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N-Tris[(2-aminoethyl)-2-(diphenylphosphoryl) acetamide)] - novel CMPO tripodand: synthesis, extraction studies and luminescent properties of lanthanide complexes

Research Article

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Abstract: A ligand system containing three carbamoylmethylphosphine oxide (CMPO) moieties attached to a tripodal platform with a central nitrogen atom has been synthesized for metal complexation and extraction from neutral and nitric acid solutions. Liquid–liquid extractions performed for Ln(III), both from neutral and acidic media, show excellent extraction properties which exceeded those for the known mono- and di-CMPO derivatives as well as the related tripodands. A considerable enhancement of the D_{Ln} values was observed in the presence of IL ([bmim][Tf_2N]) in the organic phase towards lanthanide ions from 3M HNO_3 solutions. The protonation of the central amine nitrogen atom of the ligand **1** in the acidic media provides also the effective extraction of the perrhenate anionic complexes. The europium complexes formed by mono- and tris-CMPO ligands in the solid state, as well as Eu(III) and Tb(III) complexes generated in solutions, possess intensive luminescence at 300K

Keywords: *Carbamoylmethylphosphine oxides • Lanthanides(III) • Ionic liquids • Extraction • Luminescence*

1. Introduction

Nowadays, a lot of research groups focus their efforts on the targeted design of artificial receptors for the selective recognition of cations and anions [1]. The tripodal receptors belong to a special class of acyclic ionophores, which consist of multi-armed ligands with each arm bearing functional group(s) that can coordinate with the target ion. In general the number of tripodal ligands for actinide and/or lanthanide complexation is still rather limited [2,3].

It is well known that organophosphorus compounds are inclined to form strong complexes with hard transition and rare-earth metal ions [4,5]. Among those, bidentate phosphorus analogs of acetylacetonate ligands bearing the donor oxygen atoms in 1,3-positions such as those of two phosphoryl groups or of the combination of P=O and C=O (carbonyl, carbalkoxy or carbamoyl) functions are good chelating ligands for trivalent lanthanide and actinide ions and, therefore, display useful extraction and sorptions properties towards these elements [6-10]. Among those, carbamoylmethylphosphine oxides

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(CMPO), for example (*N*,*N*-diisobutylcarbamoylmethyl) octylphenylphosphine oxide [11,12] or (*N*,*N*-dibutylcarbamoylmethyl)diphenylphosphine oxide [13], are known to be preferable among the typical extractants for processing of accumulated liquid acidic radioactive wastes in terms of cost and effectivity. The effectivity and selectivity of such ligands usually increase with an increase in the amount of CMPO residues in a molecule [14]. Attachment of CMPO groups to molecular platforms such as calixarenes [15-17] and cavitands [18-21] led to further increase of extraction efficiencies and selectivities.

However, as only three CMPO moieties are necessary for the coordination of a *f*-element ion, the corresponding tripodal CMPO ligands are of undoubted interest. Nevertheless, currently reported are only a few examples of a tripodal platform with substituted trityl [22-24] skeleton and different rearrangement of CMPO moieties, the related compounds with thiophosphoryl function [25], and those on trimethylolpropane-based tripodal framework [26]. These tripodal receptors, excluding the thiophosphoryl derivatives, show reasonable extraction properties towards lanthanides and actinides in 1,1,2,2-tetrachloroethane, and 1,1,1-tris [(diphenylcarbamoylmethylphosphine oxide N-propoxy) methyl]propane demonstrated high selectivity towards Eu^{3+} and forms a very stable complex (log β_{ML} = 28.3). However, in many cases extractions using known tripodal CMPO ligands suffer from third phase formation and the systems developed were effective at low HNO_3 concentration only.

Therefore, in continuation of our group research in the field of neutral [27-29] and ionic [30] CMPO derivatives, in this paper we report on the synthesis and extraction study of the novel tripodal CMPO ligand which shows excellent extraction properties exceeding those for the known mono- and di-CMPO derivatives as well as the related tripodands both in neutral and acidic medium. Furthermore, taking into account the growing interest in luminescent systems based on f-elements and ability of CMPO derivatives to form strong complexes with lanthanides, we describe for the first time luminescent properties of Eu and Tb complexes formed by CMPO ligands, including the novel tripodand.

