C*H*$_2$-N), 1.85-1.70 (m, 2H, P-C*H*$_2$-), 1.66-1.50 (m, 2H, P-CH$_2$- C*H*$_2$), 1.61-1.49 (m, 4H, -C*H*$_2$-CH$_2$-N),1.44-1.18 (m, 30H, -C*H*$_2$-), 0.93-0.84 (m, 9H, C*H*$_3$)
^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 166.1 (C=O), 69.8 (P-CH$_2$-O), 65.8 (C(O)-*C*H$_2$-O),48.3, 46.2 (*C*H$_2$-N), 31.8, 31.6, 29.4, 29.3, 29.2, 29.1, 27.4, 26.9, 26.8, 22.8, 22.6, 22.0 (CH$_2$), 14.3, 14.1, 13.9(CH$_3$)
HRMS-ESI [M+H]+ Calc. for $C_{27}H_{57}NO_4P$: 490.4025; found: 490.4024

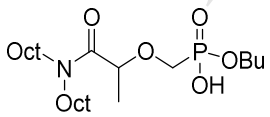
- Compound **VI** : Butyl-((*N,N*-diethylhexylcarbamoyl)-2-oxoethoxy)methyl)-phosphonate



The title compound (42%) was prepared following the general procedure starting from **4a** and **6b**. The product was purified by flash chromatography (SiO_2, ethyl acetate – methanol (methanol 0 -20%) to give the compound **VI** as an oil.

^{31}P NMR ($CDCl_3$, 162 MHz) δ(ppm): 20.6
^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 7.96 (s, 1H, O*H*), 4.37 (s, 2H, CO-C*H*$_2$-O), 4.17-4.07 (m, 2H, O-C*H*$_2$-), 3.92 (m, 4H, O-C*H*$_2$-P), 3.40-3.20 (m, 2H, C*H*$_2$-N), 3.06-3.00 (m, 2H, C*H*$_2$-N), 1.72-1.56 (m, 4H, O-CH$_2$-C*H*$_2$- & -C*H*-), 1.36-1.18 (m, 18H, -C*H*$_2$-), 0.96-0.86 (m, 15H, C*H*$_3$)
^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 166.7 (C=O), 69.7 (P-CH$_2$-O), 67.3 (P-O-*C*H$_2$-CH$_2$), 65.6 (C(O)-*C*H$_2$-O), 51.4, 48.6 (CH$_2$-N), 36.8, 38.5 (CH), 30.6, 30.4, 28.9, 28.7, 24.0, 23.9, 23.1 (CH$_2$), 14.3, 14.1, 10.9, 10.5, 10.4 (CH$_3$)
HRMS-ESI [M+H]+ Calc. for $C_{23}H_{49}NO_5P$: 450.3348 ; found: 450.3330

- Compound **VII** : Butyl-((*N,N*-diethylhexylcarbamoyl)-1-oxopropan-2-yl)methyl)-phosphonate



The title compound (56%) was prepared following the general procedure starting from **4a** and **6c**. The product was purified by flash chromatography (SiO_2, ethyl acetate – methanol (methanol 0 -20%) to give the compound **VII** as an oil.

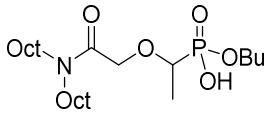
^{31}P NMR ($CDCl_3$, 162 MHz) δ(ppm): 21.8

^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 10.6 (s, 1H, O*H*), 4.47-4.20 (m, 1H, -C*H*-), 4.16-4.08 (m, 2H, O-C*H*$_2$-), 3.93 (m, 4H, O-C*H*$_2$-P), 3.49-3.12 (m, 4H, C*H*$_2$-N), 1.73-1.62 (m, 2H, O-CH$_2$-C*H*$_2$-), 1.61-1.48 (m, 4H, C*H*$_2$-CH$_2$-N), 1.47-1.37 (m, 5H, O-CH$_2$-CH$_2$-C*H*$_2$- & -CH-C*H*$_3$),1.34-1.24 (m, 20H, -C*H*$_2$-), 0.96-0.82 (m, 9H, C*H*$_3$)

^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 166.3 (C=O), 78.7 (C(O)-*C*H-O), 69.7 (P-CH$_2$-O), 67.3 (P-O-*C*H$_2$-CH$_2$), 48.3, 46.3 (CH$_2$-N), 31.8, 31.7, 29.4, 29.3, 29.2, 27.4, 26.8, 26.6, 22.9, 22.4, 22.0, (CH$_2$), 16.8, 14.3, 14.1, 13.8 (CH$_3$)

HRMS-ESI [M+H]+ Calc. for $C_{24}H_{51}NO_5P$: 464.3505 ; found: 464.3503

- Compound **VIII** : Butyl-((*N,N*-dioctylcarbamoyl)-2-oxoethoxy)ethyl)-phosphonate



The title compound (10%) was prepared following the general procedure starting from **5a** and **6a**. The product was purified by flash chromatography (SiO_2, ethyl acetate – methanol (methanol 0 -20%) to give the compound **VIII** as an oil.

