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Comparing extraction, synergism and separation of lanthanoids using acidic and neutral compounds in chloroform and one ionic liquid: Is the latter always "better"?

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The complexation properties of a pyrazolone derivative, 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one (**HL**), in chloroform were examined and it was found that it possesses improved complexation ability in comparison with 4-benzoyl, 4-(4-methylbenzoyl) and 4-(4-fluorobenzoyl)
10 derivatives. Mixed ligand chelate extractions of trivalent lanthanoids (La, Nd, Eu, Ho and Lu) with **HL** and 5,11,17,23-tetra-*tert*-butyl-25,26,27-tris(dimethylphosphinoylpropoxy)-28-hydroxy-calix[4]arene (**S1**) or 5,11,17,23-tetra-*tert*-butyl-25,27-bis(dimethylphosphinoylpropoxy)-26,28-dihydroxy-calix[4]arene (**S2**) as synergistic agents were also carried out in chloride medium at constant ionic strength $\mu=0.1$ and CHCl$_3$ as organic phase. The interactions between the extractants in
15 deuterochloroform were studied by ^{1}H, ^{13}C, and ^{31}P NMR. The composition of the extracted species was established as LnL$_3$·HL (L$^-$ represents HL anion) with HL as a single extractant, and as LnL$_3$·S in the presence of the phosphorus-containing calix[4]arene. On the basis of the experimental data, the values of the equilibrium constants were calculated. The influence of the number of P=O groups of *tert*-butyl-calix[4]arene on the extraction process was discussed. The synergistic enhancement and separation
20 factors between metals were evaluated. Finally, the extraction of La(III) and Eu(III) ions was performed by using an ionic liquid, 1-butyl-3-methylimidazolium-bis(trifluoromethanesulfonyl)imide, as a solvent and varying the type of ligands. By comparison to CHCl$_3$, the ionic liquid offers increased distribution ratios, at the expense of a levelling off the separation factors. Reasons for such a phenomenon are discussed.

25 ## Introduction

As part of our systematical work on the synergistic solvent extraction of lanthanoids,[1-8] we performed comparative studies aiming at i) improving the extraction ability of β-diketone compounds by increasing their acidity, ii) studying the
30 dependence of the extraction properties on the number of the ligating groups on a calixarene scaffold and finally, iii) understanding the role of the solvent for extraction, separation and synergism by comparing a traditional molecular solvent, chloroform, and one ionic liquid, namely 1-methyl-3-
35 butylimidazolium bis(trifluoromethanesulfonyl)imide, thereafter denoted as [C$_1$C$_4$im][Tf$_2$N]. It is our opinion that the well-assessed strategy based on the individual independent improvements of the extractants used in a synergistic system, which has proven to be quite efficient in molecular solvents,[1-8]
40 may find some limitations in ionic liquids (ILs). Ionic liquids are studied for an increasing number of applications in various aspects of chemistry and of course liquid-liquid extraction of rare earths and other metals.[9-11] It is now acknowledged that the nanodomains existing in the bulk of ILs and their supramolecular
45 organization lead to very specific solvating properties, thus of

great impact onto Ln and An complexation[12] and, consequently, on extraction from aqueous towards IL phases. Actually, many papers have evidenced tremendous favorable changes, in terms of extraction efficiency, for a variety of systems, when passing from
50 a molecular solvent to an ionic liquid. Another important general result is that the extraction model is, most of the time, very different in ILs as compared to molecular solvents.[13] In this respect, it could be envisioned that "good recipes" in molecular solvents may not be fully applicable in ILs. It is thus important to
55 investigate the possible changes induced by replacing molecular solvents by ILs on the synergism phenomenon and pre-organization effect, comparing step by step extraction, separation and then, synergism. In fact, although many synergistic systems have been investigated in traditional molecular solvents, where
60 the solvent nature has proven to be part of the parameters for getting high efficiencies, few papers have dealt so far with the question of synergism in Ionic Liquids.[14-17] In particular, calixarenes are widely studied for their extracting abilities and the benefit they offer in terms of pre-organization of the complexing
65 pattern in molecular solvents but studies on these questions in IL-based extraction systems are scarce.[18, 19] To our knowledge, only a handful of publications on synergism in ILs is available. For

example in $Am^{3+}/HNO_3//(TBP+CMPO)/[C_1C_4im][Tf_2N]$ (TBP: tri-*n*-butyl phosphate),[14] much less CMPO (N,N-diisobutylcarbamoylmethyl)octylphosphine oxide) than in the equivalent dodecane system is requested, with distribution ratios above 2×10^4 or equal to 16 in $C_1C_4imTf_2N$ and dodecane respectively. Hirayama et al.[16] investigated the system HTTA−18C6−$[C_1C_4im][Tf_2N]$ for selective extraction of La, Eu and Lu focusing on the size-fitting effect. The La(III) was efficiently extracted as $La(TTA)_2(18C6)^+$ by the cation-exchange process (TTA: 2-thenoyltrifluoroacetone, 18C6: 18-crown-6), but Eu and Lu experience small synergistic effect. The environmentally benign Sr^{2+} separation system obtained by the combination of neutral-neutral extractants was developed by Stepinski et al.[17] Addition of TBP markedly increased the extraction of Sr^{2+} into $[C_5C_1im][Tf_2N]$ by DCH18C6 (dicyclohexyl-18-crown-6) and the synergism depends on the alkyl chain length of the IL–cation.

In order to get a deeper insight into the role of ILs, we therefore focused our efforts on a newly synthesized acidic pyrazolone derivative as extractant, HL, for which we report herein synthesis and extraction properties. This compound is used either alone or in conjunction with two partially phosphorilated at the narrow rim *tert*-butyl-calix[4]arenes calixarene-based compounds, **S1** and **S2**, both in chloroform and in IL towards 5 trivalent lanthanoid ions. The reasons that prompted us to choose these various compounds are detailed below. First, 4-acylpyrazol-5-ones are among the most widely exploited O–donors in coordination chemistry[20-23] due to their lower pK_a values (2.56-4.26) in comparison with conventional β-diketones, such as acetylacetone (pK_a = 9.0) and thenoyltrifluoroacetone (pK_a = 6.25). The nature of the substituent in the fourth position of the pyrazolone ring causes significant variations in the electronic, steric, and solubility parameters of the ligand, thereby affecting complexation and extraction of metal ions including 4f- and 5f-elements.[1, 22] While 4-benzoyl, 4-(4-methylbenzoyl) and 4-(4-fluorobenzoyl) derivatives are slightly studied, 4-(4-trifluoromethylbenzoyl) pyrazolone has not been examined,[1, 21] so that the chemical challenge was one of the experimental and synthetic incentive of this work.

