

Extraction properties of β -aminophosphine oxides towards lanthanides and alkaline earth metals

Research Article

Ekaterina V. Matveeva^{1*}, Elena V. Sharova¹,
Alexander N. Turanov², Vasilii K. Karandashev³, Irina L. Odinets¹

¹A. N. Nesmeyanov Institute of Organoelement Compounds,
Russian Academy of Sciences, Moscow 119991, Russia

²Institute of Solid State Physics, Russian Academy of Sciences,
Chernogolovka 142432, Russia

³Institute of Microelectronics Technology and High Purity Materials,
Russian Academy of Sciences, Chernogolovka 142432, Russia

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Abstract: The investigation of the extraction properties of a series of polyoligodentate β -aminophosphine oxides **1-8** bearing from one to six phosphine oxide groups in a molecule towards Ln(III) and alkaline earth metals ions from neutral media has revealed that, using common diluents, the extraction efficiency increases with an increase of a number of P=O functions in a ligand. The addition of ionic liquid, namely 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([bmim][NTf₂]), significantly increasing the extraction efficiency and application of IL concentration of 0.05 M (in 1,2-dichloroethane) providing the maximum recovery of metal ions with Lu/La separation factor reaching up to 91. Hexapodal tris[bis(2-diphenylphosphorylethyl)aminoethyl]amine **8** demonstrates the highest extraction under all conditions applied and the separation factor for U and Eu of this compound exceeded 10³.

Keywords: β -aminophosphine oxides • Lanthanides(III) • Alkaline earth metals • Ionic liquids • Liquid-liquid extraction

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1. Introduction

β -Aminophosphoryl compounds are shown to exhibit a wide range of bioactivities such as antibacterial, anti-HIV, and protease-inhibiting activities [1,2]. At the same time, despite the presence of two donor centers, their coordination potential seems to be underappreciated [3-6]. However, the complexing properties of some representatives of β -aminophosphoryl derivatives evidence their usefulness in the construction of catalytically active metal complexes, as was demonstrated for ruthenium catalyzed asymmetric transfer hydrogenations [7-9], design of selective ionophores or membrane carriers [10,11] as well as liquid-liquid extraction processes. Nevertheless, to the best of our knowledge the investigations in this area are limited to the above mentioned publications and are especially scarce in the field of extraction where the known data concern the extraction from acidic media of some Ln(III) ions [12],

U [13], and I and II group metals as well as transition ones [14] with only a few ligands.

Recently we have developed a practical, efficient, easy-to-scale, and cheap synthetic approach to β -aminophosphoryl compounds via the aza-Michael reaction in water in the absence of any catalyst or co-solvent [15-17]. In contrast to the classical procedures suggested previously for this reaction, the aqueous version can readily provide, depending on the reactant ratio, both common monophosphorylethylamines and their bisphosphorylated analogues. Owing to the quantitative yields of products in most cases, the compounds of both types could be isolated via simple freeze-drying of the reaction mixtures.

Taking into account the complexing properties of these compounds and their easy availability via the suggested synthetic methodology, it seems reasonable to perform the systematic study of their extraction properties in order to estimate the influence of a ligand structure, including the

* E-mail: matveeva@gmail.com

amount of phosphoryl groups, and extraction conditions on the extraction efficiency. Herein, we report the results of this study towards lanthanide(III) and alkaline earth metal ions, obtained using both common diluents and their mixtures with 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([bmim][NTf₂]) ionic liquid. Structure-extraction properties relationships are also revealed.

2. Experimental procedure

2.1. General remarks

All chemicals were purchased as reagent grade from Acros and Aldrich and used without further purification. The NMR spectra were recorded on a Bruker AMX-400 instrument. The chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (¹H and ¹³C) or externally to H₃PO₄ (³¹P). IR spectra were recorded on a Magna-IR 750 FTIR spectrometer (Nicolet Co., resolution 2 cm⁻¹, scan number 128, KBr pellets). Melting points were determined with an Electrothermal IA9100 Digital Melting Point Apparatus and were uncorrected. 1-Butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([bmim][NTf₂]) was prepared and purified according to the published procedure [18]. Chemical and analytical grade nitrobenzene, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, and chloroform were used as diluents.

2.2. Synthesis of the ligands

The ligands **1-4,7,8** were obtained via the procedures described by us previously and their physicochemical constants fit well with the reported literature data [16]. The novel ligands **5**, **6** were prepared by the same aqueous methodology from *m*-xylylenediamine and diphenylvinylphosphine oxide used in 1:2 and 1:4 ratio, respectively.

1,3-Bis{[(diphenylphosphoryl)ethyl]aminomethyl}benzene (5). Diphenylvinylphosphine oxide (1 g, 4.4 mmol) was added to a solution of *m*-xylylenediamine (300 mg, 2.2 mmol) in water (5 ml) at room temperature and resulting mixture was stirred at 100°C for 5 h. The solvent was removed by freeze-drying to give **5** as an off-white hygroscopic powder (380 mg, 95%). M.p. 75°C; ³¹P NMR (162 MHz, CDCl₃) δ_P 31.43; ¹H NMR (400 MHz, CDCl₃) δ_H 1.70 (br. s, 2H, NH), 2.52 (dt, 4H, ²J_{PH} = 11.2 Hz, ³J_{HH} = 7.4 Hz, PCH₂), 2.96 (dt, 4H, ³J_{PH} = 11.6 Hz, ³J_{HH} = 7.4 Hz, NCH₂), 3.69 (s, 4H, CH₂C₆H₄), 7.03-7.21 (m, 4H, C₆H₄), 7.38-7.51, 7.62-7.74 (both m, 12H+8H, C₆H₅); ¹³C NMR (101 MHz, CDCl₃) δ_C 29.94 (d, ¹J_{PC} = 71.0 Hz, PCH₂), 42.09 (NCH₂), 53.19 (CH₂C₆H₄), 126.35