2. Experimental procedure

2.1. General remarks

The NMR spectra were recorded on a Bruker AMX-300 instrument in $CDCl_3$ and CD_3OH solutions. The chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^1H and ^{13}C) or externally to H_3PO_4 (^{31}P). The ^{13}C NMR spectra were registered using the JMODECHO mode; the signals for the C atoms bearing odd and even numbers of protons have opposite polarities. 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 DigitalMelting Point Apparatus and were uncorrected.

The known ligands **2**-**5** [14,31] were obtained *via* the procedures described in the literature, and their physicochemical constants matched the literature data.

N-tris[(2-aminoethyl)-2-(diphenylphosphoryl) acetamide)] 1

Phosphorus trichloride (1.1 g, 0.0077 mol) was added dropwise with stirring and cooling to 0°C (an ice-bath) to a slurry of phosphorylacetic acid (5.0 g, 0.019 mmol) in anhydrous $CHCl_3$ (15 mL). Then the bath was removed and the mixture was stirred at 20°C for 5 h and again cooled to 0°C. A solution of triethylamine (4.7 g, 0.046 mmol) and tris-(2-aminoethyl)amine (0.7 g, 0.0051 mol) in anhydrous $CHCl_3$ (5 mL) was slowly added dropwise. The reaction mixture was stirred at 20°C for 2 h and allowed to stand overnight. Then water (20 mL) and DCM (15 mL) were added, the organic layer was separated, washed with water (50 mL), dried with Na_2SO_4, and filtered. The solvent was removed *in vacuo*, and the residue was purified by recrystallization from ethanol (twice) and dried *in vacuo* over P_2O_5 to constant weight to give 1.4 g of a sodium complex of the compound. The slurry of this complex was stirred in water for 20 min, the precipitate was filtered off and washed with ether to give after being dried over P_2O_5 the desired compound as a hydrate. Yield: 32%. Mp: 192°C (dec). IR (KBr, cm^{-1}): 3277 (ν_{NH}), 3059, 2955, 2918, 2818, 1665 ($\nu_{C=O}$), 1590, 1547 (ν_{NH}), 1438 (ν_{CH2}), 1312, 1299, 1176 ($\nu_{P=O}$), 1121, 1101, 1071, 1028, 998, 847, 746, 729, 694, 517. ^1H NMR (300 MHz, $CDCl_3$, ppm, J/Hz): 2.43-2.47 (m, 6H, $NC\underline{H}_2$); 3.12-3.17 (m, 6H, $NCH_2C\underline{H}_2$); 3.63 (d, 6H, PCH_2, $^2J_{P-H}$=14.3); 7.39-7.43 (m, 12H, *m*-C_6H_5P); 7.52-7.54 (m, 6H, *p*-C_6H_5P); 7.71-7.78 (m, 12H, *o*-C_6H_5P); 8.62 (br. s, 3H, NH). ^{31}P NMR (121.5 MHz, $CDCl_3$): 30.25 ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, ppm, J/Hz): 37.58 (NCH_2), 38.81 (d, PCH_2, $^1J_{PC}$=62.6), 52.89 ($NCH_2\underline{C}H_2$), 128.45 (d, *m*-C in C_6H_5, $^3J_{PC}$=12.1), 130.69 (d, *o*-C in C_6H_5, $^2J_{PC}$=9.9), 131.79 (d, *p*-C in C_6H_5, $^4J_{PC}$=1.6), 131.99 (d, *ipso*-C in C_6H_5, $^1J_{PC}$=102.6), 164.43 (d, C(O), $^2J_{PC}$=5.5). Anal. Calcd for $C_{48}H_{51}N_4O_6P_3{\bullet}H_2O$: C, 64.71; H, 6.00; N, 6.29. Found: C, 64.73; H, 5.77; N, 6.09.

