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Insights into the Green Solvent Extraction and Selectivity of 4f-Ions by Chelating Ligands Comprised of Pyrazolone and Carboxymethyl-Bridged Saturated *N*-Heterocyclic Moieties

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Abstract

A new solvent extraction system for the removal of 4f ions (Ln^{3+}) from water by use of chelating ligands (HLn, n = 5, 6, 7, and 8) composed of heterocyclic receptors and one β-dicarbonyl fragment is reported. The covalent attachment of a β-dicarbonyl unit to a saturated N-heterocycle with variable ring size resulted in a cooperative interaction within the receptor for Ln^{3+} transfer, which remarkably enhanced the efficiency of the process. The intramolecular cooperative effect was observed only in the ionic liquid (IL) solvent system, providing a several-fold increase in extraction performance for Ln^{3+} ions (La, Nd, Eu and Dy) over chloroform. Thus, it is not possible to confirm that an identical reaction mechanism operated in both liquid systems: IL or $CHCl_3$. The existence of neutral chelates of the type LnL_3 or anionic lanthanoid complexes [LnL_4^-] in an ionic medium during the solvent extraction process applying various solvent systems has been established hitherto. Consequently, the Ln^{3+} ion was held by HLn molecules more rigidly in an IL medium ([$C_1C_nim^+$]/[$C_1C_4pyr^+$]/[$C_1C_4pip^+$][Tf_2N^-], n = 4, 6, 8, 10) than in chloroform, representing an important factor dominating the magnitude of the intramolecular cooperative effect of the chelating ligands for Ln^{3+} ions. The effect of the diluent's chemical nature on the metal extraction and separation has been studied and discussed thoroughly. Furthermore, competitive solvent extraction and separation studies with various s-, p-, d-, and f-ions of the periodic table revealed that the magnitude of the intramolecular cooperative effect depends on the suitability between the metal ion size and the cavity size or flexibility of the HLn compounds. In addition, the solvent extraction process of 12 refractory metals and 8 platinum group metals with the synthesized chelating extractants is also investigated in different organic liquid media.

Keywords: solvent extraction; chelating ligand; mechanism; ionic liquids; separation

Check for updates

Academic Editor: György Keglevich

Received: 18 January 2026
Revised: 7 February 2026
Accepted: 11 February 2026
Published: 13 February 2026

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1. Introduction

Currently, rare earth metals are classified as critical chemical elements, vital to many cutting-edge technology products. Today, due to the essential impact on modern industry, it would be highly desirable to develop effective methods for the separation of individual 4f-block elements, that is, lanthanoids [1,2]. However, such a separation process is challenging because the chemical properties of 4f-block elements are quite similar, which translates automatically into serious separation and purification technological difficulties. Generally,

solvent extraction is one, possibly the most effective, chemical technology for separating f-block elements. A lack of high-quality rare earth mineral deposits, especially in Europe, has forced countries to seek alternatives, particularly the exploitation of suitable secondary sources [3]. In other words, China holds almost 80% of rare earth reserves, the USA holds 11%, while India holds around 5% [4]. As a rule, any rare earth mineral in nature usually contains all the metals in the group; unfortunately, some of them are enriched, and some are in very low concentrations. The fact that they often occur together as a group in the same ore deposits raises additional challenges regarding selectivity. The lighter lanthanoids and those with even atomic numbers are more abundant in comparison to the heavier ones and those with odd atomic numbers. In addition, they often occur together with either the uranium or thorium decay chains, making processing even more challenging [4]. Thus, the presence of thorium and uranium in rare-earth-containing minerals is of great concern. The goals for implementing green technologies nowadays can only be achieved if the necessary mineral resources are available, while at the same time, ensuring the safety of new hydrometallurgical mechanisms for both people and the planet. It is necessary to reassess the existing resources for clean baselines and alternatives from the perspective of their more complete and environmentally friendly utilization for the implementation of an economically acceptable green transition. For example, recycling of end-of-life products, i.e., waste electronic devices [5], neodymium magnets [6,7], slag powders of nickel metal hydride (NiMH) batteries, and urban mining of industrial waste containing lanthanoids, such as phosphogypsum or bauxite residue [8], have all been suggested as an important step in achieving a sustainable, circular society [9]. In fact, depleted NiMH batteries are one of the very important sources for rare earth elements, consisting of lanthanum, cerium, praseodymium, neodymium, and yttrium together with significant amounts of other valuable metals, like nickel and cobalt [10]. Moreover, bauxite residue (red mud) is the most important aluminum ore, which contains only between 30 and 50% Al_2O_3, the rest being silica, various iron oxides, TiO_2, but also Ca, Na, and small amounts of Zn, Ga, Ni, V, Zr, Nb, Th, U, and rare earth metals [11]. On the other hand, platinum-group metals (PGMs) are widely used in many industrial sectors, and consequently, the ever-increasing demand surpasses their supply [12]. Moreover, the concentration of valuable metals in electronic scrap, i.e., urbane mine, is usually several times higher than in raw ores. As an example, approximately 13–26 times more copper and 35–50 times more gold could be obtained via e-waste recycling than from the minerals in nature from which they are usually extracted [13]. This avenue, of course, has placed serious scientific emphasis on exploiting and expanding new technologies and innovations to meet the foreseeable future necessities of this class of strategic metals. However, the recovery of critical metals from complex waste is a very tough nut to crack. In reality, the measures of environmental sustainability *vis-a-vis* metals are likely less advanced today than we would like them to be. Actually, end-of-life recycling rates for all rare earths are below 1% [14]. During the years, various strategic molecules some of them commercially available reagents, i.e., di-(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC 88A), trialkyl-methyl ammonium chloride (Aliquat 336), bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), tributyl phosphate (TBP), etc., have been associated as capable extracting agents for rare earth metals in different technological schemes [15–18]. Alternatively, extensive scientific studies have been carried out worldwide for the recovery of 4f-metals by solvent extraction process using different chelating extractants in order to develop efficient chemical processes [19,20]. In general, chelating extractants contain mainly acidic functional groups, for example, –OH, =NOH, and –SH, besides coordination functional groups like =CO, =N-, or ≡N- as well. Numerous literature reports describe the solvent extraction and separation of scandium, yttrium, lanthanoids (Ln), and other transi-

tion or s-metals using acidic *β*-diketone type extractants [6,21]. In most chelating solvent systems, likely typical β-diketone compounds [21], acylpyrazolone "hub" molecules [22,23], or the more acidic isoxazolone ligands [24–26] have been involved as strategic reagents to provoke "chelate effect". This has the supplemental advantage, so that researchers may draw on the massive library of well-known viable compounds with various structural backbones in the field of coordination chemistry, many of which are highly specific for a given group of metallic species instead of designing new complicated ones [27,28]. Nevertheless, a bird's-eye view of a century's chemistry has shown that there are still no universal extractants and, therefore, the design of suitable reagents remains crucial.

Another overarching goal is to avoid the volatile organic compounds (VOCs) as diluents and/or extractants to provide safer alternatives in the field of hydrometallurgical processes [15,29–32]. Thus, some water-immiscible ionic liquids (ILs) have already been used as excellent diluents for liquid–liquid extraction during the last two decades, like *n*-alkyl-*m*-alkylimidazolium cations ($[C_nC_mim^+]$) combined with $[(CF_3SO_2)_2N^-]$ anion [33].