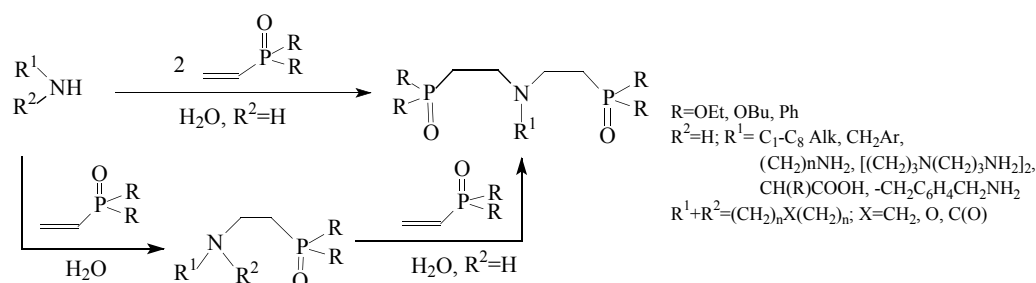
(C⁴, C⁶), 127.34 (C⁵), 128.08 (C²), 128.34 (d, ³J_{PC} = 11.6 Hz, *m*-C₆H₅), 130.34 (d, ²J_{PC} = 9.3 Hz, *o*-C₆H₅), 131.42 (*p*-C₆H₅), 132.67 (d, ¹J_{PC} = 98.5 Hz, *ipso*-C), 139.59 (C¹, C³); IR (KBr, ν , cm⁻¹): 1181 (P=O), 3286 (NH), 3316, 3350 (br., H₂O); Anal. Calcd for C₃₆H₃₈N₂O₂P₂•1.5 H₂O: C, 69.79; H, 6.14; N, 4.52%. Found: C, 69.91; H, 6.38; N, 4.58%.

1,3-Bis{[(N,N-bis[(diphenylphosphoryl)ethyl])aminomethyl]benzene (6)} was prepared in an analogous manner from diphenylvinylphosphine oxide (0.68 g, 3 mmol) and *m*-xylylenediamine (100 mg, 0.75 mmol) over 24 h. After freeze-drying the crude product was purified by column chromatography (SiO₂, CHCl₃:methanol, 100:5). Off-white powder (465 mg, 60%); m.p. 142°C; ³¹P NMR (162 MHz, CDCl₃) δ_P 31.45; ¹H NMR (400 MHz, CDCl₃) δ_H 2.31-2.35 (m, 8H, PCH₂), 2.74-2.78 (m, 8H, NCH₂), 3.42 (s, 4H, CH₂C₆H₄), 6.91-6.92 (m, 3H, C₆H₄), 7.02 (t, 1H, ³J_{HH} = 6.9 Hz, C₆H₄), 7.38-7.46, 7.60-7.67 (both m, 24H+16H, C₆H₅); ¹³C NMR (101 MHz, CDCl₃) δ_C 30.02 (d, ¹J_{PC} = 70.0 Hz, PCH₂), 45.15 (NCH₂), 55.23 (CH₂C₆H₄), 126.35 (C², C⁴), 128.10 (C³), 129.03 (C⁶), 130.15 (d, ³J_{PC} = 11.2 Hz, *m*-C₆H₅), 130.64 (d, ²J_{PC} = 9.0 Hz, *o*-C₆H₅), 132.26 (*p*-C₆H₅), 132.84 (d, ¹J_{PC} = 97.5 Hz, *ipso*-C), 139.15 (C¹, C⁵); IR (KBr, ν , cm⁻¹): 1180 (P=O), 3429 (br., H₂O); Anal. Calcd for C₆₄H₆₄N₂O₄P₄: C, 73.27; H, 6.15; N, 2.67%. Found: C, 72.88; H, 5.90; N, 2.43%.

2.3. Extraction properties

Extractant solutions in the organic diluents were prepared from precisely weighed amounts of the reagents. The initial concentration of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, U, Th, Ca, Sr, and Ba was 1×10⁻⁵ M for each element. All lanthanides (III) (except Pm) were present in the initial aqueous phase when simultaneous extraction of Ln(III) was studied. The experiments were carried out in ampoules with ground stoppers at 20-25°C. The volumes of both organic and aqueous phases were equal to 2 mL. The solution was stirred on a rotary mixer for an hour to achieve the equilibrium. Preliminary experiments showed that this time period was more than sufficient for chemical equilibrium to be reached. After the extraction, 0.5 mL of the aqueous solution was taken for further analysis. A portion of the organic phase was transferred to another glass tube, and an equal volume of the 1-hydroxyethane-1,1-diphosphonic acid solution was added. The mixture was shaken for 20 min resulting in back extraction of used element (Ln(III), U(IV), Th(IV), Ca(II), Sr(II), and Ba(II)) into the aqueous phase.

Metal concentrations in the initial and equilibrium aqueous solutions after extraction and back extraction were determined by inductively coupled plasma mass-



Scheme 1. General method for the synthesis of β -aminophosphoryl compounds via the aza-Michael reaction in water.

spectrometry (ICP-MS) on a X-7 mass spectrometer with quadrupole mass analyzer (Thermo Scientific, US) [19]. The distribution ratios of metal ions (D) were calculated as the ratio of concentrations in the equilibrium organic and aqueous phases. The duplicate experiments showed that the reproducibility of the D measurements was generally within 10%.

3. Results and discussion

3.1. Synthesis of the ligands

The ligands **1-8** used in the study were obtained starting from diphenylvinylphosphine oxide and primary amines or polyamines, according to the general route depicted in the Scheme 1. Note that different ratios of the reactants allowed to synthesize the ligands differing not only in the main molecular scaffold and substituents at the nitrogen atom but also in the amount of diphenylphosphoryl groups in a molecule.