$[Eu\{N(CH_2CH_2NHC(O)CH_2P(O)Ph_2)_3\}Cl_3]$

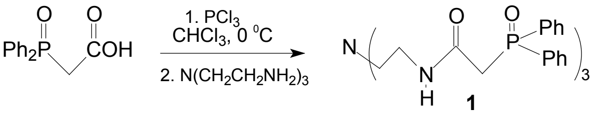
An ethanolic solution (3 mL) of the $EuCl_3$ (46 mg, 0.126 mmol) was added dropwise to a solution of the ligand **1** (113.0 mg, 0.129 mmol) in 4 mL of C_2H_5OH

and in 2 mL CH_3CN. The resulting mixture was left under ambient conditions for 2 h and evaporated to a volume of ~1 mL. Addition of ether (5 mL) to the reaction solution afforded precipitation of the corresponding complex which was filtered off, washed with 10 mL of Et_2O and dried in vacuum. Yield: 77%. Mp: 194°C (dec.). IR (KBr, cm^{-1}): 3348, 3219, 3056, 2949, 2897, 1625 ($\nu_{C=O}$), 1590, 1566, 1438 (ν_{CH2}), 1399, 1330, 1160 ($\nu_{P=O}$), 1139, 1124, 1096, 1072, 1027, 997, 847, 734, 694, 527, 508. ^{31}P NMR (121.5 MHz, CD_3OD): 0.70 ppm. Anal. Calcd for $C_{48}H_{51}Cl_3EuN_4O_6P_3$: C, 50.97; H, 4.54; N, 4.95. Found: C, 50.84; H, 4.57; N, 4.81.

2.2. Extraction properties

Chemical- and analytical-grade nitrobenzene, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, and chloroform were used as diluents. 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, Re, Fe, Al, Cu, Pb, Zn, Cd, Ni, Co, Mn, Ca, Sr, and Ba was 1×10^{-5} M for each element. All lanthanides (III) (except Pm) were presented in the initial aqueous phase when simultaneous extraction of Ln(III) was studied. The experiments were carried out in ampules with ground stoppers at 20-25°C. The volumes of both organics and aqueous phases were equal to 2 mL. The solution was stirred on a rotary mixer for an hour at 60 rpm to achieve equilibrium. Preliminary experiments showed that this time exceed the time required for the system to reach the equilibrium. 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 a specific volume of the 1-hydroxyethane-1,1-diphosphonic acid solution was added. The mixture was shaken for 20 min and Ln(III) in the organic phase were back extracted into the aqueous phase.

The metal concentrations in the initial and equilibrium aqueous solutions after extraction and back extraction were determined by inductively coupled plasma mass-spectrometry (ICP-MS) on a PlasmaQuad mass spectrometer with quadrupole mass analyzer (VG Elemental, GB) [32]. The distribution ratios of metal ions (D) were calculated as the ratio of concentrations in the equilibrium organic and aqueous phases. Duplicate experiments showed that the reproducibility of the D_{Ln} measurements was generally within 10%. The nitric acid concentration in the equilibrium aqueous solutions was determined by potentiometric titration with KOH solution.



Scheme 1. Synthesis of the tris-CMPO ligand **1**.

2.3. Luminescence

The luminescence spectra of the complexes in a solid state and in solutions were registered on a luminescent spectrometer SDL-1 (St.-Peterburg). The Hg lamp equipped with UFS-2 colour filter for detachment of most intensive mercury lines 313 and 365 nm was used for excitation. The luminescence was measured on solid samples put into 10×5×45 mm cuvette with 1 mm deepening and 7 mm diameter. For solutions, quartz 10×10×45 mm cuvette was used.