Second, calixarenes are a versatile class of supramolecular compounds widely exploited as molecular platforms for the introduction of specific ligating arms in a reorganized pattern suitable for metal ions complexation.[1-8, 24-26] Depending on the nature of the ligating groups, on the dimension of the macrocyclic scaffold and on the hydrophobicity, calixarenes have shown immense selectivity in the separation of alkaline and alkaline earth ions,[27] heavy metals[28] and f-elements.[1, 29] The latter and the tunable shape of the molecules make them ideal candidates for building blocks and molecular scaffolds in the design of new and more sophisticated ligands. There are two basic features to modify these unique three-dimensional structures with almost unlimited derivatization abilities: introduction of variable substituents and additional functional groups both at the lower (OH side) and upper (alkyl branch side) rims. As is well-known, compounds possessing P=O group like phosphonates, phosphines and phosphine oxide derivatives, have shown high affinity for f-elements. Combined with calixarene extracting properties, ligands with phosphorus containing pendant arms at the lower rim have led to a substantial enhancement of the extraction effectiveness and selectivity in molecular solvents.[1, 30, 31] Some have proven to be better extractants for lanthanoids than TOPO (tri-n-octylphosphine oxide) or CMPO used in the nuclear waste management.[31] It has been noted by Ludwig et al.[32] that the cavity size, the position and kind of donor groups as well as the ligand hydrophobicity have a pronounced impact on the extraction ability and selectivity. The intra-group separation efficiencies of the partial-cone isomers of calix[4]arene substituted by phosphoryl and amide groups have been evaluated in a competitive extraction process of 11 rare-earth metal ions by Yaftian et al.[33] It is noteworthy that the more effective extraction has been accompanied with better selectivity.[31] The authors established also that the distribution ratios increase with the polarity of the molecular solvents in the order chloroform< dichloromethane<1,2-dichloroethane<nitrobenzene.[31,33] Contrary to the studies on the efficiency of calixarenes as single extractant, the records on their efficacy as synergistic agents in the field of solvent extraction are quite limited.[2-6, 34] This gave us therefore another impulse for this work.

Experimental

Reagents

All reagents were purchased from Merck and Fluka and were used without any further purification. Fluka silica gel/TLC-cards 60778 with fluorescent indicator 254 nm were used for TLC chromatography. The melting point of pyrazolone was determined in a capillary tube on SRS MPA100 OptiMelt (Sunnyvale, CA, USA) automated melting point system. The NMR spectra were recorded on a Bruker Avance II+ 600 spectrometer (Rheinstetten, Germany) at 25°C; the chemical shifts were quoted in ppm in δ-values against tetramethylsilane (TMS) as an internal standard or against H_3PO_4 as external standard in ^{31}P spectra; the coupling constants were calculated in Hz.

The pyrazolone derivative, 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one (**HL**),[35] was obtained according to an adapted literature procedure[36] in excellent yield (Scheme 1). The experimental details and full characterization of the ligand are given in the Supporting information together with the original 1D and 2D NMR spectra (Figures S1-S6).
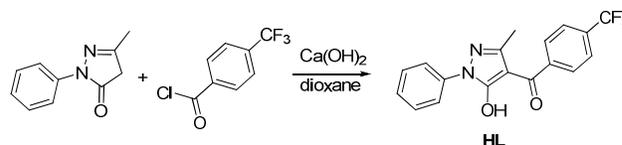
Scheme 1. Synthesis of 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one (**HL**).

The lower rim partially substituted calix[4]arenes, 5,11,17,23-tetra-*tert*-butyl-25,26,27-tris(dimethylphosphinoylpropoxy)-28-hydroxy-calix[4]arene (**S1**) and 5,11,17,23-tetra-*tert*-butyl-25,27-bis(dimethylphosphinoylpropoxy)-26,28-dihydroxy-calix[4]arene (**S2**), shown on Figure 1, were synthesized by one-pot alkylation of commercially available *tert*-butylcalix[4]arene as already published by us.[37]
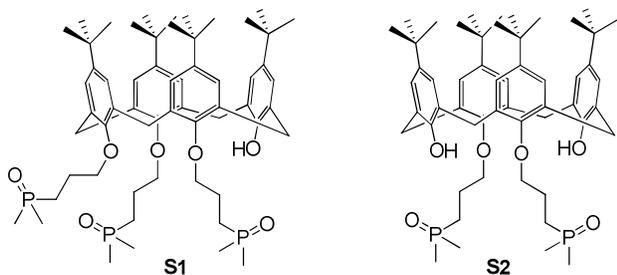
Figure 1. Structural formulas of ligands **S1** and **S2**.

The solvents were CHCl₃ (Merck, p.a.) and 1-butyl-3-methyl imidazolium-bis(trifluoromethanesulfonyl)imide (Solvionic,
5 France). Stock solutions of metals at concentration equal to 2.5×10^{-3} mol dm⁻³ were prepared from their oxides (Fluka, puriss) by dissolving in concentrated hydrochloric acid and diluting with distilled water to the required volume. Arsenazo III (Fluka) was of analytical grade purity as were the other reagents used.
10

Solvent Extraction Procedure

The experiments were carried out using 10 cm³ volumes of aqueous and organic phases. The samples were shaken mechanically (Orbital Shaker OS-20, Boeco, Germany, 120 rpm)
15 for 45 minutes at room temperature ($22 \pm 2°C$) which was sufficient to reach equilibrium.[1-8] After the separation of the phases, the metal concentration in the aqueous phase was determined spectophotochemically (S-20 Spectrophotometer Boeco, Germany) using Arsenazo III.[38] The concentration of the
20 metal ion in the organic phase was calculated by subtraction of the determined amount in the aqueous phase from the total amount present. The acidity of the aqueous phase was measured by a digital pH meter (pH 211 HANNA, USA) with an accuracy of 0.01 pH units. The ionic strength was maintained at 0.1 M with
25 (Na, H)Cl. The initial concentration of the metals was 2.5×10^{-4} mol dm⁻³ in all experiments.