3.2. Extraction properties

3.2.1. Extraction of lanthanides(III) from neutral media

Taking into account that the protonation of the amine nitrogen atom in an acidic medium will result in P(O)-monodentate extractants instead of P(O),N-bidentate ones (vide infra), all extraction studies were performed in neutral media.

It is well known, that lanthanide(III) ions are extracted with neutral organophosphorus compounds as solvates LnL_sA_3 (where L is a neutral extractant, A is a counterion, and s is Ln:L stoichiometric ratio), and hydrophobicity of solvates formed and their transfer to the organic phase are highly depended on the nature of a counterion. So the Eu(III) extraction efficiency from 1 M NH_4Cl , 1 M NH_4NO_3 and 1 M NH_4ClO_4 solutions using 0.01 M solution of representative compound **7** in 1,2-dichloroethane increases in a series $\text{NH}_4\text{Cl}(\log\text{DEu} = -1.80) < \text{NH}_4\text{NO}_3(\log\text{DEu} = 0.07) < \text{NH}_4\text{ClO}_4(\log\text{DEu} = 1.70)$ along with the decreasing hydration energies of the relevant anions. At the same time, the nature

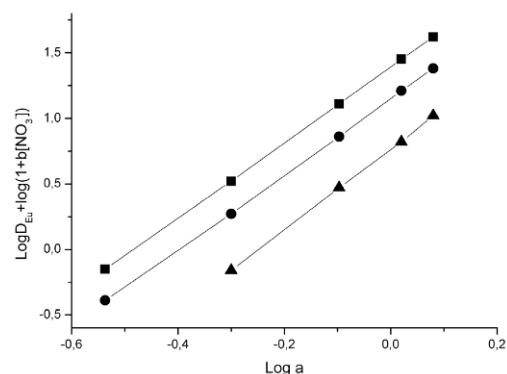
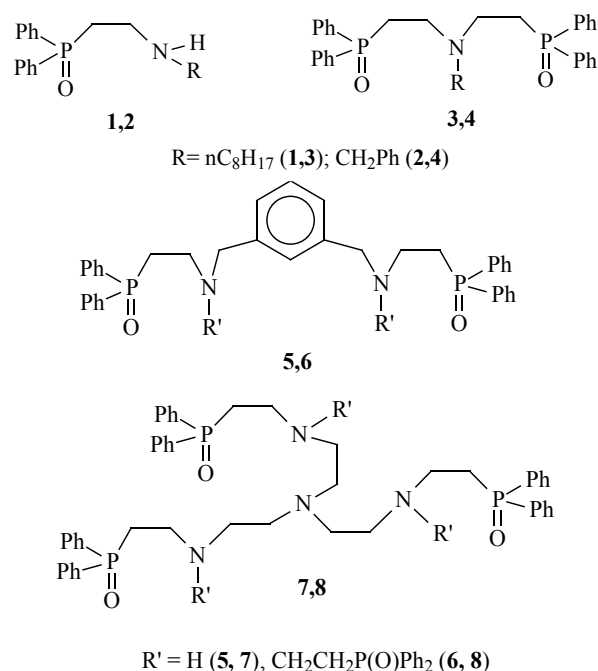


Figure 1. Dependence of Eu(III) extraction on the activity of NH_4NO_3 in aqueous phase with 0.01 M solutions of compounds **3**, **6** and **7** in 1,2-dichloroethane.

of an organic diluent also substantially affects the lanthanides(III) extraction efficiency, and over Eu(III) extraction from 4 M NH_4NO_3 with 0.025 M solutions

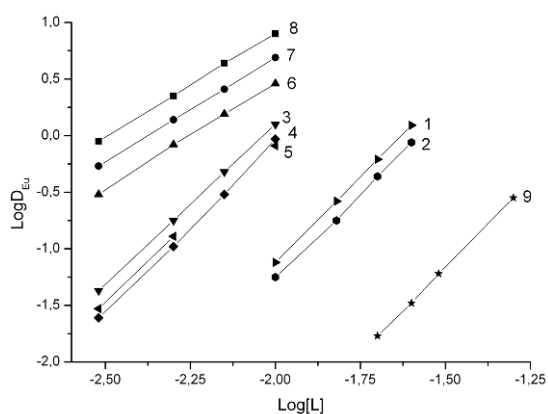


Figure 2. Influence of the concentration of the extractants **1-8** in 1,2-dichloroethane on the extraction of Eu(III) from 4 M NH_4NO_3 solutions. The data for diphenylethylphosphine oxide **9** are provided for comparison.

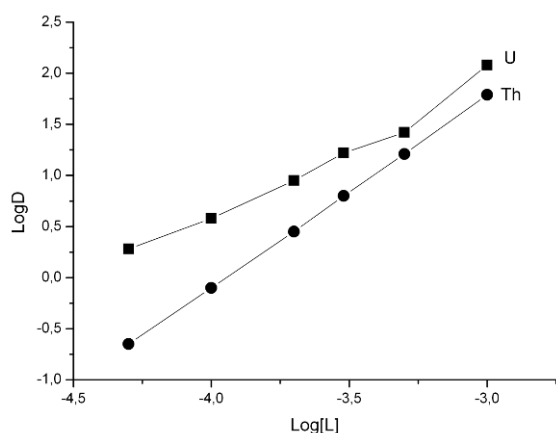
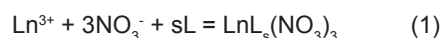


Figure 3. Influence of the concentration of compound **8** in dichloroethane on the extraction of Th(IV) and U(VI) from 4 M NH_4NO_3 solutions.

of compound **3**, D_{Eu} values increases as follows: chloroform ($\log D_{\text{Eu}} = -0.75$) < 1,1,2,2-tetrachloroethane ($\log D_{\text{Eu}} = 0.20$) < 1,2-dichloroethane ($\log D_{\text{Eu}} = 0.87$) < nitrobenzene ($\log D_{\text{Eu}} = 1.65$). Such tendency of the D_{Ln} values increasing in parallel with an increase of the dielectric constant of a diluent and its solvating power was previously observed by Rozen *et al.* [20] in the study of the diluent effect on the extraction of Eu(III) and Am(III) with neutral bidentate organophosphorus compounds and explained by the specific solvation of the complex extracted with an organic diluent.