The aim of this scientific study is thus to investigate in detail the solvent extraction behaviour of four new organic molecules containing *N*-heterocyclic fragments with variable size attached to a pyrazalone scaffold in ionic liquid media or typical organic diluents, as seen in Figure 1. The goal is to develop new compounds, i.e., tested herein for the first time, with a heterocyclic framework that can provide a strong platform for selective complexation of various metal ions, such as s-, p-, d-, and especially from the 4f-series, as well as to comply with the CHON "green" principal requirement [34]. As a part of a systematic study of the metal solvent extraction, the present work was undertaken also to investigate the effect of diluents, an IL ($[C_1C_nim^+]/[C_1C_4pyr^+]/[C_1C_4pip^+][Tf_2N^-]$, n = 4, 6, 8, 10) or molecular one (C_6H_6, CCl_4, C_6H_{12}, $CHCl_3$, $C_2H_4Cl_2$) with a comparison purpose, on the extraction behaviour of trivalent ions of the 4f series. In addition, the work discusses the results in terms of a reaction mechanism based on the "slope analysis method" as an effort to determine the feasible stoichiometry of the lanthanoid complex formed in solution. Besides the main objective, i.e., to determine the possibilities for separation of the lanthanoids and other groups of metals in the periodic table, another aim of the proposed investigation is to study the solvent extraction of refractory metals (Ge, Hf, Mo, Nb, Sb, Si, Sn, Ta, Te, Ti, W, and Zr) together with platinum group metals (Ru, Rh, Pd, Re, Os, Ir, Pt, and Au) with a series of four chelating extractants with different heterocyclic radicals. There is a handful of comprehensive extraction research studies of a large number of metals from the periodic table—37 in [23], 56 in [35], or 74 in [36]—in the scientific literature.

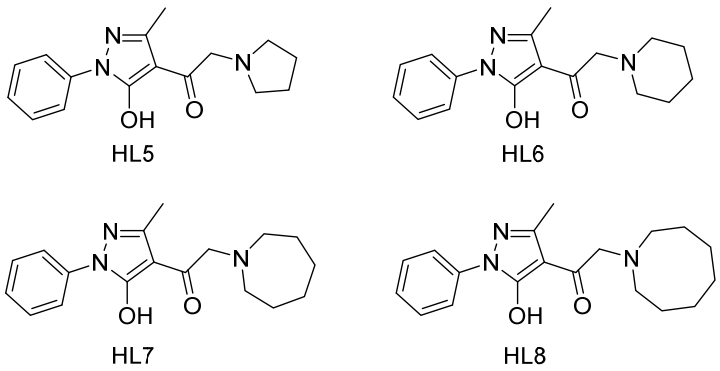


Figure 1. Chemical structures of chelating extractants employed in this study, HL5–HL8.

2. Results and Discussion

2.1. Investigation of Ligand's Solubility in the Aqueous Phase by NMR Analysis

In general, the so-called S-criteria are requested for successful design of a solvent system in order to achieve an efficient chemical process: synthesis, safety, stability, solubility,

speed, separation, strength, and selectivity [37,38]. The main role of chelating reagents during liquid–liquid distribution is to facilitate the transfer of the metal ions from aqueous to an organic phase. However, only metal chelates that are practically insoluble in aqueous media (water) but readily soluble in organic diluents can be quantitatively extracted. Thus, on the basis of solubility data, it is possible to find the most suitable metal chelate for each technological separation scheme by the solvent extraction method. The lipophilic reagents must possess several key physicochemical properties to be used in solvent systems [39,40], such as the formation of stable (preferably chelated) complexes with the target metal ion(s) and the discrimination against competing species present in the aqueous phase. Other essential features required are to maintain good phase compatibility (sparing mutual solubility) with the organic diluent, as well as the easy partitioning from the aqueous medium. Finally, the smooth release of the target metal under suitable chemical conditions so essential for the stripping procedures is of predominant importance. In other words, rapid kinetics of formation (complexation) and destruction (decomplexation) of the metal complex should be expected. Of course, low solubility of the ligand molecule in the aqueous phase is expected by all means, as well as low coextraction of water molecules. Additionally, the ideal ligand should be inexpensive and, more importantly, conform to the twelve principles of green chemistry regarding sustainability. Furthermore, it should consist, if possible, only of C, H, O, and N atoms (the "CHON principle"), making it fully combustible to gaseous products after use [40]. Therefore, one of the tested ligands was chosen for the purpose of analyzing its solubility in water, i.e., whether there would be a loss of some amount of it during the solvent extraction process. The possible solubility of the ligand HL5 ([HL5] = 1×10^{-2} mol/dm^3 diluted in [$C_1C_6im^+$][Tf_2N^-]) in the aqueous phase was investigated using different nitric acid media, i.e., D_2O, 1×10^{-1}, 1×10^{-2}, and 1×10^{-3} mol/dm^3 DNO_3; Figures 2, S1 and S2 (see Supplementary Materials). As can be seen from the results obtained from the proton NMR spectra, the aqueous phase does not contain detectable amounts of the studied ligand, and it can be assumed that it is insoluble in water. This pattern is valid for all experiments and shows that the ligand does not possess water solubility. On the other hand, the observed transfer of the ionic liquid [$C_1C_6im^+$] cation into the aqueous phase is a common feature and well-studied phenomenon; see refs. [33,41]. The average value of IL cation solubility for the alkyl chain length n = 6 is ca. 6 mM in the pH range from 1 to 8 [41].

2.2. Solvent Extraction and Selectivity Across the Periodic Table and 4f-Series

For instance, a real selectivity could be estimated by performing competitive solvent extraction experiments with the objective of assessing the applicability of the solvent systems outlined herein. Thus, the solvent extraction ability of four synthesized ligands was investigated towards various metal cations from the periodic table using two types of diluents. The aim was to establish the influence of both the size and flexibility of the heterocyclic receptor, as well as the chemical nature of the applied diluent; Figures 3 and S3. Notwithstanding, ILs are very expensive chemical products, and before any applications can be envisioned, it is necessary to evaluate their exact contribution compared with conventional systems with typical organic diluents ($CHCl_3$) under the same experimental conditions. In general, for all studied solvent systems, the use of an ionic liquid as a diluent leads to better results for the majority of the studied metal ions. Further, the 4f-series stands out, in which the ligand HL6 is more effective than the other three synthesized chelating molecules. As a whole, the following order of effectiveness can be roughly deduced concerning Ln^{3+} ions: HL6 > HL5 > HL7 > HL8. The results also show that the HL6 compound is a better complexing agent for the s-series ions, including Ag^+. In addition, the four new ligands are extremely effective with nearly equal capacity for trivalent ions

like Fe^{3+} and Bi^{3+} when dissolved in an IL. From the research studies conducted to analyze the capacity of ligand HL6 for solvent extraction of various metals from the periodic table (Figure 3), it is seen that the use of an IL medium is a very advantageous way compared to cases with chloroform. Therefore, the ligand HL6 is somehow a remarkably suitable compound in coordination chemistry as dissolved in $[C_1C_4im^+][Tf_2N^-]$ and could be applied with success for solvent extraction processes of various metal ions from the d- and f-series, typical p-metals, for example, Tl^+, Pb^{2+}, and Bi^{3+} or s-ions as well. Maybe, the bite angle of the HL6 molecule adapts more easily to fit the specific metal's coordination geometry and the corresponding ionic radius: increase or decrease. Only for the chemical element Ba^{2+} were similar results obtained (5% extractability) regardless of the chemical nature of the used diluent: molecular or ionic. However, it should be emphasized that aluminum can only be extracted with the solvent system HL6/$CHCl_3$. The ligand HL6 dissolved in $CHCl_3$ could also be used for the qualitative extraction of Hg^{2+}, Ag^+, Cu^{2+}, and Mg^{2+} cations with more than 30% extraction efficacity. On the other hand, this solvent system is not effective for metal ions like Bi^{3+}, Re^{7+}, Sr^{2+}, and K^+, which can only be extracted if the diluent is $[C_1C_4im^+][Tf_2N^-]$ (Figure 3).