In order to determine metal distribution ratios using ionic liquid as organic media for La(III) and Eu(III) extraction, 2.5 cm³ of organic and aqueous phases of specific composition identical
30 with those used when CHCl₃ was employed were stirred for 60 minutes at room temperature ($22 \pm 2°C$), phases were separated and metal content was determined.

Results and Discussion

35 ### Extraction, synergism and separation in CHCl₃
Solvent Extraction of Ln(III) Ions with HL, S1 or S2 alone
Based on the preceding results,[1,4,39] the extraction equilibria of lanthanoids with 4-acylpyrazolones can be described by the equation:

40 $$Ln^{3+}_{(aq)} + 4HL_{(o)} \leftrightarrow LnL_3 \cdot HL_{(o)} + 3H^+_{(aq)} \qquad (1)$$
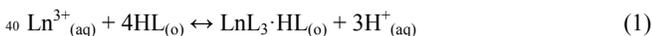
where Ln^{3+} denotes lanthanoid and the subscripts "aq" and "o" indicate the species in the aqueous and organic phase.

The extraction constant, K_L, is defined as

$$K_L = \frac{[LnL_3.HL]_{(o)}[H^+]^3_{(aq)}}{[Ln^{3+}]_{(aq)}[HL]^4_{(o)}} = D_L \frac{[H^+]^3_{(aq)}}{[HL]^4_{(o)}} \qquad (2)$$

45 where D_L is the lanthanoid distribution ratio. As seen from online resource Figure S7 the plots of logD_L vs pH and log[HL] are linear, with slopes very close to 3 and 4, in accordance with eq.1.

The equilibrium constants for the extraction of lanthanoids with 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-
50 one were calculated on the basis of eq. 3 and summarized in Table 1.

$$\log K_L = \log D_L - 3pH - 4\log[HL] \qquad (3)$$

The values of logK_L are approximately 1.50, 1.20 and 0.9 logarithmic units higher than those obtained with 3-methyl-4-(4-
55 methylbenzoyl)-1-phenyl-pyrazol-5-one (HPMMBP), 3-methyl-4-benzoyl-1-phenyl-pyrazol-5-one (HP) and 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one (HPMFBP) respectively. This difference is due to the fact that HL is a slightly stronger acid (pK$_a$=3.40[23]) than HPMMBP (pK$_a$=4.02),
60 HP (pK$_a$=3.92) and HPMFBP (pK$_a$=3.52).[1, 21] The acidity of the extracting agent is increased by the electron-withdrawing effect of the fluorinated group, and the extracting agent can be used to extract metal ion from more acidic aqueous solutions, the equilibrium values increase as the pK$_a$ value decreases.
65 By contrast, the experimental data showed that the lanthanoid ions extraction with 5,11,17,23-tetra-tert-butyl-calix[4]arenes with two and three dimethylphosphinoylpropoxy ligating groups at the narrow rim used alone is negligible under the experimental conditions of the present study in CHCl₃. The latter is probably
70 due to deactivation of the basic phosphoryl groups by H-bonding with the solvent.[40, 41]

Interactions between HL and S1 or S2
An important problem for systems containing mixtures of
75 extractants used for solvent extraction of metals is their possible interaction.[1, 7] The unfavorable role of the extractant interaction was noted by Zhang.[42] 45 years ago Marcus and Kertes[43] have also pointed out that the interaction between an acidic and a neutral extractant is a reason for the destruction of the synergism.
80 The interactions between acidic (HL) and neutral (S) extractant applied in the present study were examined by NMR experiments in the same solvent used in the extraction. Slight upfielding of the signals for methyl and methylene groups of the alkyl substituents of calixarenes with the addition of HL were detected both in
85 proton and carbon spectra (Figures S8-S11), while phosphorus signals were downfielded, as shown on Table 2 and Figure S12. The values of the shifting of the signals increase with the increase of the HL content, which is an indication that the effects are dependent on the extractants' ratio. Negligible chemical shift
90 changes were registered in the spectra of HL upon mixing with S. However, the methyl protons give broad signals (Figures S8-S9) and the methyl group and quaternary carbon at the 3rd position do not appear in the carbon spectra even in S:HL 1:3 mixtures with both calixarenes (Figures S10 and S11). This pattern is
95 compatible with slow exchange between two sites, resulting from the rotation of the acyl group, i.e. between molecules with C=O in the CH₃-3 and OH side, which influenced mainly the methyl group at position 3 and quaternary C$_q$-3 atom due to the carbonyl anisotropy. The latter shows that the strong H-bond between
100 hydroxyl proton and carbonyl oxygen in HL molecule is partially destroyed due to interaction with P=O of the calixarene molecule.

The existence of two exchangeable sites is an indication that the interactions between the components of the extracting systems are localized on the pyrazolone hydroxyl group and do not involve the carbonyl function.

Table 2. ^{31}P chemical shits of calixarenes (**S**) and **S**:**HL** mixtures.

^{31}P	S	S:HL 3:1		S:HL 1:1		S:HL 1:3	
	δ	δ	Δδ	δ	Δδ	δ	Δδ
2/3 S1*	43.75	43.88	+0.13	44.04	+0.29	44.33	+0.58
1/3 S1*	45.13	45.34	+0.21	45.60	+0.47	45.92	+0.79
S2	43.56	43.63	+0.07	43.80	+0.34	44.19	+0.63

* Calixarene **S1** shows a single intensity signal for ^{31}P of the substituent at 26 position and a double intensity one for those at 25 and 27 positions; indicated as 1/3 S1 and 2/3 S1, respectively.