Taking into account the analogy in the behavior of a variety of neutral organophosphorus compounds and β -aminophosphine oxides under study, the extraction of Ln(III) ions with the latter ones from nitrate media may be described by Eq. 1



Herein, an extractant is suggested to be present in dichloroethane as a monomer and mononuclear Ln(III) complexes are extracted when the initial concentration of Ln(III) is equal to 1×10^{-5} M. The corresponding extraction equilibrium constant K_{ex} is

$$K_{\text{ex}} = D_{\text{Ln}} (1 + \beta[\text{NO}_3^-]) a^{-3} [\text{L}]^{-s} \quad (2)$$

wherein β is the equilibrium constant of the formation of $\text{Ln}(\text{NO}_3)_3$ complexes and a is the activity of NO_3^- ions in the aqueous phase. At the constant concentration of an extractant in the organic phase, a slope of the plot $\log D + \log(1 + \beta[\text{NO}_3^-])$ vs. $\log a$ corresponds to the number of NO_3^- ions in the complex extracted. For the Eu(III) ions extraction with dichloroethane solutions of compounds **3**, **6**, and **7** this slope is close to 3 (Fig. 1), indicating the compensation of Eu^{3+} charge and extraction of neutral REE nitrates.

At the constant concentration of NO_3^- ions in the aqueous phase, the tilting of the plot $\log D_{\text{Eu}}$ vs. $\log[\text{L}]$ is close to 2 for the extraction using compounds **6**, **7** and **8** or 3 in the case of compounds **1-5** (Fig. 2), indicating Eu(III) ion transfer to the organic phase as di- and trisolvates, respectively. To compare, Fig. 2 shows also the corresponding data obtained for diphenylethylphosphine oxide $\text{Ph}_2\text{P}(\text{O})\text{Et}$ **9**, being the structural analog of the compounds under investigation but lacking the amine nitrogen atom, which also extracts Eu(III) as a trisolvate similar to the ligands **1-5** [21].

To compare the extraction efficiency for lanthanides and actinides, the influence of the concentration of compound **8** in dichloroethane on U(VI) and Th(IV) extraction from 4 M NH_4NO_3 solution was considered (Fig. 3). Evidently, Th(IV) is extracted as a disolvate. For the U(VI) extraction, the observed non-integer slope of the $\log D_{\text{U}}$ vs. $\log[\text{L}]$ curve can result from the formation of a mixture of mono- and disolvates. The difference in stoichiometry of the extracted U(VI) and Th(IV) complexes leads to the decrease of the separation factor (SF) for these elements ($\text{SF}_{\text{U/Th}} = D_{\text{U}}/D_{\text{Th}}$) along with the increase of the ligand concentration in organic phase (Fig. 3). The separation factor for U and Eu over the extraction from 4 M NH_4NO_3 solution using 0.001 M solution of compound **8** in dichloroethane exceeded 10^3 .

The influence of the structure of β -aminophosphine oxide on the extraction efficiency of the lanthanide ions from nitrate media was estimated by comparison of D_{Ln} values determined over the simultaneous extraction of Ln(III) ions (excluding Pm) and Y(III) from 4 M NH_4NO_3 with 1,2-dichloroethane solutions of compounds **1-8** (Fig. 4).

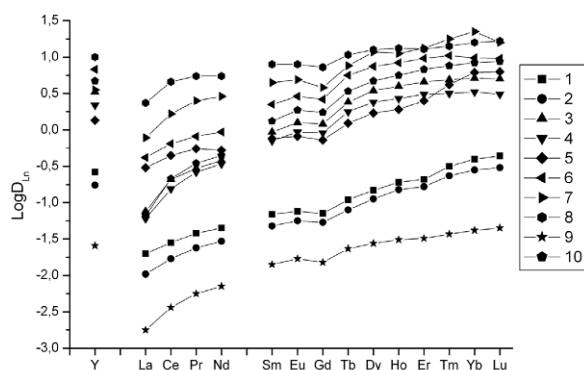


Figure 4. Simultaneous extraction of lanthanides(III) from 4 M NH_4NO_3 solutions with compounds **1-10** in 1,2-dichloroethane. Initial extractant concentrations are 0.01 M for **1-8**, **10** and 0.02 M for phosphine oxide $\text{Ph}_2\text{P}(\text{O})\text{Et}$ **9**.

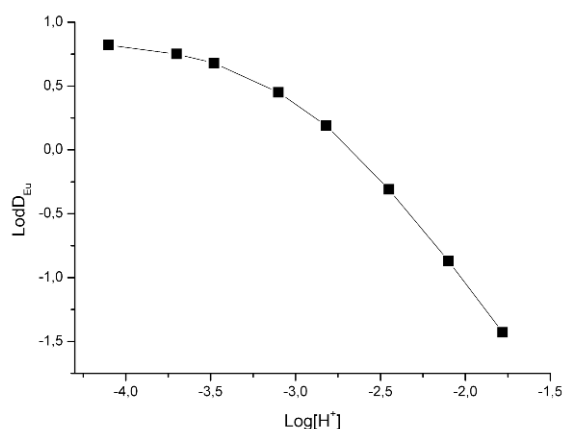


Figure 5. Influence of the equilibrium concentration of H^+ ions in the aqueous phase on the extraction of $\text{Eu}(\text{III})$ using 0.025 M solution of compound **3** in 1,2-dichloroethane from 4 M NH_4NO_3 solution.