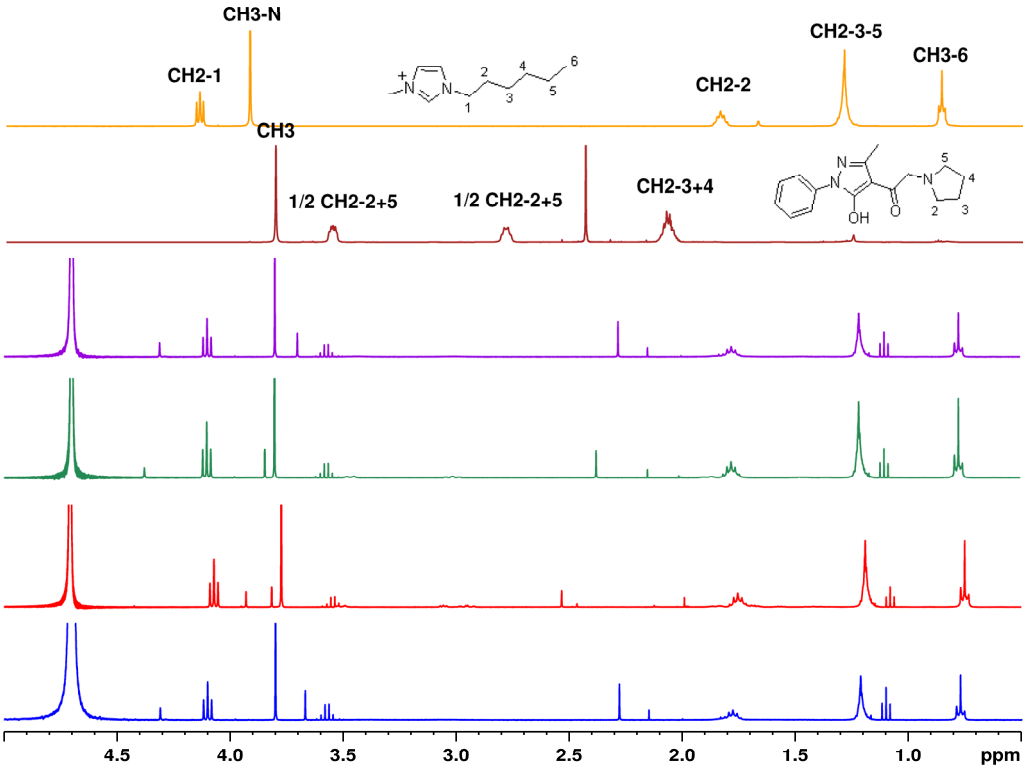


Figure 2. Partial NMR spectra investigating the HL5 solubility in the aqueous phase: D_2O (blue); 0.1 mol/dm^3 DNO_3/D_2O (red); 0.01 mol/dm^3 DNO_3/D_2O (green); and 0.001 mol/dm^3 DNO_3/D_2O (violet); as well as HL5 diluted in $CDCl_3$ (brown) and $[C_1C_6im^+][Tf_2N^-]$ diluted in $CDCl_3$ (orange).

Furthermore, competitive solvent extraction of all rare earths, excluding the radioactive Pm^{3+}, and two 5f-ions with the chelating ligand HL6 was investigated applying six ILs and five molecular diluents; see Table S1. Obviously, the applied experimental conditions, i.e., the low pH of the aqueous phase, are not so favourable for the extraction of metals. But on the other hand, this step can be used for internal 4f-group separation of metals as well as the separation of different Ln/Th pairs. For example, scandium is extracted better than other representatives of group 3 of the periodic table. Thus, the HL6 compound is an excellent ligand for the separation of pairs like Sc/Y, Sc/La, as well as most of the Sc/Ln pairs. In other words, the applied solvent system would be beneficial for both

chemical processes, solvent extraction and separation of Sc^{3+}, taking into account the fact that it is a very expensive metal due to its scarcity and the rather complicated metallurgical processes for its purification and recovery [42]. As a whole, the IL $[C_1C_4pip^+][Tf_2N^-]$ gives better results likely compared to $[C_1C_4pyr^+][Tf_2N^-]$ or $[C_1C_4im^+][Tf_2N^-]$ IL compounds for all investigated 18 f-ions. For example, the thorium element showed a maximum extraction efficiency among the other tested 17 f-ions when the solvent systems involved an IL compound. In traditional liquid–liquid separation processes, great volumes of risky or hazardous diluents are usually generated (VOCs). Therefore, the development of sustainable research and implementation of green chemical technologies with greater adoption of clean and environmentally sound innovations is an indispensable objective to protect the environment and ensure healthy lives. The results presented in Table S1 clearly show that tasted traditional organic diluents are an ineffective organic liquid medium, with a few exceptions *ca*. Sc^{3+}, Pr^{3+}, Sm^{3+}, and Er^{3+}. The effect of organic diluent on the solvent extraction of Pr^{3+} and Er^{3+} ions shows that the extraction ability increases in the order: chloroform < carbone tetrachloride < 1,2-dichloroethane < cyclohexane. This tendency is not observed for Sc^{3+} extraction into chloroform, which is a relatively nonpolar diluent, or the Sm^{3+} ion. In general, the diluent effect, when chloroform is excluded, increases when both the dielectric constant and dipole moment of the diluent decrease [43]. The ionic liquid $[C_1C_{10}im^+][Tf_2N^-]$ is likely the most fitting organic medium for the solvent extraction of rare earth metals among other hydrophobic ILs of the type $[C_1C_nim^+][Tf_2N^-]$; Table S1. Therefore, an additional study was conducted with the participation of the other remaining chelating extractants under the same experimental conditions in $[C_1C_{10}im^+][Tf_2N^-]$; Figure 4. The data obtained indicates that HL6 compound has better coordinating ability compared to the other three molecules, especially for metals in the middle of the 4f-series and 5f-ion U as well. On the other hand, the exact opposite could be reported for thorium, where molecules with a larger heterocycle fragment, such as HL7 and HL8, showed better extraction ability. Typically, the bulkiness of the ligand or its physical size causes steric hindrance, affecting the overall spatial architecture of the metal complex, but adjusting to larger bite angles likely favoured thorium in this case.