Synergistic solvent extraction of Ln(III) ions with mixtures of HL and S1 or S2

The experimental data for the synergistic solvent extraction of the lanthanoid(III) ions with mixtures of **HL** and **S1** or **S2** are given in figures 2-4. The plots of log$D_{L,S}$ versus pH and log[HL] are linear with slopes close to three and the plots of log$D_{L,S}$ vs. log[S] with slopes close to one. Therefore, in the presence of phosphorus-containing calix[4]arenes, the lanthanoid extraction can be expressed by the equation:

$$Ln^{3+}_{(aq)} + 3HL_{(o)} + S_{(o)} \leftrightarrow LnL_3 \cdot S_{(o)} + 3H^+_{(aq)} \quad (4)$$
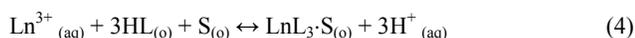
The observed extraction model in the two used systems is identical. This shows that the lanthanoid extraction behavior was not influenced qualitatively by the number of dimethylphosphinoylpropoxy groups of calix[4]arene.

Similar mixed complexes LnL$_3$·S with involvement of one molecule of tetraphosphorylated at the narrow rim calix[4]arene in the extracted species, have been found in our previous studies.[1,3,4,6]

Taking into account that the transfer of pyrazolones[21] and the calixarene[37] to the aqueous phase is very low, the overall equilibrium constant values $K_{L,S}$ can be determined by the equation:

$$\log K_{L,S} = \log D_{L,S} - 3\log[HL] - \log[S] - 3 \text{ pH} \quad (5)$$

The formation of mixed complexes in the organic phase can be described by the following equation:

$$LnL_3 \cdot HL_{(o)} + S_{(o)} \leftrightarrow LnL_3 \cdot S_{(o)} + HL \quad (6)$$
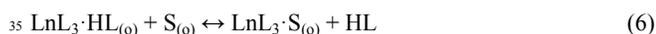
The equilibrium constant $\beta_{L,S}$ for the organic phase synergistic reaction can be determined as:

$$\log\beta_{L,S} = \log K_{L,S} - \log K_L \quad (7)$$

The values of the equilibrium constants $K_{L,S}$ and $\beta_{L,S}$ calculated from the experimental data are given in Table 1. The equilibrium constants are based on the assumption that the activity coefficients of the species do not change significantly under the experimental conditions i.e. they are concentration constants. The data presented in Table 1 show that the addition of **S1** and **S2** to the system Ln(III)–HL leads to a very large increase of the values of $K_{L,S}$ in comparison with those of K_L (4-5 orders of magnitude).

The values of logK_L and log$K_{L,S}$ increase from La to Lu, in agreement with the increasing charge density resulting from the lanthanoid contraction. The obtained log$K_{L,S}$ with **S1** are a little bit larger i.e. this agent exibits better extraction properties and is more efficient than the corresponding **S2** homologue compound. So, the number of the flexible narrow rim ligating groups, two and three, of the studied p-t-butylcalix[4]arenes causes quantitative changes in the synergistic solvent extraction of lanthanoids. The crucial role of the phosphoryl groups in the complexation of the rare earth ions was reported by Yaftian et al.[33] This finding was corroborated by extraction studies with narrow rim substituted cone-calix[4]arenes containing two, three and four phosphoryl groups. The authors unambiguously established that a higher number of –CH$_2$P(O)Ph$_2$ groups tethered to a calix[4]platform favors the extraction of rare-earth metal ions. Another example of the functional group affinity, that calixarenes bearing one to three CMPO residues are less efficient extractants than the tetra-CMPO calix[4]arene was also reported by Arnaud-Neu et al.[30]

The synergistic enhancement obtained for the combination of two extractants can be evaluated by calculating the synergistic coefficients (SC) as: SC = log [($D_{1,2}$) / (D_1+D_2)] where $D_{1,2}$, D_1 and D_2 denote the distribution ratio of a metal ion using mixture of extractants ($D_{1,2}$) and using the same extractants separately (D_1 and D_2). The calculated values of the synergistic coefficients of the lanthanoid ions are given in Table 1. It is seen that all Ln(III) ions are extracted synergistically (SC>0). The addition of the two calix[4]arenes to the chelating extractant improves the extraction efficiency of Ln(III) ions and produces large synergistic effects up to 10^3. **S1** produces a more significant effect on the lanthanoids extraction and highly enhances it. The synergistic enhancement did not show any great change from La to Lu. The obtained SC values for Ln(III) ions in the present study are in the most cases a little bit higher than those when phosphorus containing calix[4]arene with four P=O donor groups was used as synergistic agent in combination with HP, HPMMBP and HPMFBP[1,4] but HL is a stronger acidic chelating extractant.

Separation factors and abilities for HL and HL–S

When the metal ions form complexes of the same type (as in the present case), the separation of the lanthanoids using HL alone and HL–S mixtures can be assessed by the separation factors (SF) calculated as a ratio of the equilibrium constants K_L or $K_{L,S}$ of two lanthanoids (the heavier and the lighter one). Their values are also given in Table 1. It is seen that the SF obtained for the extraction of the Ho/Eu pair with HL alone is approximately 2 times higher than those obtained for the synergistic extraction. It is generally believed that the synergistic extraction makes the separation of metals worse, compared with the extraction with a chelating ligand only.[3, 4] The obtained SF values are higher for the two synergistic systems used especially for the first pair, Nd/La. It should also be noted that a loss of separation selectivity is observed across the 4f-series due to the cation radii decrease of approximately 20 % from La to Lu. If both the extraction efficiency and the separation selectivity are taken into account, the synergistic combination of HL–S1 shows some advantage under comparable conditions. The comparison of the results show that the SFs of the pairs Ho/Eu and Lu/Ho obtained in this study

are similar to those found for the synergistic extraction of lanthanoids with the chelating extractants HPMFBP and HPMMBP in combination with 5, 11, 17, 23-tetra-*tert*-butyl-25,26,27,28-

tetrakis(dimethylphosphinoylmethoxy)calix[4]arene.[1] Concerning the SF values, a moderate selectivity has been noticed with the present systems as compared to the case when similar extraction systems were used.[6]