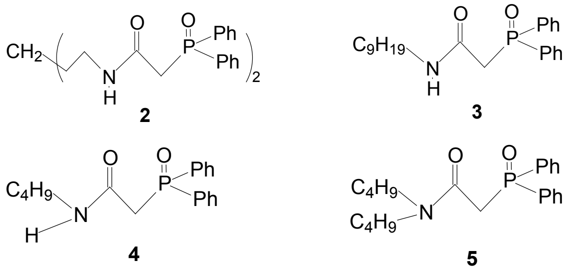
3. Results and discussion

3.1. Synthesis of the ligands

The desired tripodand **1** was synthesized using the general synthetic procedure detailed by us earlier, namely *via* the reaction of diphenylphosphorylacetic acid chloride generated in situ in the presence of phosphorus trichloride with amines [21]. For construction of tripodal framework, we used tris(2-aminoethyl)amine as N-nucleophile. Note that after the ordinary work-up procedure involving drying over sodium sulfate, the final ligand was isolated as the corresponding sodium complex which was destroyed by water treatment (see experimental). Therefore, to avoid such complex formation, application of typical driers should be excluded from this procedure.

The pure ligand **1** demonstrates a singlet at *ca.* 30 ppm in the ^{31}P NMR spectrum, *i.e.*, the region characteristic for the given phosphorus atom environment.The ^1H NMR spectrum corresponds to the depicted structure and is comprised of a doublet of protons of the PCH_2 group at 3.63 ppm with a coupling constant of 14.3 Hz along with the other characteristic signals of the hydrogen atoms located in the typical regions. In the IR spectrum characteristic absorption bands at 1665 cm^{-1} (C=O) and 1176 cm^{-1} (P=O) along with absorption of NH group appearing as a broad band at 3277 cm^{-1} (valent oscillations) and a band at 1547 cm^{-1} (component frequencies of NH deformation oscillations and C-N oscillations) were observed.

For comparison, experiments in the extraction study and luminescence properties of the complexes we performed also the synthesis of related derivatives **2**-**5** differing in the amount of CMPO groups in the molecule and substituents at the nitrogen atom. These comparative ligands were obtained *via* the direct



2 **3** **4** **5**

Scheme 2. The comparative mono- and bis-CMPO ligands used in the study.

amination of ethyl diphenylphosphorylacetate *via* the other general procedure developed by us previously [14-31].

3.2. Extraction experiments

3.2.1. Extraction of lanthanides(III) from neutral media

As known lanthanide(III) ions are extracted with neutral organophosphorus compounds as solvates LnL_sA_3 (where L is neutral extractant, A - a counterion, and s - Ln:L stoichiometric ratio). The nature of the counterion affected significantly hydrophobicity of solvates formed and their transfer from aqueous to organic phase. Thus, efficiency of extraction of Eu(III) by 0.002 M solution of compound **1** in 1,2-dichloroethane from 1 M NH_4Cl, 1 M NH_4NO_3 and 1 M NH_4ClO_4 solutions increases in a series $NH_4Cl(\log D_{Eu} < -2.5) < NH_4NO_3(\log D_{Eu} = -0.9) < NH_4ClO_4(\log D_{Eu} = 3.15)$ with decreasing hydration energies of the relevant anions, that is, with increasing hydrophobicity of extracted Ln(III) complexes as far as hydrophobic properties of a counterion increased. The nature of an organic diluent also substantially affects the lanthanides(III) extraction efficiency. For example, in the extraction of Eu(III) from 4 M NH_4NO_3 solutions the efficiency increased in the order: chloroform ($\log D_{Eu} = -0.55$) < 1,1,2,2-tetrachloroethane ($\log D_{Eu} = -0.43$) < 1,2-dichloroethane ($\log D_{Eu} = -0.22$) < nitrobenzene ($\log D_{Eu} = 0.2$) in parallel with an increase of dielectric constant of a diluent and its solvating power. The same tendency noted previously by Rozen *et al*. [33] in the study of the diluent effect on the extraction of Eu(III) and Am(III) with neutral bidentate organophosphorus compounds, namely tetraphenylmethylenediphosphine dioxide and diphenyl(dibutylcarbamoylmethyl)phosphine oxide, was explained by the specific solvation of the complex extracted by an organic diluent.