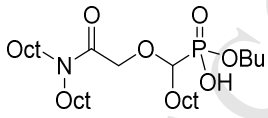
^{31}P NMR ($CDCl_3$, 162 MHz) δ(ppm): 22.3

^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 4.48-4.19 (m, 2H, CO-C*H*$_2$-O), 4.21-4.01 (m, 2H, O-C*H*$_2$-), 3.97-3.88 (m, 1H, O-C*H*-P), 3.30 (m, 2H, C*H*$_2$-N), 3.13 (t, 2H, C*H*$_2$-N), 1.73-1.61 (m, 2H, O-CH$_2$-C*H*$_2$-), 1.60-1.36 (m, 9H, -C*H*$_2$-CH$_2$-N-CH$_2$-C*H*$_2$- ; O-CH$_2$-CH$_2$-C*H*$_2$- & -CH-C*H*$_3$),1.37-1.21 (m, 20H, -C*H*$_2$-), 0.93-0.85 (m, 9H, C*H*$_3$)

^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 166.7 (C=O), 81.3 (P-CH-O), 69.7 (P-CH$_2$-O), 65.6 (C(O)-*C*H$_2$-O), 48.3, 46.3 (CH$_2$-N), 31.8, 31.7, 29.4, 29.3, 29.2, 27.4, 26.8, 26.6, 22.9, 22.4, 22.0, (CH$_2$), 14.2, 14.1, 13.8, 10.6 (CH$_3$)

HRMS-ESI [M+H]+ Calc. for $C_{24}H_{51}NO_5P$: 464.3505 ; found: 464.3507

- Compound **IX** : Butyl-((*N,N*-dioctylcarbamoyl)-2-oxoethoxy)nonyl)-phosphonate



The title compound (22%) was prepared following the general procedure starting from **5b** and **6a**. The product was purified by flash chromatography (SiO_2, ethyl acetate – methanol (methanol 0 -20%) to give the compound **IX** as an oil.

^{31}P NMR ($CDCl_3$, 162 MHz) δ(ppm): 22.1

^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ(ppm): 9,85 (s, 1H, O*H*), 4.34-4.19 (m, 2H, CO-C*H*$_2$-O), 4.16-4.0 (m, 2H, O-C*H*$_2$-), 3.68-3.64 (m, 1H, O-C*H*-P), 3.29 (m, 2H, C*H*$_2$-N), 3.21 (m, 2H, C*H*$_2$-N), 1.90-1.84 (m, 2H, -C*H*$_2$-CH-P), 1.72-1.65 (m, 2H, O-CH$_2$-C*H*$_2$-), 1.59-1.47 (m, 4H, -C*H*$_2$-CH$_2$-N-CH$_2$-C*H*$_2$-), 1.47-1.35 (m, 2H, O-CH$_2$-CH$_2$-C*H*$_2$-), 1.34-1.18 (m, 32H, -C*H*$_2$-), 0.93-0.81(m, 12H, C*H*$_3$)

^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ(ppm): 166.7 (C=O), 81.3 (P-CH-O), 69.7 (P-CH_2-O), 65.6 (C(O)-CH_2-O), 48.3, 46.3 (CH_2-N), 31.8, 31.7, 29.4, 29.3, 29.2, 27.4, 26.8, 26.6, 24.7, 22.9, 22,6 22.4, 22.0, 21.6 (CH_2), 14.2, 14.1, 13.9, 13.4 (CH_3)

HRMS-ESI [M+H]+ Calc. for $C_{31}H_{65}NO_5P$: 562.4600 ; found: 562.4604

4.2. Extraction experiments from H_3PO_4 solutions

To illustrate the entire rare earth elements series two light rare earth elements (LRREs): La and Nd and three heavy rare earth elements (HREEs): Gd, Dy and Yb, have been chosen for the extraction experiments. Rare earth elements stock solutions were prepared at the desired acidity from lanthanum(III) nitrate hexahydrate (Sigma Aldrich, 99.99%), neodymium(III) nitrate hexahydrate (Alfa Aesar, 99.99%), gadolinium(III) nitrate hexahydrate (Alfa Aesar, 99.9%), dysprosium(III) nitrate hexahydrate (Alfa Aesar, 99.9%), ytterbium(III) nitrate hexahydrate (Alfa Aesar, 99.9%).

The desired concentrations (typically 5 mmol/L of $Ln(NO_3)_3$ in H_3PO_4, equimolar concentrations of metals = 1 mmol/L) were prepared by dilution using ultrapure water (MilliQ, Millipore, 18 MΩ.cm^{-1}) and the acidity (typically H_3PO_4 0.5 to 5 M) was adjusted with phosphoric acid. The initial concentrations of metals were measured by inductively coupled plasma/atomic emission spectroscopy (ICP/AES Spectro Arcos).

The organic phase was prepared by dissolving ligands (from 5 to 100 mmol/L) in dodecane.

Organic phases were pre-equilibrated with an aqueous phase at the same acidity as the extraction step without REE cations. The pre-equilibrated organic phases were then mixed with an equal volume of an aqueous acidic stock solution of REEs in a thermostated shaker (Infor-ht® Ecotron) at 25°C and 400 rpm for 1 h, (this time is sufficient to reach thermodynamic equilibrium).

Phases were separated after centrifugation at 4000 rpm for 30 minutes (sigma 3-16 PK). After centrifugation, the separated aqueous phases were subjected to ICP-AES analysis in order to determine i) the distribution ratio (D_M), which is the ratio of the total concentration of metal M in the organic phase to the total concentration of the same metal in the aqueous phase, *i.e.,* $D_M = [M_{org}]/[M_{aq}]$ and ii) the extraction efficiency $E\%=D_M/(D_M+(A/O))$ with A/O the aqueous to organic phase volumetric ratio (typically =1).

The experiments were carried out in duplicate measurements with precision of ± 5%.

Associated Content

Supporting Information: additional data on extraction behaviour and characterization of compounds (Figure SI-1 to Figure SI-4,Table SI-1 and Table SI-2, NMR spectra).

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