Extraction, synergism and separation in IL
Preliminary experiments

Actually, pure IL phases of the imidazolium family are known to extract various metal ions. For example, the extraction behavior of Ce(IV) along with that of Th(IV) and Ln(III) (Ln=Ce, Gd, Yb) by pure $[C_8C_1im][PF_6]$ was investigated by Li et al..[44] The authors established that $[C_8C_1im][PF_6]$ alone showed good extraction ability for Ce(IV), while it was inefficient for Th(IV) and Ln(III). Other examples from the imidazolium family can be found for Pu(IV)[45,46] (for a review of this effect for An and Ln, see:[11]) and Au(III)[47] while several d-block metals can be extracted with phosphonium ILs.[48] This prompted us to check the possibility of Eu(III) quantitative extraction by $[C_1C_4im][Tf_2N]$. The results indicate that this pure IL does not act as an extracting phase at the investigated pH value (2.67). This result is in line with previous ones obtained for ILs of the same family under various acidic conditions (in particular, 1 M nitric acid).[49] As a consequence, all extraction results obtained in the present study in IL phase are due to the presence of the extracting agents.

In a second step, the solubility of the compounds in IL was investigated. As previously reported,[50] neutral extractants are readily soluble in imidazolium-based ILs, however acidic extractants showed poor solubility and this greatly affects the extraction performance. **S1** and **S2** have excellent solubility in $[C_1C_4im][Tf_2N]$, while HL needs time to be fully soluble (ex. 8.6×10^{-3} mol/dm³, 1-2 h).

Third, the interactions between the ionic liquid (IL) and the components of the extracting systems were studied. Such interactions are not expected due to the absence of functional groups in IL. Only weak H-bonding of IL nitrogen with **HL** OH can be assumed. Therefore, their interactions were studied at different molar ratios by proton and carbon NMR experiments. All samples were prepared separately by using pure dry compounds dissolved in deuterated solvents. Deuterobenzene was chosen due to its inert nature. As seen on Figures S15 and S16, the proton and carbon resonances of both IL and HL have the same values in the spectra of the individual compounds and in those of their 1:1 mixture. The latter is an indication that no interactions between the ionic liquid (IL) and acidic extractant (HL) occur in the inert solvent benzene-d₆. The interactions were further studied in deuteroacetonitrile (Figures S17 and S18) and in deuterochloroform (Figures S19-S24), H-bond acceptor and donor, respectively, and the same pattern was observed.

Extraction by individual compounds HL, S1 and S2

In order to investigate the role of ionic liquid on the extraction process, a set of experiments was performed under conditions of the aqueous phase comparable with those carried out in CHCl₃. The distinct extraction behavior of the corresponding systems

towards La was described in Figures S25 and S26 and towards La and Eu in Figure S27. The present results show great change in the extraction percentage at approximately 1.7 times lower concentration of the chelating extractant (HL), Figure S27 and the stoichiometry of the La(III)–HL complex in IL and CHCl₃ is different. From the obtained results (Figure S25) the extraction process of La(III) with HL in $[C_1C_4im][Tf_2N]$ can be described by the equation:

$$Ln^{3+}_{(aq)} + 3HL_{(o)} \leftrightarrow LnL_{3(o)} + 3H^+_{(aq)} \tag{8}$$

The equilibrium constant was calculated and presented in Table 3:

$$\log K_L = \log D_L - 3pH - 3\log[HL] \tag{9}$$

In ILs, it has been shown that lanthanoids maintain the usual coordination number they display in molecular solvents.[12] Consequently, in equation 8 above, the complex LnL_3 has an unsaturated first coordination sphere. In an IL solution, the completion of the coordination sphere can be achieved either through binding with the Tf_2N^- anions or by water molecules that are known to transfer to the IL phase: ca. 12000 ppm under such chemical conditions.[49] Furthermore, it has been shown by EXAFS and Molecular Dynamics that in IL solutions, Eu(III) (and other metal ions) display in fact two successive well-defined coordination spheres, of alternate charge, that closest to the metal centre being either composed of Tf_2N^- or $C_1C_4im^+$ ions, depending on the neat charge of the metal entity.[51, 52] Finally, it has been shown that Tf_2N^- is one of the weakly coordinating anions ever, and does not compete favourably with H_2O for Eu(III) coordination sphere in many cases.[10]

Higher extraction efficiency of various extractants in ILs as compared to traditional molecular solvents is a common feature and different stoichiometries of the extracted species are usually found,[9, 11] but not always.[51] The HL behavior is perfectly in line with these general results. Albinsson has concluded that in the organic phase (C_6H_6) at least two complexes exist, $LnAa_3$ and the self-adduct $LnAa_3 \cdot HAa$ as well as for the lower lanthanoids (especially La) a second self-adduct, $LnAa_3(HAa)_2$ was supposed to be extracted with acatylacetone.[53,54] In addition, Binnemans also noted that at low HTTA concentration neutral $[Ln(TTA)_3(H_2O)_x]$ complexes are extracted into the IL phase.[10] In the IL phase, only deprotonated moieties are binding to the metallic center (eq.8). This is of course ascribable to changes in the coordination sphere in the IL as compared to CHCl₃, linked to changes in the solvent properties.

S1 used alone in $[C_1C_4im][Tf_2N]$ also shows a considerable effect to extract lanthanoids: as it is seen from Figure S27, **S1** acts as an excellent ligand for 4f-ions. In $[C_1C_4im][Tf_2N]$, a slope of 1 obtained from the plot indicates that one molecule of **S1** is involved in the extraction step, Figure S26. The calculated value of $\log K_S$ as $\log K_S = \log D_S - \log[S1]$ is also presented in Table 3. In line with other results for different Eu extraction systems in ionic liquids[49,55] we therefore propose that La extraction by **S1** alone in $[C_1C_4im][Tf_2N]$ proceeds through cationic exchange according to the following equilibrium:

$$Ln^{3+}_{(aq)} + S1_{(o)} + 3\,C_1C_4im^+_{(o)} \leftrightarrow [LnS1]^{3+}_{(o)} + 3C_1C_4im^+_{(aq)} \tag{10}$$
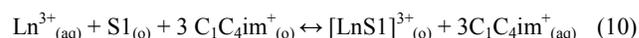
Table 3. Values of the equilibrium constants K_L, K_S and $K_{L,S}$ and synergistic coefficient for La(III) extraction with **HL**, **S1** and **HL–S1** mixture.