The effect of the number of CMPO groups in the molecule of the ligand on the efficiency of lanthanides(III) extraction was examined using the related derivatives **2** and **3.** In other words, the simultaneous extraction of Ln(III) ions from 4 M NH_4NO_3 by solutions of compounds **1**-**3** in 1,2-dichloroethane was carried out. The ratio of the initial concentrations of the ligands was [**1**]:[**2**]:[**3**] was 1:1.5:3 in order to achieve the similar concentration of $Ph_2P(O)CH_2C(O)N<$ moieties in the organic phase. Fig. 1 indicates that an increase in the amount of bidentate complexing $Ph_2P(O)CH_2C(O)N<$ groups in a molecule results in the increase in the extraction efficiency towards Ln(III). For compound **2**, the extraction of lanthanides(III) increased from La(III) to Sm(III) and later on decreased from Sm(III) to Lu(III). Similar pattern of lanthanide extraction was observed for compound **2** [14] as well as other neutral bidentate ligands such as tetra(*p*-tolyl)methylenediphosphine dioxide [34] carbamoylmethylphosphine oxides (CMPO) [35], N,N'-dimethyl-N,N'-diphenylmalonamide [36] as well as calix[4]- and calix[5]arenes modified by a few $Ph_2P(O)CH_2C(O)N$ functions at their wide rim [17] in nitric acid systems. These trends in $\log D_{Ln}$ *vs*. atomic number (Z) were explained [35] by an increase in the hydration energy of the Ln^{3+} ion as Z increased, thereby decrease in the ability of extractants to dehydrate Ln^{3+} over the extraction. For compound **1,** D_{Ln} tends to increase as Z increases (Fig. 1) probably due to participation of the central nitrogen atom in complexation with heavy Ln(III) over the extraction from neutral media. In this context, it should be mentioned that exchange of the ether oxygen in the molecule of podand $Ph_2P(O)(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2P(O)Ph_2$ for -NBu group results in sufficient increase of Ln(III) extraction efficiency from neutral NH_4NO_3 solutions [37]. At the same time, when this nitrogen atom is protonated in 4 M HNO_3 solution the inversion of the trend $\lg D_{Ln}$ *vs*. Z for compound **1** (Fig. 2) was observed and the difference in the D_{Ln} values $D_{Ln}(NH_4NO_3)/D_{Ln}(HNO_3)$ increased with an increase of Z.

3.2.2. Extraction of lanthanides(III) from nitric acid solutions

Fig. 3 shows the effect of HNO_3 concentration in the aqueous phase on the simultaneous extraction of lanthanides(III) by solution of compound **1** in 1,2-dichloroethane. As one may see, the log D_{Ln} *vs*. log $[HNO_3]$ curve exhibits maxima at $[HNO_3]$ = 3 M for La - Tb and at $[HNO_3]$ = 4 M for Tm and Ho. These maxima are commonly observed in metal extraction by neutral organophosphorus compounds and are explained by combined effect of HNO_3 salting out and competition for the extractant molecule by co-extraction of HNO_3. The maximum of log D_{Ln} shift towards higher $[HNO_3]$ values on passing from La(III) to Ho(III), which is evidently associated with an increase in the hydration energy of the Ln^{3+} ion, as Z increases. For the heavier Ln(III), D_{Ln} increases with the increase of HNO_3 concentration up to 7 M HNO_3 (Fig. 3).

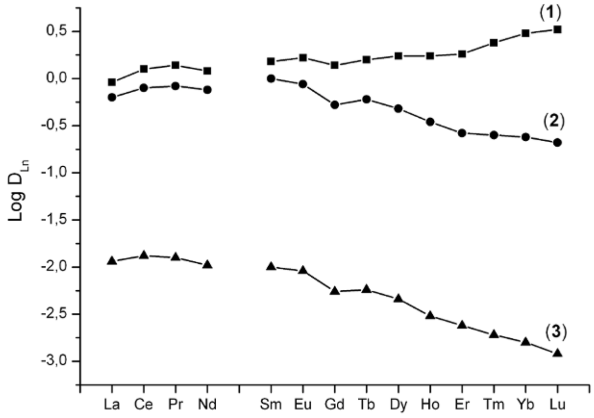


Figure 1. The extraction of lanthanides(III) from 4 M NH_4NO_3 media with solutions of compounds **1-3** in 1,2-dichloroethane. Initial extractant concentrations are 0.00333 M (compound **1**), 0.005 M (compound **2**) and 0.01 M (compound **3**).