Further, to begin the assessment concerning the lanthanoids intragroup selectivity, the better solvent system HL6/$[C_1C_4pip^+][Tf_2N^-]$ can be examined by the separation factors (SFs) calculated as a ratio of the distribution ratios of two adjacent lanthanoids (the heavier and the lighter one). Their values are given in Table S2. It should be noted that a considerable loss of separation selectivity is observed across the 4f series. Additionally, it is also seen that the SF obtained for the solvent extraction of some investigated lanthanoid ions is almost similar, i.e., Lu/Ln or Ln/Gd, Ln/Nd, Ln/Tb, and Ln/Dy. Although in such solvent systems implicating an IL, an increased extractability can usually be obtained, and the selectivity is often not improved at all [15]. Unfortunately, what is usually seen in the field is that the similar size of adjacent trivalent lanthanoid cations causes the SFs to be much too small to allow for the separation of individual lanthanoids in a single extraction stage [33]. In the case under consideration, however, the high solvent extraction rate is accompanied by extremely good separation of neighbouring metals in the first half of the 4f-series (La–Eu) as well as Ln/Er pairs. The calculated SFs between lanthanum and other lanthanoid(III) ions are very high. In general, the chemical element lanthanum is present as a major constituent of monazite or fluorocarbonate ores, bauxite, and associated residues, as well as tailings and waste liquors consisting of rare earths, etc. [15,33]. Therefore, the development of new extraction systems possessing a high lanthanum selectivity in the areas of recovery and recycling is a probable improvement trend for future research studies. It should also be emphasized that the high selectivity is obtained with the participation of metals such as Gd, Tb, Dy, and Ho and the light lanthanoids in the 4f-series. For example,

the values of the SFs for pairs Gd/Ce (27), Tb/Pr (38), Ho/Sm (8), as well as the adjacent ion pair Gd/Eu (6), are more than excellent and should be highlighted as significant in the recycling chemistry of valuable metals.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Li(I) 10% 80%										$CHCl_3$ IL4	HL 6 pH_{eq}= 1.65			
Na(I) – –	Mg(II) 71% 91.6%											Al(III) 6.7% –		
K(I) – 41.2%	Ca(II) – –	Sc(III)	Ti(IV)	V(V)	Cr(III) 3.4% 100%	Mn(II) –	Fe(III) 11.2% 85.2%	Co(II) 4.3% 100%	Ni(II) 3.5% 96.5%	Cu(II) 29.9% 95.3%	Zn(II) 2.9% 92.5%	Ga(III)		
Rb(I)	Sr(II) – 89.2%	Y(III)	Zr(IV)	Nb(V)	Mo		Ru(III)	Rh(III)	Pd(II)	Ag(I) 81.5% 100%	Cd(II) 4.0% 98.0%	In(III)		
Cs(I)	Ba(II) 4.7% 5.0%	Ln(III)	Hf(IV)	Ta(V)	W(VI)	Re(VII) – 93.0%	Os(IV)	Ir(III)	Pt(IV)	Au(III)	Hg(II) 68% 96%	Tl(I) 8% 100%	Pb(II) 8.7% 93.6%	Bi(III) – 100%

La(III)	Ce(III)	Pr(III)	Nd(III)	Sm(III)	Eu(III)	Gd(III)	Tb(III)	Dy(III)	Ho(III)	Er(III)	Tm(III)	Yb(III)	Lu(III)
4.7% 98.7%	5.5% 97.4%				3.0% 97.9%	2.9% 100%							3.7% 100%

Figure 3. Solvent extraction performance of HL6 ligand (2×10^{-2} mol/dm^3) diluted in $[C_1C_4im^+][Tf_2N^-]$ or $CHCl_3$ for 27 metal ions ($[M^{n+}]_{in}$ = ~2.5×10^{-4} mol/dm^3). The reported extraction percentage values (%) represent the average of three measurements with a deviation of less than 5%.

3														
Sc – 6.5 8.5 –	IL 10													
Y – 6.0 – –	HL 5 6 7 8													
L	a	n	t	h	a	n	o	i	d	s				
La – 1.3 – –	Ce – 2.0 – –	Pr 1.9 – 6.0 4.9	Nd – 2.6 – –	Pm	Sm – 0.7 – –	Eu – 0.4 – –	Gd – 4.3 – –	Tb – 2.8 – –	Dy – 2.1 – –	Ho – 3.4 – –	Er 0.4 – 4.0 2.8	Tm – 2.6 – –	Yb – 1.4 0.3 –	Lu – 1.5 – –
A	c	t	i	n	o	i	d	s						
	Th 70.6 10.7 96.4 91.9		U – 3.8 – –											



Figure 4. Solvent extraction performance of HL5, HL6, HL7, and HL8 ligands (2×10^{-2} mol/dm^3) diluted in $[C_1C_{10}im^+][Tf_2N^-]$ for rare earth metal ions and two actinoids. The reported extraction percentage values (%) represent the average of three measurements with a deviation of less than 5%.

A second point of consideration is the evaluation of selectivity between adjacent ions in the 4f-series using two solvent systems involving the HL6 ligand, with the data presented in Figure 5. What is seen from the calculated SFs is that the nature of the diluent in use does not affect the separation of only one pair too much, e.g., U/Th ($CHCl_3$: 0.5; IL: 0.3). In fact, the chemistry of uranium solvent extraction is highly complex due to the existence of multiple oxidation states ranging from II to VI. So, the type of ligand with a desired higher affinity for uranyl ions, even in the presence of competing metal anions and cations, plays a crucial role in the efficient separation and extraction process for the sustainable utilization of uranium resources and environmental protection [44]. On the other hand, what is clearly seen is that the IL $[C_1C_{10}im^+][Tf_2N^-]$ provided a favourable mass transfer environment and separation for seven of the investigated lanthanoid pairs and Th/Lu ($CHCl_3$: 2.1; IL: 7.6), while the molecular diluent $CHCl_3$ is a better medium for metal pairs like La/Y (2.3), Pr/Ce (7.4), Sm/Nd (1.4), Er/Ho (1.0), and Yb/Tm (5.3). Therefore, the effect of a diluent clearly occurs during the extraction process of rare earth metals and could be used as a selective strategy in the field. So, the choice of diluent is a very crucial step not only for extraction enhancement but also for the effective separation of metals. The obtained results may have a great significance in the mutual separation of trivalent Lns, as a different scientific approach with regard not only to the choice and design of new "remarkable" molecules but also to applying different organic media as well.

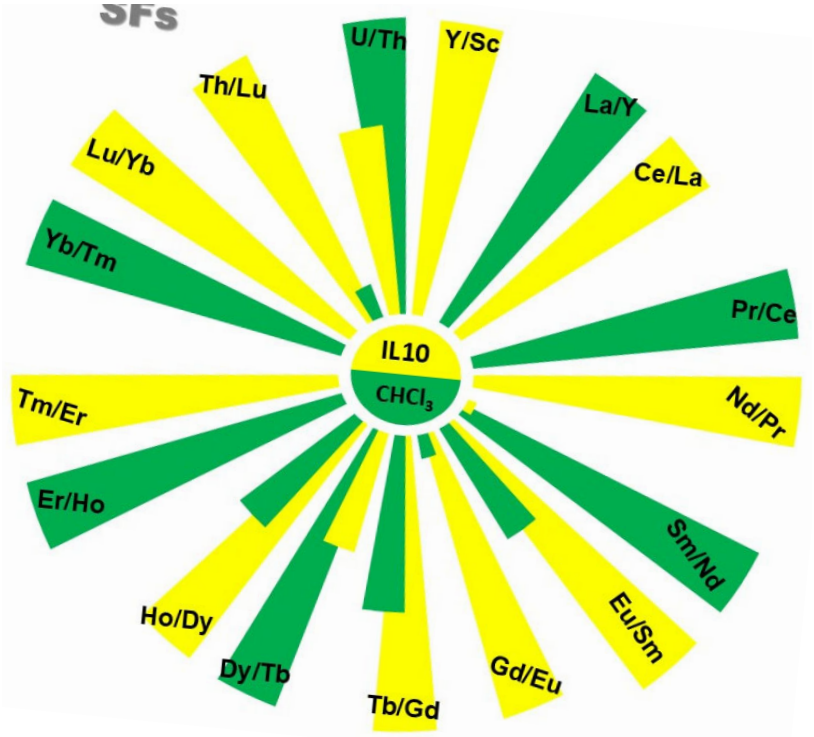


Figure 5. The SFs data visualization of two HL6 solvent systems, including $CHCl_3$ and $[C_1C_{10}im^+][Tf_2N^-]$ diluents, with a Nightingale rose diagram.