logK_L	logK_S	log$K_{L,S}$	log$\beta_{L,S}$	SC
-2.33	3.30	3.34	5.67	2.52

Under the chemical conditions of our experiments, the amount of H$^+$ and Cl$^-$ ions dissolved in the IL phase is known to be negligible, thus rendering ionic exchange through H$^+$ impossible.[56] The liquid-liquid extraction of trivalent rare earth ions by neutral calix[n]arenes usually proceeds via formation of a complex ion pair of stoichiometry 1:1, metal:ligand in molecular solvents: (CHCl$_3$, 1,2-dichloroethane, nitrobenzene).[31] The analysis of the extraction equilibrium obtained by Yaftian et al.[33] from a mixture of four rare earths (La, Eu, Er and Y) revealed that the extracted species (ML(NO$_3$)$_3$, nitric acid solution 1M) have also a 1:1 ratio for both (cone-1 and partial-cone-1) ligands in 1,2-dichloroethane. However, it is seen that the distribution ratios of La(III) and Eu(III) decrease several times upon change of **S1** with **S2**, Figure S27 so we did not perform a detailed study of the extraction mechanism with this compound. It is well-known that slight modifications in the nature and arrangement of the ligating groups affect enormously the interaction of an organic extractant with selected cations in molecular solvents[32,33] and such effects have also been observed in ILs.[57] It has been reported by Dung and Ludwig[58] that a much lower Hg(II) and Pb(II) extraction in toluene solutions was achieved in the presence of two –CH$_2$COOH groups in comparison with the extractability of the corresponding calix[4]arene-based compound bearing four CO$_2$H groups.

The chemical nature of the solvent usually has some significant importance on the extraction equilibria.[3,31,33] The distribution ratios increase with the polarity of the organic phase. As a general rule, replacing a traditional molecular solvent by an IL leads to drastic enhancement effects on the distribution ratios, whatever the type of extracting agent (amine, phosphine oxide, etc). Usually, the advantage of IL compared with classical solvents is expressed as a lower concentration of the extracting moiety to be dissolved in the IL in order to obtain an identical *D* value, with a concentration benefit in the range of a factor 4 to 30[14,59] or even 500.[60] Nakashima et al.[59] also reported that the use of ILs greatly enhanced the extraction efficiency and selectivity of CMPO as an extractant for rare earth metals compared to n-dodecane used as the extracting solvent. For the specific case of calixarene based-extractants, similar enhancement effects have been observed: For example, Shimojo and Goto[19] reported that the extraction performance of pyridinocalix[4]arene towards silver ions was greatly enhanced by dissolution in ionic liquid (1-alkyl-3-methylimidazolium hexafluorophosphate) compared to chloroform.

Synergism HL–S1

Going from individual extractants to mixed systems, i.e. to the cooperative binding ability of two different extractants, the synergistic mixture **HL–S1** shows a similar extraction model towards La(III) ions using [C$_1$C$_4$im][Tf$_2$N] and CHCl$_3$ as solvents, as described by reaction (4). The log*D* values of La(III) using the IL phase with the **HL–S1** mixture are plotted as a function of the aqueous phase pH and [HL] or [S] concentration. These plots are shown in Figure 5. The overall equilibrium constant $K_{L,S}$ for La(III) obtained with the **HL–S1** mixture using IL is approximately 2 orders of magnitude higher than that obtained using CHCl$_3$ as a solvent. However, **HL** alone and **S1** alone are already efficient extractants in ILs, and the overall synergism ability of the **HL–S1** mixture in IL, although noticeable, is not as good in [C$_1$C$_4$im][Tf$_2$N] as it is in CHCl$_3$: The SC obtained in CHCl$_3$ and in [C$_1$C$_4$im][Tf$_2$N] are 3.13 and 2.52 respectively. So, a moderate decrease of synergism is observed in IL for this system. Our result in this new system HL–S1/IL is in line with the work of Shimojo and co-workers, who observed that the combination of a crown-ether and an acidic extractant for Sr(II) extraction neither provides a better extraction in IL as compared to chloroform, nor offers significant synergism as compared to the individual extractants in the chosen IL, namely [C$_1$C$_2$im][Tf$_2$N].[60] Similarly, Hirayama et al.[16] showed that the addition of a crown-ether to HTTA in [C$_1$C$_4$im][Tf$_2$N] was of no help as regard synergism for Lu and Eu.

It has been shown[61] that synergism in molecular solvents using an acidic (**HL**) extractant in conjunction with a neutral (**S**) extractant, is due to the efficient complexation by **L**, which allows formation of a neutral species to be dissolved in the molecular solvent, while **S** helps withdrawing the remaining water molecules from the metal coordination sphere, in order to further enhance the solubility in the molecular solvent. As demonstrated above, in [C$_1$C$_4$im][Tf$_2$N], for the mixtures **HL–S1** involvement of 3 **HL** moieties is not enough to fulfill the 8 or 9 lanthanide coordination sphere requirement that we have evidenced in various IL phases.[62, 63] In this respect, the situation appears to be quite similar in CHCl$_3$ and IL. However, [C$_1$C$_4$im][Tf$_2$N] does tolerate large amounts of water in its bulk,[56] and highly or fully hydrated lanthanoid ions easily dissolve in this IL.[64] As a consequence, the presence of **S1** does not appear as mandatory as it is in chloroform to improve extraction efficiency. This is in line with the involvement of only three **HL** moieties in the absence of **S1**: there is in fact no absolute need for a water-free coordination sphere to get high extraction distribution ratio when using [C$_1$C$_4$im][Tf$_2$N]. In other words, the limited synergistic effect observed in [C$_1$C$_4$im][Tf$_2$N] is in line with the observation made in several molecular solvents that an increase in water solubility leads to a decrease in synergism.[61]

Selectivity across the Ln series in IL

To assess the possibility to separate La over Eu as well as to know the selectivity performance of the corresponding systems in [C$_1$C$_4$im][Tf$_2$N], the separation factors between La and Eu defined as the ratio of the respective distribution ratios (Figure S27) were calculated and depicted in Table 4.