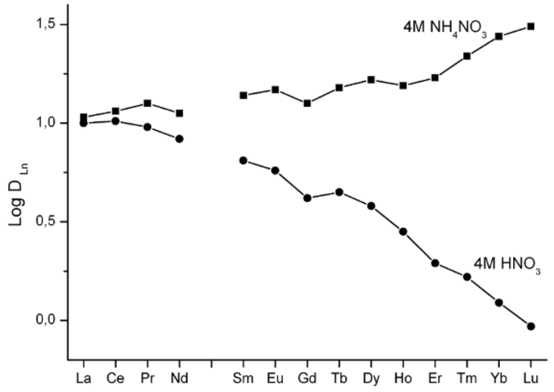


Figure 2. The extraction of lanthanides(III) from 4 M NH_4NO_3 and 4 M HNO_3 solutions with 0.01 M solution of compound **1** in 1,2-dichloroethane.

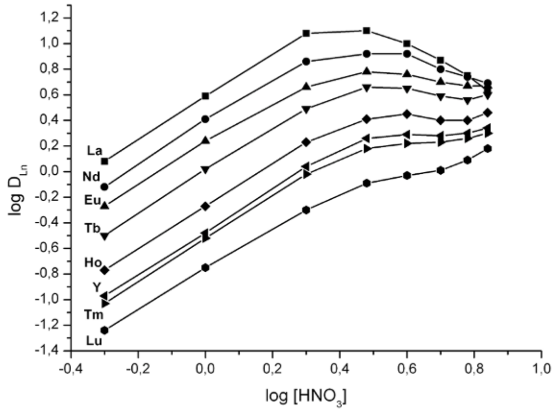


Figure 3. The effect of HNO_3 concentration in the aqueous phase on the extraction of lanthanides(III) with 0.01 M solutions of compound **1** in 1,2-dichloroethane.

The variations in D_{Ln} as a function of concentration of the tripodand **1** in 1,2-dichloroethane for 3M HNO_3 systems are shown in Fig. 4. To compare the extraction efficiency of compound **1** towards Ln(III) with that for actinides, the extractant dependences for U(VI) and Th(IV) were studied at the same HNO_3 concentration in the aqueous phase. Fig. 4 demonstrates that both Th(IV) and U(VI) are extracted with compound **1** more effectively than Ln(III).

The second power dependence of D_{Ln} on [L] indicates that Ln(III) are extracted from nitric acid solutions by compound **1** as disolvates. In contrast, mono-CMPO derivative **3** extracts Ln(III) from 3M HNO_3 solutions as tri- and tetra-solvates (Fig. 4). Therefore, the tripodand CMPO-derivative extracts Ln(III) ions more effectively compared with compound **3**. The difference in extraction ability for compounds **1** and **2** is less pronounced, *e.g.* in the case of the extraction with 0.005 M solutions in dichloroethane from 3 M HNO_3 the D_{Eu} values were 1.75 and 0.77 [14], respectively. Furthermore, comparison of the Eu(III) extraction from 1 M HNO_3 with 0.014 M solutions in 1,1,2,2-tetrachloroethane of compound **1** and its structural analog – tripodand 1,1,1-tris[(diphenylcarbamoylmethylphosphine oxide N-propoxy)methyl] propane [26], demonstrates that the former possess better extraction ability (D_{Eu} = 1.55 and 0.26 [26], respectively).