2.3. Chemical Mechanism of Lanthanoids Solvent Extraction Process

The ionic character of IL compounds has an essential influence on the solvent extraction process of metallic species from the aqueous phase, and the reaction mechanisms are often quite different without an analogue in VOC-based solvent systems [15,33]. The stoichiometry of the metal–ligand complex formed during the equilibrium in the organic layer can be obtained by the slope analysis method, which is the most widely used technique in solvent extraction chemistry, employing traditional organic diluents because of its simplicity and effectiveness [19,45]. In IL solvent systems, the slope analysis of Ln^{3+}

extraction with the tested four ligands was investigated as a function of pH in the aqueous phase and HLn concentration in the IL phase in order to determine the reaction mechanism and the stoichiometry of the Ln^{3+}–HL complexes formed in the $[C_1C_6im^+][Tf_2N^-]$ organic phase. The variation in log*D* for La^{3+}, Nd^{3+}, Eu^{3+}, and Dy^{3+} ions as a function of HLn concentrations is shown in Figures 6, 7, S4 and S5. It is noted that only the Dy^{3+} ion could be extracted with lower concentrations of the examined ligands, such as 3×10^{-3} mol/dm^3. Moreover, the experiment was performed in the presence of four metal ions in the aqueous phase (La^{3+}, Nd^{3+}, Eu^{3+}, and Dy^{3+} as representatives of light, middle, and heavy ions in the 4f-series), i.e., not for a single metal ion. The log-log dependences obtained represent straight lines with slopes of nearly 3 or 4 when applying the different solvent systems.

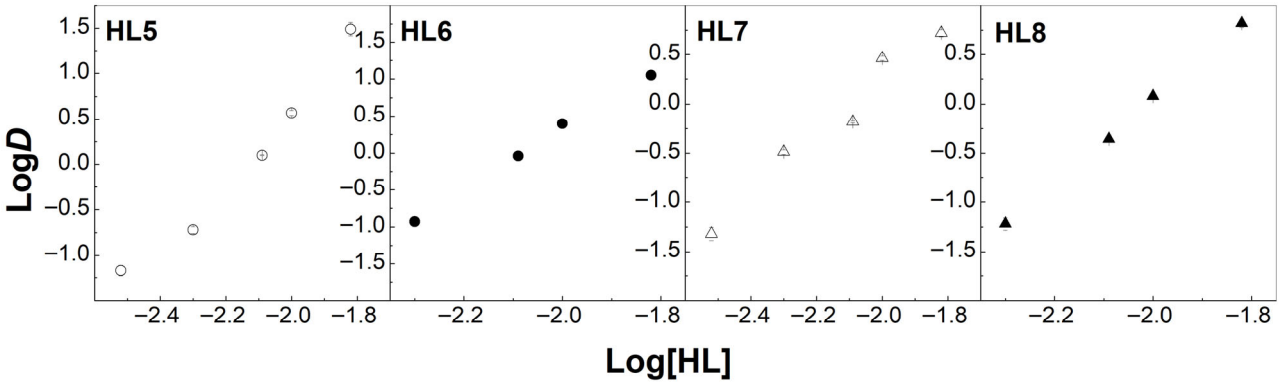


Figure 6. Log *D vs.* log $[HL]_{IL}$ plots at pH = 2.40 for Eu^{3+} ion in $[C_1C_6im^+][Tf_2N^-]$ (slopes 3.81, 4.15, 2.92, and 4.27).

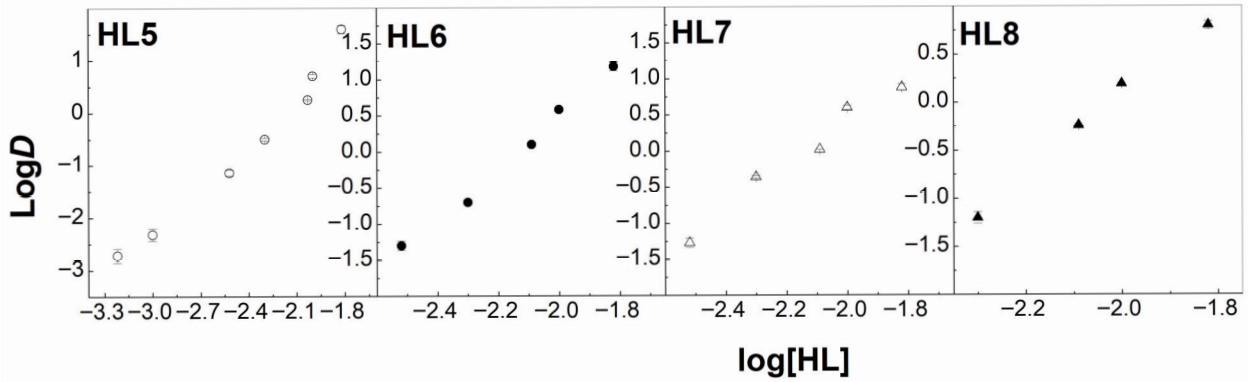


Figure 7. Log *D vs.* log $[HL]_{IL}$ plots at pH = 2.4 for Dy^{3+} ion in $[C_1C_6im^+][Tf_2N^-]$ (slopes 2.97, 3.63, 3.07, and 4.20).

The results indicate that three protons from the HLn molecules were exchanged for one La^{3+} ion during the solvent extraction process; Figure S4. The neutral chelates of the type LnL_3 were established for the following researched systems too: Nd^{3+}–HL7/HL8, Eu^{3+}–HL7, and Dy^{3+}–HL5/HL7. In this study, the slope analysis of La^{3+} extraction clearly expresses the formation of neutral chelates in the $[C_1C_6im^+][Tf_2N^-]$ media, applying the four studied compounds. The reaction mechanism—when a metal cation forms a chelate complex with available ligands and moves into the organic phase as a single, neutral, uncharged species—was represented by the following equation:

$$Ln^{3+}{}_{aq} + 3HL_{IL} \leftrightarrow LnL_{3IL} + 3H^+{}_{aq} \quad (1)$$

where the subscript "aq" denotes aqueous phase and "IL" denotes organic, ionic liquid phase.

Furthermore, it seems that the La^{3+} ion extraction behaviour in the IL medium is influenced qualitatively but quantitatively by the nature of heterocyclic substituents of the

HL molecule. The values of distribution ratios (*D*) increased in the following approximative order of heterocyclic receptor size, i.e., 8 < 6 < 7 < 5. This result is thought to originate in a size-fitting effect of HLn molecules to the lighter Ln^{3+}, lanthanum. Thus, simple modification of the structural features of a chelating reagent represents a significant change in this regard [34].