Fig. 4 shows that D_{Ln} values for compounds **1** and **2** are substantially higher than those observed for diphenylethylphosphine oxide **9**, therefore, the presence of the nitrogen atom results in the increase of the extraction efficiency towards lanthanides(III) from neutral media due to the participation of the β -nitrogen atom in such compounds in $\text{Ln}(\text{III})$ complexation in O,N -bidentate chelate mode. It should be noted that trioctylamine (TOA) did not extract $\text{Ln}(\text{III})$ under these conditions ($\log D_{\text{Ln}} < -2$), while the significant synergistic effect was observed in the $\text{Eu}(\text{III})$ and $\text{Am}(\text{III})$ extraction with mixtures of TOA and neutral monodentate organophosphorus ligands such as trioctylphosphine oxide and tributylphosphate [22,23].

The presence of the second phosphorylethyl moiety at the nitrogen atom in a ligand structure, as in compounds **3** and **4**, increased the extraction efficiency

compared with that for the related ligands **1**, **2** having the same scaffold and one $\text{P}(\text{O})$ group. However, the extraction potency of these compounds is less than that mentioned in the literature for their N -Me substituted analog $[\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2]_2\text{NMe}$ **10** [24] and decreases in a series **10**>**3**>**4**. This fact may be explained by a steric factor as well as reduced donor properties of the nitrogen atom in the ligand **4**.

The same tendency, *i.e.*, the increase of the extraction efficiency along with an increase of the amount of phosphoryl groups in a ligand structure, was observed also in the case of compounds **5** and **6** containing two and four phosphoryl groups in the molecule, respectively. Nevertheless, the increase of the amount of phosphine oxide groups up to six in compound **8** compared with three ones in compound **7** resulted in the increase of D_{Ln} for the light $\text{Ln}(\text{III})$ and $\text{Y}(\text{III})$ but slightly affected the extraction of Dy - Lu .

In the extraction systems under consideration, the tendency of D_{Ln} increasing along with the increase of lanthanide atomic number (Z) was observed (Fig. 4). Such a character of D_{Ln} vs. Z plot can be explained by the increase of $\text{Ln}(\text{III})$ complexes stability with hard (according to Pirson) ligands as charge density of Ln^{3+} ion increases due to decrease of its ionic radius with Z increase [25].

Using the ligand **3** as a model compound, it was demonstrated that the protonation of the nitrogen atom resulted in the decrease of D_{Eu} value in parallel with the increase of H^+ ions concentration in the aqueous phase at the constant concentration of NO_3^- ions (Fig. 5). This fact unambiguously indicates the participation of the nitrogen atom of the β -aminophosphine oxide ligands in complex formation with $\text{Ln}(\text{III})$ ions. Indeed, in the case of their structural analogs, *e.g.* 1,4-diphenylphosphorylbutane $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_4\text{P}(\text{O})\text{Ph}_2$ and bis(2-diphenylphosphorylethyl) ether $[\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2]_2\text{O}$, the pH variation in the range 2-4 does not exert any significant effect on the $\text{Ln}(\text{III})$ extraction from nitrate media [20].

In this context it should be underlined that the protonation of β -aminophosphoryl compounds resulted in the formation of so-called task-specific (TSILs) or functionalized (FILs) ionic liquids [26-30] bearing a quaternary ammonium cation and complexing phosphoryl moiety. The analogs of these compounds, namely, $[(\text{BuO})_2\text{P}(\text{O})\text{X}(\text{CH}_2)_n\text{NR}_3]^+[\text{NTf}_2]^-$ ($\text{X}=\text{NH}$, O or absent) described recently by Ouadi *et al.* [31] were found to be useful as $\text{U}(\text{VI})$ extractants from HNO_3 solutions using $[\text{Me}_3\text{NBu}][\text{NTf}_2]$ as the organic phase.

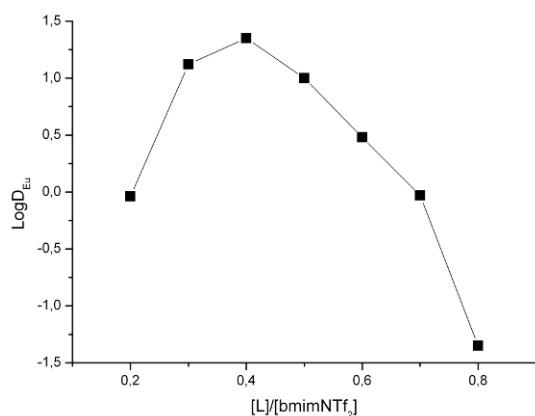


Figure 6. Extraction of Eu(III) from 1.10^{-5} M $\text{Eu}(\text{NO}_3)_3$ solutions with a mixture of compound **8** and $[\text{bmim}][\text{NTf}_2]$ in 1,2-dichloroethane. $[\mathbf{8}] + [\text{IL}] = 0.005$ M.

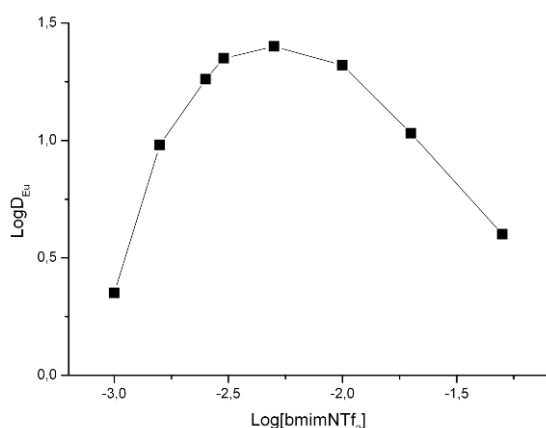


Figure 7. Influence of $[\text{bmim}][\text{NTf}_2]$ concentration on the extraction of Eu(III) from 1×10^{-5} M $\text{Eu}(\text{NO}_3)_3$ solutions with 0.002 M solution of compound **8** in 1,2-dichloroethane.