Table 4. Values of separation factors of Eu/La pair obtained with different systems.

Systems	Eu/La	Solvent	Systems	Eu/La	Solvent
HL	2.4	IL	HL–S2	1.0	IL
S1	0.4	IL	HL	5.8	CHCl$_3$
S2	1.2	IL	HL–S1	20.8	CHCl$_3$
HL–S1	1.4	IL	HL–S2	18.2	CHCl$_3$

Concerning the SF values obtained with **HL**, the value in

chloroform is much higher than in $[C_1C_4im][Tf_2N]$. In the case of the synergistic mixtures **HL–S1** or **HL–S2**, a striking detrimental effect of the IL is seen, as SF values are drastically decreased in this solvent, being now close to one, indicating an almost negligible separation efficiency and an unfavorable effect of mixing extractant in view of selective extraction in $[C_1C_4im][Tf_2N]$. ILs dramatically increase extraction abilities, being very good at enhancing extraction performances of any compound but, by doing so, they logically tend to level off separation factors. This can be put in parallel with the leveling off of complexation abilities of inorganic ligands towards metallic cations as already observed and discussed.[65]

Conclusions

The extraction of a chelating extractant 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one (**HL**) in the presence of partially phosphorylated at the narrow rim calix[4]arenes (**S**) as synergistic agents towards five Ln(III)-ions was studied in $CHCl_3$. The composition of the extracted species was established as $LnL_3 \cdot HL$ and $LnL_3 \cdot S$. The NMR investigations on the interaction between the extractants showed that the P=O groups of **S** form moderate H-bonds with pyrazolone hydroxyl function in chloroform solutions. The addition of the phosphorus-containing p-tert-butylcalix[4]arenes produces large synergistic effect up to 10^3 and improves the selectivity among the lighter lanthanoid ions in comparison with HL alone. The best results regarding extractive efficacy were obtained with the tris-phosphorylated compound. La(III) and Eu(III) ions were efficiently extracted using different compound systems in ionic liquid under conditions comparable as those in chloroform. The NMR experiments showed that no interactions occur between IL and HL independently on the solvent nature: benzene, acetonitrile and chloroform.

As a general rule, our results indicate that this "green media" has fantastic extraction potential which results in less selectivity. As a consequence, ILs appear to be of limited interest for the effective individual separation of lanthanoids from an aqueous mixture arising from dissolution of industrial scraps or end-of-cycle processes although they could provide very high extraction distribution ratios. However, separating each Ln from such mixtures to mix them again to obtain new magnets, for example, may appear quite inefficient and it might be better to recover all Ln taken as a mixture, separated from d-metals.[66] In this perspective, the levelling off separation factors as obtained in ILs, at values around 1 by use of "ineffective synergistic mixtures", together with the very high distribution ratios, would be an interesting property of such solvents.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and characterization of HL, Figures S1–S6 and extraction of Ln(III) ions with chelating extractant, HL only (Figure S7), Figures S8-
65 S18 concerning the extractants interaction as well as Figures S19-21 presenting the extraction results in IL. See DOI: 10.1039/b000000x/

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Table 1. Values of the equilibrium constants K_L, $K_{L,S}$ and $\beta_{L,S}$, synergistic coefficients and separation factors for lanthanoids extraction with mixtures HL–S.

Ln^{3+}	$\log K_L$	$\log K_{L,S}$		$\log\beta_{L,S}$		S.C.			SF			
		HL–S1	HL–S2	HL–S1	HL–S2	HL–S1	HL–S2			HL	HL–S1	HL–S2
La	-3.24	1.22	1.14	4.46	4.38	3.13	2.99	Nd/La		3.2	8.7	7.6
Nd	-2.74	2.16	2.02	4.9	4.76	3.51	3.37	Eu/Nd		1.8	2.4	2.4
Eu	-2.47	2.54	2.40	5.01	4.87	3.62	3.48	Ho/Eu		3.8	2.0	1.8
Ho	-1.88	2.86	2.67	4.74	4.55	3.35	3.16	Lu/Ho		1.8	1.9	2
Lu	-1.62	3.14	2.97	4.76	4.59	3.37	3.20					

Notes: The values of the equilibrium constants are calculated on the basis of the 35 experimental points; statistical confidence is 95% and standard deviation is less than ±0.05. S.C.: pH=2.20, [HL]=1.5×10^{-2}mol/dm^3, [S]=7×10^{-4}mol/dm^3.
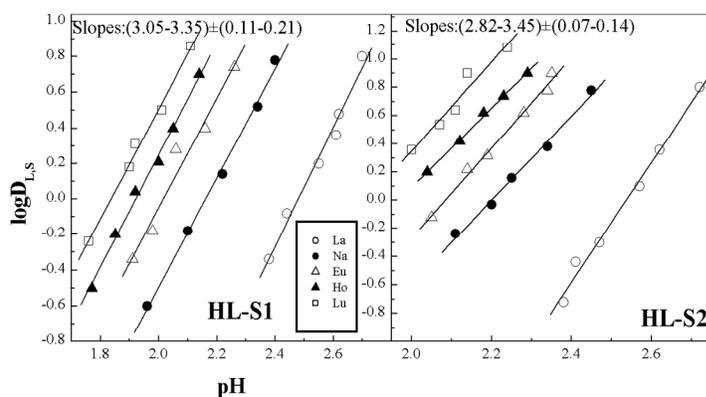
Figure 2. Log$D_{L,S}$ vs. pH for the extraction of lanthanoid(III) ions with mixtures HL–S at [HL]=1.5×10^{-2} mol/dm^3 and [S]= 7×10^{-4}mol/dm^3 in CHCl$_3$.
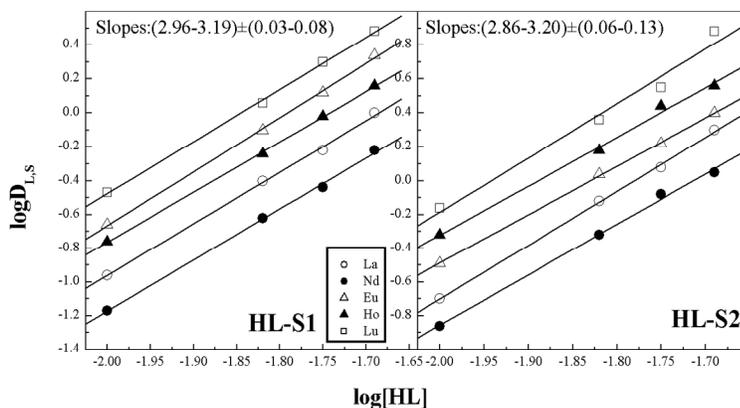