However, the studied plots of log*D vs.* chelating ligand concentrations were linear with a slope of ~4 for the Nd^{3+} ion with HL5 or HL6 ligands, for Eu^{3+} with HL5, HL6, and HL8, as well as for the Dy^{3+} solvent extraction with HL6 or HL8 compounds. Thus, four HL molecules were required to extract one Ln^{3+} ion into the $[C_1C_6im^+][Tf_2N^-]$ phase in a 1:4 metal-to-ligand ratio in these investigated research cases. Consequently, an anionic tetrakis complex is formed in the organic phase: $[LnL_4{}^-]$, (L^- represents the HL anion). Additionally, the coordination numbers of mononuclear β-dicarbonyl lanthanoid complexes are generally high, varying from 6 to 12, with 8 being rather common [46]. While metal ions generally exist in the form of neutral hydrophobic complexes in molecular liquids, charged metallic complexes highly soluble in the IL phase may pertain in the ionic solvation environment [19,21,29,46]. The solvent extraction of anionic complexes is possible by the exchange of the IL anions ($[Tf_2N^-]$) into the aqueous phase, so that the extraction process of Ln^{3+} ions with the HLn molecule in the IL system can be expressed by the following equation:

$$Ln^{3+}{}_{aq} + 4HL_{IL} + Tf_2N^-{}_{IL} \leftrightarrow LnL_4{}^-{}_{IL} + 4H^+{}_{aq} + Tf_2N^-{}_{aq} \quad (2)$$

For instance, it is obvious that these two different chemical reaction mechanisms are in competition regarding the complementarity between the size of the metal cation and the size of the heterocyclic receptor of HLn molecules (*n* = 5, 6, 7, and 8). It cannot be ignored that larger molecules are usually much more flexible for coordination assignment in solutions due to their rigidity. Therefore, by appropriate means, the chemical structure of the heterocycles can be modified in "tune" to make the ligands suitable for use in separation and coordination chemistry. When the reaction in the organic phase is via the ion-exchange mode, the solvent extraction of metal ions is more efficient in the solvent system of a shorter alkyl IL's chain due to the hydrophobicity of IL ions, of course [30]. Generally, the great variety of possible lanthanoid−HL complexes, however, affords the chemical ionic systems considerable freedom in selecting between solvent extraction mechanisms involving neutral, cationic, or anionic species depending on the experimental purpose [15,33,47–49]. Thus, the chemical picture regarding the reaction mechanism is less straightforward in an ionic medium.

Secondly, a common picture is obtained when the diluent $[C_1C_6im^+][Tf_2N^-]$ is replaced by chloroform, i.e., a much higher concentration of the ligands is required to extract the metals, which is a serious disadvantage, more than 1×10^{-2} mol/dm^3. Under the experimental conditions applied herein, only the HL5 ligand extracts the Ln metals without lanthanum; Figure S6. Thus, an increase in the extraction efficiency is observed going from La^{3+} to Lu^{3+} at these experimental concentrations of the chelating extractants and pH of the aqueous phase. The overall quantitative extraction process is basically achieved in moderately acidic solutions (pH $\geq$ 2 for middle and heavy Ln^{3+}) [50]. However, the remaining three ligands do not show extraction ability at this relatively low pH of the aqueous phase in equilibrium, ca. 2.15. Hence, the unique physicochemical properties of ionic type organic liquid phase induced better solvent extraction performance in comparison to a molecular one ($CHCl_3$).

Moreover, after forward solvent extraction, the four Ln^{3+} ions studied were subsequently stripped from the investigated organic ionic phases. The achieved 4f-metals removal percentage is *ca.* 95% using 1 mol/dm^3 HNO_3 acid as a stripping agent for the

back extraction procedure. In general, stripping action can be achieved easily for similar IL-based systems with chelating molecules applying mineral acid solutions [15,33,46].

2.4. Solvent Extraction and Selectivity Among Platinum Group Metals and Refractory Metals

As a matter of fact, 16 systems involving the four ligands and four diluents were studied for their application in the solvent extraction chemistry for noble metals (PGMs), Figures 8 and S7–S9. What is clearly visible from the obtained results is that Ru and Rh are somehow extracted only with the solvent system HL5/$CHCl_3$. On the other hand, Pd can be extracted with all ligands when two of the diluents are used, i.e., $CHCl_3$ and $[C_1C_{10}im^+][Tf_2N^-]$. This is also characteristic of Ir, but with the difference that the HL8 ligand is not active in chloroform medium. One of the three ionic liquids, namely $[C_1C_{10}im^+][Tf_2N^-]$, is the diluent with extremely pronounced selectivity for the solvent extraction of Re. However, it should be emphasized that only the HL5 compound dissolved in two other diluents is effective for this metal; Figure S7. Moreover, two of the investigated metals, Os and Au, are extracted quantitatively (in most cases $\geq$ 90%) with all 16 tested solvent systems. To some extent, this is also observed for Pt but excluding the ionic liquid medium $[C_1C_4pip^+][Tf_2N^-]$. Furthermore, it can be concluded categorically that the compound $[C_1C_{10}im^+][Tf_2N^-]$ is the most suitable diluent for this group of metals. All of these findings will be useful to one degree or another, given that almost all worthy secondary materials that typically have a higher concentration of PGMs are more readily available than natural resources, rendering them a perfect choice for accessing and future valorization.

7	8	9	10	11
			HL 6	
	Ru – – – –	Rh – – – –	Pd 35.2% – 64.1% –	$CHCl_3$ IL4 IL10 IL4pip
Re – – 70.0% –	Os 92.0% 65.2% 96.7% 70.2%	Ir 1.2% – 61.3% –	Pt 68.9% 27.9% 93.9% –	Au 98.2% 92.6% 98.8% 94.3%

Figure 8. Solvent extraction performance of HL6 ligand (2×10^{-2} mol/dm^3) diluted in $CHCl_3$ or three ILs, $[C_1C_4im^+][Tf_2N^-]$, $[C_1C_{10}im^+][Tf_2N^-]$, and $[C_1C_4pip^+][Tf_2N^-]$ for 8 platinum group metals. The reported extraction percentage values (%) represent the average of three measurements with a deviation of less than 5%.

A comparative analysis of the solvent extraction of 12 refractory metals with the synthesized four ligands using two types of diluents was also performed. From the data presented in Figure 9, it can be seen that the ligand HL5 extracts only tin (W) when dissolved in chloroform and tantalum (Ta) when an ionic liquid is used. The two ligands HL7 and HL8 can also be used for the selective extraction chemistry of tantalum. On the other hand, partial extraction of tin with them has also been observed when using chloroform. Among the four ligands tested, only HL6 dissolved in $CHCl_3$ was effective for the solvent extraction process of almost all metals from this series, i.e., Ti, Ge, Sb, Zr, Nb, Mo, Hf, and Ta, without Sn. In other words, 100% extraction of the metals was achieved with the system HL6/$CHCl_3$. Unfortunately, the solvent system involving the

ionic liquid [$C_1C_4im^+$][Tf_2N^-] resulted in the negligible extraction of only silicon (Si). The observed chemical trend is probably due to the better solubility of the chelating ligands in chloroform compared to the ionic liquid. This is also one of the main disadvantages of these compounds used as diluents, which is also the main reason for the not-so-effective interfacial reactions observed in solvent extraction chemistry. It cannot be ignored that, generally, organic molecules have different solubility in organic diluents affected by the size of the side ring (n = 5, 6, 7, and 8).