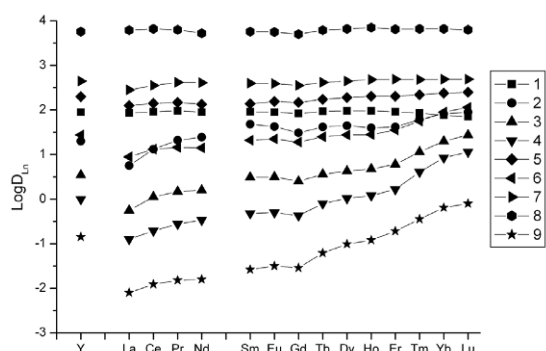


Figure 8. Simultaneous extraction of lanthanides(III) from aqueous solutions of their nitrates (each 4×10^{-6} M) with 0.01 M solutions of compounds **1-8** and **9** in 1,2-dichloroethane containing 0.05 M $[\text{bmim}][\text{NTf}_2]$. Vo:Vw = 1:10 (for **9** Vo:Vw = 1:1).

3.2.2. Extraction of lanthanides(III) from aqueous solutions into organic phase containing ionic liquid

The application of ionic liquids (ILs) as new separation media has been actively considered as an alternative

for the organic phase in liquid-liquid solvent extraction systems, e.g. for the separation of *f*-elements [32–36]. Indeed, imidazolium ionic liquids are relatively radiation resistant and do not undergo significant radiolysis upon exposure to high radiation doses [37]. For example, Visser and Rogers [32] showed that the extraction of Pu(IV), Th(IV) and U(VI) into 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{bmim}][\text{PF}_6]$) with a mixture of octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) and tri-*n*-butylphosphate is at least an order of magnitude higher than the extraction observed for the same extractant concentration in dodecane. CMPO-ligand dissolved in $[\text{bmim}][\text{PF}_6]$ was found to enhance the extractability and the selectivity of lanthanide cations extraction compared to its solutions in conventional solvents, and excess of NO_3^- ions in the aqueous phase was not required for actinides and lanthanides recovery [38]. ILs can be also used as synergetic additive in the extraction of Ln(III) with solutions of neutral extractants in common solvents, as was demonstrated by us recently [39].

Therefore, it seems reasonable to estimate whether ILs could affect the extraction of lanthanides with β -aminophosphine oxides. The continuous variation experiments performed for the extraction of Eu(III) from aqueous $\text{Eu}(\text{NO}_3)_3$ solution using compound **8** and 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($[\text{bmim}][\text{NTf}_2]$) in 1,2-dichloroethane have revealed a significant synergetic effect (Fig. 6). A similar effect was observed for the Eu(III) extraction from EuCl_3 aqueous solution. Note that both ligand **8** and $[\text{bmim}][\text{NTf}_2]$ alone do not extract Eu(III) from aqueous $\text{Eu}(\text{NO}_3)_3$ or EuCl_3 solutions ($\log D_{\text{Eu}} < -2$). The most probable reason for synergism in the presence of IL is the incorporation of hydrophobic IL anions into extracted solvates, which makes extracted Ln(III) complexes more hydrophobic compared with those with nitrate anions. A similar process was suggested to be responsible for the considerable enhancement of the extraction of Ln(III) and Am(III) with CMPO in the presence of hydrophobic picrate [40] or chlorinated cobalt dicarbollide [41] anions.

Fig. 7 demonstrates the influence of $[\text{bmim}][\text{NTf}_2]$ concentration in the organic phase on a Eu(III) extraction from aqueous $\text{Eu}(\text{NO}_3)_3$ solutions. According to these data, the $\log D_{\text{Eu}}$ vs. $\log [\text{IL}]$ curve exhibits maximum at $[\text{IL}] = 0.005$ M. This maximum can be explained by the combined effect of $[\text{IL}]$ on the formation of extracted Ln(III) complexes and reduction of the concentration of the free extractant in the organic phase due to its interaction with cation of ionic liquid. Similar dependences of $\log D_{\text{Ln}}$ on $\log [\text{IL}]$ were observed previously for the Ln(III) extraction with neutral extractants in the presence of ILs [39].

Table 1. Lu/La separation factors for the lanthanides(III) extraction from 4 M NH_4NO_3 solutions with compounds **1-8** in 1,2-dichloroethane and from aqueous $\text{Ln}(\text{NO}_3)_3$ solutions with compounds **1-8** in 1,2-dichloroethane containing 0.05 M $[\text{bmim}][\text{NTf}_2]$. Extractant concentrations are 0.01 M.

Compound	$\text{SF}_{\text{Lu/La}}$	
	1,2-dichloroethane	1,2-dichloroethane with $[\text{bmim}][\text{NTf}_2]$
1	28.8	0.83
2	21.9	15.8
3	66.1	49.0
4	51.3	91.2
5	20.9	2.0
6	22.9	12.9
7	20.4	1.7
8	7.1	1.0

Table 2. Extraction of Ca^{2+} , Sr^{2+} and Ba^{2+} from aqueous solutions with 0.05 M solutions of compounds **1-8** in 1,2-dichloroethane containing 0.05 M $[\text{bmim}][\text{NTf}_2]$.

Compound	Log D		
	Ca(II)	Sr(II)	Ba(III)
1	0.25	-0.15	-0.43
2	0.02	-0.48	-0.70
3	1.76	0.89	0.34
4	1.71	0.70	0.02
5	1.17	0.28	0.20
6	2.28	1.42	1.15
7	2.55	1.80	1.36
8	2.90	2.20	1.72

The data on the simultaneous extraction of Ln(III) ions from the aqueous solutions of the corresponding nitrate salts using 0.01 M solutions of the ligands **1-8** in 1,2-dichloroethane containing 0.05 M $[\text{bmim}][\text{NTf}_2]$ are presented in Fig. 8 and shows the retention of D_{Ln} increase along with the increase of lanthanide atomic number (Z) trend. At the same time, the influence of a ligand structure on the extraction efficiency in this case differs from that which was observed in the absence of the ionic liquid. Thus, in the presence of $[\text{bmim}][\text{NTf}_2]$, D_{Ln} values are significantly higher for compounds **1** and **2** compared with their bisphosphorylated analogs **3** and **4**, as well as for compound **5** in comparison with its bisphosphorylated counterpart **6**. Apparently, this fact is connected with more pronounced interaction of IL with β -aminophosphine oxides **3**, **4**, and **6** bearing greater amount of P(O) groups resulting, in turn, in the lower concentration of these free extractants. Nevertheless, compound **8** bearing six phosphoryl groups is the more effective extractant than its counterpart **7** having only three P=O functions.