Figure 3. Log$D_{L,S}$ vs. log[HL] for the extraction of lanthanoid(III) ions with mixtures HL–S at [S]= 7×10^{-4}mol/dm^3 in CHCl$_3$. HL–S1: La, pH=2.35; Nd, pH=1.95; Eu, pH=2.00; Ho, pH=1.85; Lu, pH=1.85. HL–S2: La, pH=2.50; Nd, pH=2.10; Eu, pH=2.10; Ho, pH=2.05; Lu, pH=2.00.
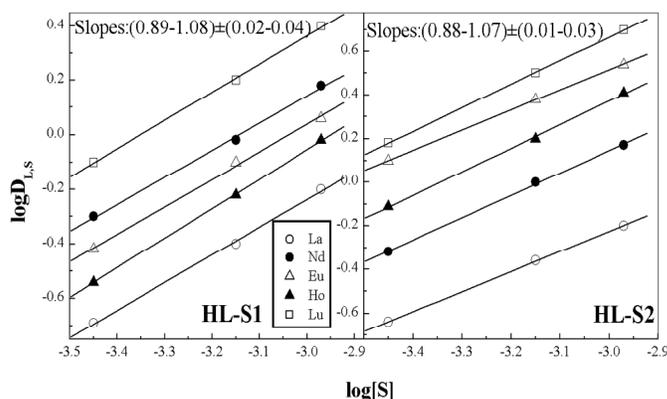
Figure 4. Log$D_{L,S}$ vs. log[S] for the extraction of lanthanoid(III) ions with mixtures HL–S at [HL]= 1.5×10^{-2}mol/dm^3 in CHCl$_3$. HL–S1: La, pH=2.35; Nd, pH=2.15; Eu, pH=2.00; Ho, pH=1.85; Lu, pH=1.90. HL–S2: La, pH=2.45; Nd, pH=2.20; Eu, pH=2.20; Ho, pH=2.05; Lu, pH=2.05.
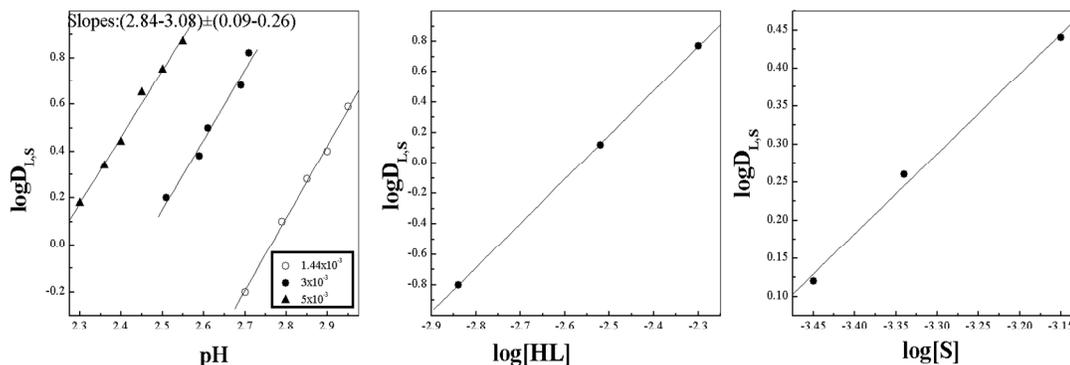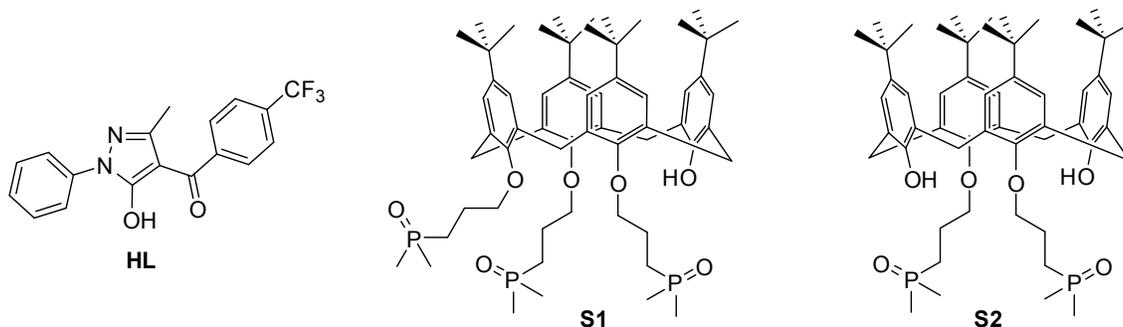

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Figure 5. Log$D_{L,S}$ vs. pH for La(III) extraction with HL–S1 at [S]=7x10^{-4}mol/dm^3 in IL. Log$D_{L,S}$ vs. log[HL] (3 concentrations) for La(III) ion extraction at [S]=7x10^{-4}mol/dm^3 and pH=2.50, slope 0.98±0.06. Log$D_{L,S}$ vs. log[S] (3 concentrations) for La(III) ion extraction at [HL]=3x10^{-3} mol/dm^3 and pH=2.60, slope 1.04±0.12.

10 **Graphic entry for the Table of Contents**

Five lanthanoid ions were extracted with 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one alone and in combination with partially substituted calix[4]arenes by phosphinoyl functions as synergistic agents using CHCl$_3$ and an

15 ionic liquid, 1-butyl-3-methylimidazolium-bis(trifluoromethanesulfonyl)imide, as solvents. The composition of the extracted species was determined. The interaction between the extractants has been studied by NMR spectroscopy.