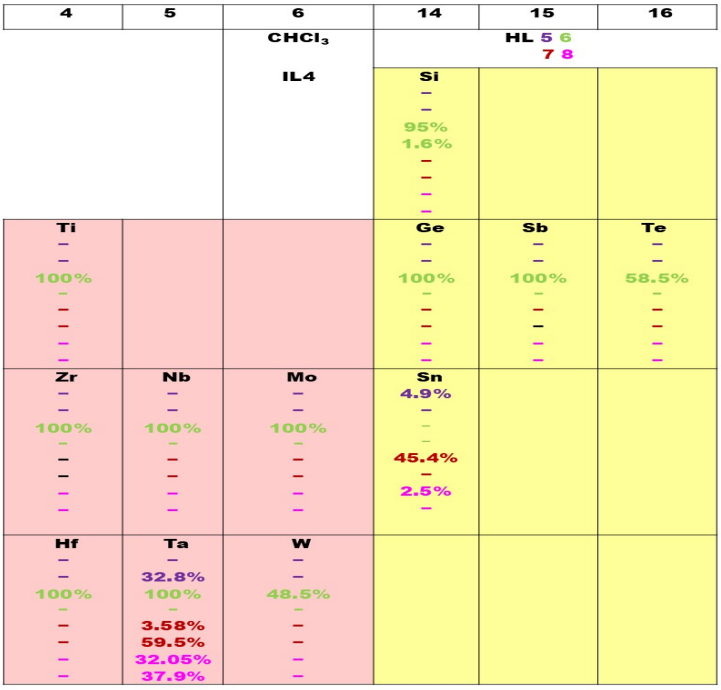


Figure 9. Solvent extraction performance of HL ligands (1×10^{-2} mol/dm^3) diluted in [$C_1C_4im^+$][Tf_2N^-] or $CHCl_3$ for 12 refractory metal ions. The reported extraction percentage values (%) represent the average of three measurements with a deviation of less than 5%.

3. Materials and Methods

3.1. Materials

All reagents were purchased from Aldrich (San Diego, CA, USA), Merck (Darmstadt, Germany), and Fluka (London, UK) were used without further purification. The diluents were 1-butyl-, 1-hexyl-, 1-octyl-, 1-decyl-3-methylimidazolium-bis(trifluoromethanesulfonyl)imides, (purity, 99.5%, average water content is *ca*. 200 ppm) purchased from Solvionic (Toulouse, France), 1-butyl-1-methylpiperidinium bis(trifluoromethanesulfonyl)imide (Sigma-Aldrich, Taufkirchen, Germany 97%), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Sigma-Aldrich, ≥98%), C_6H_6 (Merck, 99,7%), CCl_4 (Fluka, p.a.), $C_2H_4Cl_2$ (Merck, p.a.), $CHCl_3$ (Merck, p.a.), and C_6H_{12} (Merck, p.a.).

The deuterated diluents were purchased from Deutero GmbH (Kastellaun, Germany). The mineral acid DNO_3 (65%) in D_2O, (99 atom % D), was purchased from Sigma-Aldrich.

The ligands HL5–HL8, shown in Figure 1, were synthesized as described previously by us in ref. [34]. Shortly, a mixture of 4-(chloroacetyl)-3-methyl-1-phenyl-pyrazol-5-one, the corresponding cyclic amine, and caesium carbonate as a base in acetonitrile was stirred at room temperature until full conversion, followed by column chromatography purification on silica gel.

ICP-MS refractory elements standard—12 components: 10 mg/dm^3 ± 0.022–0.059 mg/dm^3 each of Ge, Hf, Mo, Nb, Sb, Si, Sn, Ta, Te, Ti, W, and Zr (CPAchem Ltd., Bogomilovo, Bulgaria.)—was used. ICP MISA Standard 1 (from CPAchem Ltd., Bogomilovo, Bulgaria),

Rare earth metals, and 18 components were used: 100 mg/dm^3 each of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, U, Y, and Yb in 5% HNO_3. ICP Standard solution of 8 components 100 mg/dm^3 each of Au, Ir, Os, Pd, Pt, Re, Rh and Ru was used (from CPAchem Ltd., Bulgaria). The following metal salts were used: $Eu(NO_3)_3 \cdot 5H_2O$ (Sigma Aldrich, 99.9%), $La(NO_3)_3 \cdot 6H_2O$ (Sigma Aldrich, 99.9%), $Dy(NO_3)_3 \cdot H_2O$ (Sigma Aldrich, 99.9%), and $Nd(NO_3)_3 \cdot 6H_2O$ (Sigma Aldrich, 99.9%). All other commercially available analytical grade reagents were used without any further purification.

Stock solutions of La^{3+}, Nd^{3+}, Eu^{3+}, and Dy^{3+} ions (1.5×10^{-3} mol/dm^3) were prepared from corresponding nitrate salts by dissolving and diluting with distilled water to the required volume. The Ln(III) ion initial concentration was 5×10^{-4} mol/dm^3. Nitric acid 65% was used (Merck, p.a.) to adjust the pH of the aqueous solutions and was added to 0.1 mol/dm^3 2-morpholinoethanesulfonic acid (MES) buffer (Alfa Aesar, 98% (Karslruhe, Germany)).

3.2. Solvent Extraction Studies

Solvent extraction experiments were carried out at room temperature by mixing the two immiscible liquid phases in a 1:1 v/v ratio (1.5 mL) for 2 h (1500 rpm), which was sufficient for attaining equilibrium. After the separation of the liquid phases, the Ln(III) ion concentration in the aqueous phase was determined by using ICP-OES spectroscopy ("Prodigy" High dispersion ICP-OES, Teledyne Leeman Labs, Mason, Ohio, USA). The concentration of the metal ion in the organic phase was obtained by material balance. Extractant solutions in an IL were prepared by precisely weighted samples. The acidity of the aqueous phase at equilibrium was measured by a pH meter (pH 211 HANNA, Smithfield, RI, USA) with an accuracy of 0.01 pH unit.

For competitive extraction tests, a volume of 2 mL of the prepared aqueous solution containing various M^{n+} metal ions (initial ~2.5×10^{-4} mol/dm^3; the corresponding nitrate salts were used $M^{n+}(NO_3)_n/M^{n+}(NO_3)_n \cdot xH_2O$), f-ions (initial ~$3.3 \times 10^{-4}$ mol/dm^3), platinum group metals (initial ~3.3×10^{-4} mol/dm^3), or various refractory elements (initial: ~1×10^{-4} mol/dm^3) was equilibrated for 3 h (1500 rpm) with 2 mL organic phase, which includes the studied ligand molecule, HLn. After phase separation, the metal ion concentrations in the aqueous solution were determined by ICP-OES.

The distribution ratio (D) at equilibrium was calculated as:

$$D = \frac{[M^{n+}]_{aq,in} - [M^{n+}]_{aq,f}}{[M^{n+}]_{aq,f}} \times \frac{V_{aq}}{V_{IL}} \quad (3)$$

where $[M^{n+}]_{aq,in}$ is the concentration of M^{n+} ion in the aqueous phase before liquid–liquid extraction tests, and $[M^{n+}]_{aq,f}$ is the concentration of the same metal ion in the aqueous phase after extraction. In general, V_{aq} and V_{IL} are the volumes of aqueous and organic phases used to perform experiments, herein, a 1:1 v/v extraction. For instance, duplicate experiments showed that the reproducibility of D measurements was generally within 95%.

The extraction percentage (% E) was evaluated as:

$$\% \, E = \frac{[M^{n+}]_{aq,in} - [M^{n+}]_{aq,f}}{[M^{n+}]_{aq,in}} \times 100 \quad (4)$$

The metal separation between elements in the periodic table can be estimated using separation factors (SF) determined as a ratio of distribution ratios of two metal ions, the heavier and lighter one:

$$SF = D_{(Z+n)}/D_{(Z)} \quad (5)$$

3.3. Investigation of Ligand's Solubility in Water Through NMR Spectroscopy

The possible solubility of the ligand HL5, ([HL5] = 1×10^{-2} mol/dm^3) diluted in [$C_1C_6im^+$][Tf_2N^-]), in the aqueous phase was investigated using nitric acid media, i.e., D_2O, 1×10^{-1}, 1×10^{-2}, and 1×10^{-3} mol/dm^3 DNO_3. Equal volumes of the two liquid phases (2 cm^3) were equilibrated for 2 h at (22 ± 2) °C by mechanical shaking. After centrifugation and phase separation, the upper phase (the term "aqueous" refers to D_2O) was taken for measurements. The NMR spectra were recorded on a Bruker Avance NEO 400 spectrometer (Rheinstetten, Germany). The spectra were processed with the Topspin 3.6.3 program.