Table 1 lists the separation factors ($\text{SF}_{\text{Lu/La}} = D_{\text{Lu}}/D_{\text{La}}$) between Lu and La, defined as the ratios of the respective distribution ratios. It is obvious

that both in presence of IL and without it, $\text{SF}_{\text{Lu/La}}$ values increased as the number of phosphoryl groups at the nitrogen atom in the extractant molecule increases (cf **1,3**), except for tris-amine derivatives **7,8**. The addition of IL to the extractant solutions improves the simultaneous extraction, decreasing selectivity, therefore, it can be concluded that the separation of the heavier lanthanides can be reached using compounds **3** and **4**.

3.2.3. Extraction of alkaline earth metal ions from aqueous solutions into organic phase containing ionic liquid

β -Aminophosphine oxides in the presence of $[\text{bmim}][\text{NTf}_2]$ in the organic phase also extract efficiently alkaline earth metal ions from aqueous solutions (Table 2), while alone (without IL) compounds **1-8** did not extract Ca^{2+} , Sr^{2+} , Ba^{2+} ions from aqueous medium ($\log D < -2$). The extraction efficiency of alkaline earth metal ions increases in the order $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+}$ in parallel with the increase in the positive charge density of M^{2+} ions. This tendency suggests that the interaction between these ligands and M(II) is predominantly electrostatic one [42]. Table demonstrates that increase in the number of phosphoryl groups in a ligand molecule improves extraction of these cations under the above conditions (compare the data for pairs **1** and **3**, **2** and **4**, **5** and **6**, and **7** and **8**, respectively). The observed dependence differs from that for the extraction of Ln(III) cations with these ligands in the presence of $[\text{bmim}][\text{NTf}_2]$ and its general pattern is similar to that for lanthanides in the absence of IL. Such difference is apparently connected with the application of more concentrated extractant solutions in the case of alkaline earth metal ions extraction and that results in the less appreciable decrease of the free ligand concentration in the organic phase. Note that hexapodal tris[bis(2-diphenylphosphoryl)ethyl]aminoethylamine **8** demonstrated the highest extraction efficiency in this case as well. Apparently, the unique properties of this compound are connected with the preorganization of the ligand in solutions, favorable for the formation of strong complexes with different metals.

4. Conclusions

The investigation of the extraction properties performed for a series of β -aminophosphine oxides differing in their structure demonstrated the potential of these compounds for the extraction of lanthanides and alkaline earth metals from neutral solutions, where addition of 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ionic liquid sufficiently increases the extraction efficiency. In general, using common diluents,

the extraction efficiency increased with the increase of a number of P=O functions in a ligand of this type. In the case of monophosphine oxides, the steric and electronic properties of the substituent R at the nitrogen atom affected also the extraction efficiency while its influence is negligible for bis(phosphorylethyl)amines. Decreasing of D_{Ln} values with an increase of H^+ ions concentration in aqueous phase at the constant concentration of NO_3^- ions, *i.e.*, with the protonation of the ligand nitrogen atom, confirmed the participation of the latter in complex formation with Ln(III) ions. In the presence of ionic liquid in a mixture with 1,2-dichloroethane as a solvent, the application of IL concentration of 0.05 M (in 1,2-dichloroethane) provided the maximum recovery of metal ions and improved the separation of the heavier lanthanides (the Lu/La separation factor reaching up to 91). Interestingly, in the presence of [bmim][NTf₂] the influence of the ligand structure on the extraction

efficiency towards alkaline earth metals demonstrated a similar tendency that was observed in the case of Ln(III) ions extraction. Nevertheless, hexapodal tris[bis(2-diphenylphosphorylethyl)aminoethyl] amine **8** demonstrated the highest extraction under all conditions applied and this ligand is the most promising among β -aminophosphine oxides under consideration.