4. Conclusions

In the present study, the solvent extraction behaviour of lanthanoids with four new chelating compounds (HLn) was comprehensively investigated in different organic liquid media: ~11. These coordination reagents were designed with the CHON principle in mind, regarding, for example, extractant recycle or organic waste minimization that can be factored into a more environmentally friendly approach to hydrometallurgical separation processes. The following order of effectiveness can be roughly deduced concerning Ln^{3+} ions: HL6 > HL5 > HL7 > HL8. The lanthanoid solvent extraction process was confirmed to proceed through a proton-exchange scheme, forming 1:3 complex (LnL_3) or anionic tetrakis entities (LnL_4^-) in [$C_1C_6im^+$][Tf_2N^-] medium due to the different researched solvent systems. Furthermore, the mutual separation abilities of HLn compounds towards lighter Lns (La-Ce-Pr) and Sc are higher than the heavier representatives of the 4f-series. It was found that the IL compound [$C_1C_4pip^+$][Tf_2N^-], used as an organic medium, gives better results compared to the other two cations, i.e., [$C_1C_4pyr^+$] or [$C_1C_4im^+$], for all 18 investigated f-ions. Lastly, the unique physicochemical properties of the ionic type organic liquid phase induced better solvent extraction performance in comparison to the molecular one.

Finally, testing was carried out for the applicability of these new chelating ligands for the competitive removal of rare earth ions from leach solution containing various s-, p-, and d-cations. All the metals from the periodic table were quantitatively transferred from acidic nitrate solutions with the HL6 compound, showing higher selectivity for refractory metals in [$C_1C_4im^+$][Tf_2N^-] media or platinum group metals in [$C_1C_{10}im^+$][Tf_2N^-]. The effectiveness of the reagent HL6 has considerable coordination ability and selectivity viz.: (i) the excellent separation of Sc^{3+} from 4f metal ions; (ii) the possible future recycling of Ni^{2+} and Co^{2+} from electronic wastes or spent lithium-ion batteries; (iii) considering the 3d series, its extraction efficiency was in the following order: $Cr^{3+} \approx Co^{2+} > Ni^{2+} \approx Cu^{2+} > Zn^{2+} > Fe^{3+}$; (iv) the capacity of selective recovery of Os, Au, and Pt. That is to say, the nature of the metal ion definitely has a fundamental relevance. The present scientific findings will be a serious contributor to further developments in separation solvent extraction chemistry for various metal ions, where selective ligand coordination plays a crucial role.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules31040656/s1, Figure S1. NMR spectra of HL5/D_2O (blue); HL5/$CDCl_3$ (red); and $C_1C_6imTf_2N$/$CDCl_3$ (green). Figure S2. NMR spectra investigating the HL5 solubility in the aqueous phase: D_2O (blue); 0.1 mol/dm^3 DNO_3/D_2O (red); 0.01 mol/dm^3 DNO_3/D_2O (green); and 0.001 mol/dm^3 DNO_3/D_2O (violet); as well as L5 diluted in $CDCl_3$ (yellow) and [$C_1C_6im^+$][Tf_2N^-] diluted in $CDCl_3$ (orange). Figure S3. Solvent extraction performance of HL5, HL7, and HL8 ligands (2×10^{-2} mol/dm^3) diluted in [$C_1C_4im^+$][Tf_2N^-] or $CHCl_3$ for 27 metal ions ($[M^{n+}]_{in}$ = ~2.5×10^{-4} mol/dm^3). The reported extractability values (%) represent the average of three measurements with a deviation of less than 5%. Table S1. Competitive solvent extraction of rare earths and two 5f-ions with the chelating ligand [HL6] = 2×10^{-2} mol/dm^3 at pH_{in} = 0.51

of the aqueous phase (V_{aq}:V_o = 2 mL:2 mL; 0.5 mL 0.1 mol/dm^3 MES). The reported extractability values (%) represent the average of three measurements with a deviation of less than 5%. Table S2. Values of the SFs of two adjacent Lns (the heavier and the lighter one) with the HL6 ([HL6] = 2 × 10^{-2} mol/dm^3)/[$C_1C_4pip^+$][Tf_2N^-] system. Figure S4. Log *D vs.* log $[HL]_{IL}$ plots at pH = 2.4 for La^{3+} ion in [$C_1C_6im^+$][Tf_2N^-] (slopes 3.12, 3.02, 3.11, and 3.25). Figure S5. Log *D vs.* log $[HL]_{IL}$ plots at pH = 2.4 for Nd^{3+} ion in [$C_1C_6im^+$][Tf_2N^-] (slopes 4.00, 4.3, 2.88, and 2.99). Figure S6. Solvent extraction performance of HL5 ligand (1.5 × 10^{-2} mol/dm^3 or 1 × 10^{-2} mol/dm^3) at pH = 2.15 diluted in $CHCl_3$ for 4 Ln ions (1—La, 2—Nd, 3—Eu, 4—Dy). The reported extractability values (%) represent the average of three measurements with a deviation of less than 5%. Figure S7. Solvent extraction performance of HL5 ligand (2 × 10^{-2} mol/dm^3) diluted in $CHCl_3$ or three ILs ([$C_1C_4im^+$][Tf_2N^-], [$C_1C_{10}im^+$][Tf_2N^-], and [$C_1C_4pip^+$][Tf_2N^-]) for 8 platinum group metals. The reported extractability values (%) represent the average of three measurements with a deviation of less than 5%. Figure S8. Solvent extraction performance of HL7 ligand (2 × 10^{-2} mol/dm^3) diluted in $CHCl_3$ or three ILs ([$C_1C_4im^+$][Tf_2N^-], [$C_1C_{10}im^+$][Tf_2N^-], and [$C_1C_4pip^+$][Tf_2N^-]) for 8 platinum group metals. The reported extractability values (%) represent the average of three measurements with a deviation of less than 5%. Figure S9. Solvent extraction performance of the HL8 ligand (2 × 10^{-2} mol/dm^3) diluted in $CHCl_3$ or three ILs ([$C_1C_4im^+$][Tf_2N^-], [$C_1C_{10}im^+$][Tf_2N^-] and [$C_1C_4pip^+$][Tf_2N^-]) for 8 platinum group metals. The reported extractability values (%) represent the average of three measurements with a deviation of less than 5%.

Author Contributions: Conceptualization, M.A.; methodology, M.A.; validation, M.A.; investigation, M.A., V.K. and S.T.; writing—original draft preparation, M.A.; writing—review and editing, M.A. and V.K.; visualization, M.A. and V.K.; project administration, M.A.; funding acquisition, M.A. All authors have read and agreed to the published version of the manuscript.

Funding: The research leading to those results received funding from the Bulgarian Science Fund: Grant Agreement No. KP-06-H69/5(2022), "*Green twist to synergistic solvent extraction and separation of rare earth metals*" as well as by the European Union-NextGenerationEU, through the National Recovery and Resilience Plan of the Republic of Bulgaria, project No. BG-RRP-2.004-0002, "BiOrgaMCT".

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflicts of interest.

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