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References

- [1] F. Palacios, C. Alonso, J.M. de los Santos, *Chem. Rev.* 105, 899 (2005) and references therein
- [2] M.S. Rahman, M. Oliano, H. Kuok, *Tetrahedron: Asymmetry* 15, 1835 (2004)
- [3] C.A. Ghilardi, P. Innocent, S. Misollini, A. Orlandini, *J. Chem. Soc., Dalton Trans.* 2075 (1986)
- [4] E.I. Sinyavskaya, L.V. Tsymbal, K.B. Yatsimirskii, S.A. Pisareva, T.Ya. Medved, M.I. Kabachnik, *Russ. Chem. Bull.* 35, 160 (1986)
- [5] G. Newton, H.D. Caughman, R.C. Taylor, *J. Chem. Soc., Dalton Trans.* 258 (1974)
- [6] F. Kosoarek, Z. Travnicek, M. Posolda, Z. Sindelar, J. Marek, *J. Coord. Chem.* 44, 61 (1998)
- [7] M. Maj, K.M. Pietrusiewicz, I. Suisse, F. Agbossou, A. Mortreux, *Tetrahedron: Asymmetry* 10, 831 (1999)
- [8] M. Maj, K.M. Pietrusiewicz, I. Suisse, F. Agbossou, A. Mortreux, *J. Organomet. Chem.* 626, 157 (2001)
- [9] X. Cheng, P.N. Horton, M.B. Hursthouse, K.K. Mimi Hii, *Tetrahedron: Asymmetry* 15, 2241 (2004)
- [10] E. Gumienna-Kontecka, J. Galezowska, M. Drag, R. Lataika, P. Kafarski, H. Kozlowski, *Inorg. Chem. Acta* 357, 1632 (2004)
- [11] R.A. Cherkasov, A.R. Garifzyanov, N.V. Kurnosova, E.V. Matveeva, I.L. Odinets, *Russ. Chem. Bull.* 1, 171-178 (2012)
- [12] M.N. Rusina, Yu.M. Polikarpov, G.F. Yaroshenko, L.M. Timakova, *Zhurn. Obsch. Khim.* 43(2), 238 (1973) (In Russian)
- [13] B.N. Laskorin, L.A. Fedorova, N.P. Stupin, M.I. Kabachnik, T.Ya. Medved, Yu.M. Polikarpov, *Radiokhimiya* 12, 335 (1970) (In Russian)
- [14] A.N. Turanov, V.K. Karandashev, N.A. Bondarenko, E.M. Urinovich, E.N. Tsvetkov, *Russ. J. Inorg. Chem.* 41, 1658 (1996)
- [15] E.V. Matveeva, P.V. Petrovskii, I.L. Odinets, *Tetrahedron Lett.* 49, 6129 (2008)
- [16] E.V. Matveeva, P.V. Petrovskii, Z.S. Klemenkova, N.A. Bondarenko, I.L. Odinets, *C. R. Chimie* 13, 864 (2010)
- [17] E.V. Matveeva, A.E. Shipov, P.V. Petrovskii, I.L. Odinets, *Tetrahedron Lett.* 52, 6562 (2011)
- [18] P. Bonhote, A.-P. Dias, P. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* 35, 1168 (1996)
- [19] A.N. Turanov, V.K. Karandashev, V.E. Baulin, *Solvent Extr. Ion Exch.* 14(2), 227 (1996)
- [20] A.M. Rozen, A.S. Nikiforov, Z.I. Nikolotova, N.A. Kartasheva, *Dokl. Akad. Nauk USSR* 286, 667 (1986) (In Russian)
- [21] A.N. Turanov, V.K. Karandashev, V.E. Baulin, A.N. Yarkevich, Z.V. Safronova, *Solvent Extr. Ion Exch.* 27(4), 551 (2009)
- [22] B.Ya. Spivakov, Yu.A. Zolotov, B.F. Myasoedov, M.K. Chmutova, N.E. Kochetkova, *Zhurn. Neorgan. Khim.* 57, 3334 (1972) (In Russian)
- [23] B.F. Myasoedov, B.Ya. Spivakov, Yu.A. Zolotov, N.E. Kochetkova, V.M. Shkinev, M.K. Chmutova, *Zhurn. Neorgan. Khim.* 59, 1379 (1974) (In Russian)
- [24] A.N. Turanov, V.K. Karandashev, N.A. Bondarenko, *Russ. J. Inorg. Chem.* 56, 1137 (2011)
- [25] K.L. Nash, M.P. Jensen, *Sep. Sci. Techn.* 36, 1257

- (2001)
- [26] J.H. Davis, Jr, *Chem. Lett.* 33, 1072 (2004)
- [27] Z. Fei, T.J. Geldbach, D. Zhao, P.J. Dyson, *Chem. Eur. J.* 12, 2122 (2006)
- [28] H. Xue, R. Verma, J.M. Shreeve, *J. Fluorine Chem.* 127, 159 (2006)
- [29] X. Li, D. Zhao, Z. Fei, L. Wang, *Science in China, Series B* 49, 385 (2006)
- [30] S.-G. Lee, *Chem. Commun.* 1049 (2006)
- [31] A.Ouadi, O. Klimchuk, C. Gaillard, I. Billard, *Green. Chem.* 9, 1160 (2007)
- [32] A.E. Visser, R.D. Rogers, *J. Solid State Chem.* 171, 109 (2003) and references therein
- [33] K. Binnemans, *Chem. Rev.* 107, 2592 (2007) and references therein
- [34] I. Billard, A.Ouadi, C. Gallard, *Anal. Bioanal. Chem.* 400, 1555 (2011) and references therein
- [35] C. Gaillard, A. Chaumont, A Ouadi, *Inorg. Chem.* 44, 8355 (2005)
- [36] S. Mekki, C.M. Wai, I. Billard, G. Moutiers, J. Burt, B. Yoon, J.S. Wang, C. Gaillard, A. Ouadi, P. Hesemannet, *Chem. Eur. J.* 12, 1760 (2006)
- [37] G.M.N. Baston, A.E. Bradley, T. Gorman, I. Hamblett, C. Hardacre, J.E. Hatter, M.J.F. Healy, B. Hodgson, R. Lewin, K.V. Lovell, G.W.A. Newton, M. Nieuwenhuyzen, W.R. Pitner, D.W. Rooney, D. Sanders, K.R. Seddon, H.E. Simms, R.C. Thied, *ACS Symp. Ser.* 818, 162 (2002)
- [38] K. Nakashima, F. Kubota, T. Maruyama, M. Goto, *Anal. Sci.* 19, 1097 (2003)
- [39] A.N. Turanov, V.K. Karandashev, V.E. Baulin, *Solvent Extr. Ion Exch.* 26(2), 77 (2008)
- [40] H. Naganawa, H. Suzuki, S. Tachimori, A. Nasu, T. Sekine, *Phys. Chem. Chem. Phys.* 3, 2509 (2001)
- [41] J. Rais, S. Tachimori, *J. Radioanal. Nucl. Chem. Lett.* 188, 157 (1994)
- [42] S. Tachimori, S. Suzuki, Y. Sasaki, A. Apichaibukol, *Solvent Extr. Ion Exch.* 21(5), 707 (2003)