3.2.3. Extraction of metal ions from nitric acid solutions in the presence of picric acid

The Ln(III) extraction with CMPO is known to increase significantly in the presence of picric acid. This fact is connected with the participation of hydrophobic Pic^- anions in the formation of extractable complexes [38]. The same synergistic effect is observed over the extraction of Ln(III) from slightly acidic solution with the ligand **1** in the presence of HPic in the organic phase. In this case the Ln(III) extraction decreased as the concentration of HNO_3 in the aqueous phase increased (Fig. 5a) and that may be connected with the inhibition of the HPic dissociation and decrease of Pic^- anion concentration in the aqueous phase. Figs. 5b and 5c indicate that the stoichiometric ratio Ln:L:Pic in extracted complexes is 1:2:3. The simultaneous extraction of lanthanides(III) by solutions of compound **1** in 1,2-dichloroethane in the presence of picric acid has revealed that tris-CMPO **1** is significantly more effective than its mono-CMPO analogue **3** in such systems (Fig. 6).

The simultaneous extraction of some tri- and dicharged cations by the solution of compound **1** and picric acid in 1,2-dichloroethane was also studied. Thus, the ligand **1** was found to be an effective extractant for alkaline earth metal ions from the diluted HNO_3 solutions in the presence of HPic in the organic phase (Table 1). To compare the extraction efficacy of compounds **1**, **2** and **3** towards these ions, Table 2 shows distribution coefficients for the extraction of Ca^{2+}, Sr^{2+}, and Ba^{2+} from

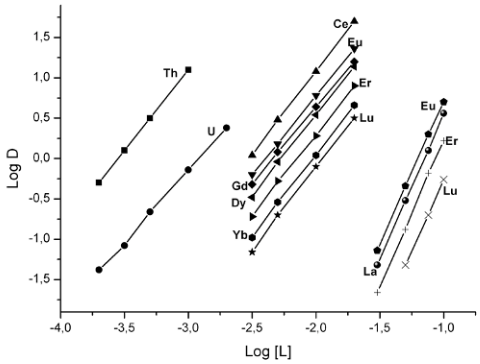


Figure 4. The effect of the concentration of extractants **1** and **3** in 1,2-dichloroethane on the extraction of Ln(III), Th(IV) and U(VI) from 3 M HNO_3 solutions.

HNO_3 solutions. Obviously, the extraction efficiency increases in the order **3** < **2** < **1** along with the increase of the number of CMPO moieties in the ligand molecule. Note that for the ligands **2** and **3** the efficiency of alkaline earth metal ions increases in the order Ba^{2+} < Sr^{2+} < 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) has mainly the electrostatic character [39].

In contrast, the efficiency of alkaline earth metal ion extraction increases in the order Ca^{2+} < Sr^{2+} < Ba^{2+} in the case of tris-CMPO **1** (Table 2) and the same order was observed for the extraction of these ions with macrocyclic ligands. The difference in the stoichiometry of the extracted complexes of the alkaline earth metal ions has been also revealed: in the system based on compound **1** complexes of the composition M:Pic:L = 1:2:1 transfer to the organic phase, while in the system formed with the analogs **2**,**3** this ratio was 1:2:2.

3.2.4. Extraction of lanthanides(III) from nitric acid solutions into ionic liquid

The application of ionic liquids (ILs) as new separation media has been actively investigated recently [40-43]. Visser and Rogers [42] showed that the extraction of Pu(IV), Th(IV), and U(VI) into 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) by a mixture of CMPO and tri-n-butylphosphate is at least an order of magnitude higher than that observed for the same extractant concentration in dodecane. Furthermore, CMPO dissolved in [bmim][PF_6], greatly enhances the extractability and the selectivity towards lanthanide cations compared with the solutions in conventional solvents [43]. We have compared the extraction efficiency of tris-CMPO **1** in 1,2-dichloroethane and 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([bmim][Tf_2N]) solvents towards lanthanide ions from 3M HNO_3 solutions. A considerable enhancement of the D_{Ln} values was observed in the presence of IL in the organic phase (Fig. 7). An increase in the efficiency of Ln(III) extraction with the ligand **1** into IL is apparently connected with incorporation of hydrophobic IL anions into extracted solvates, which makes them more hydrophobic. Similar effect is responsible for the considerable enhancement in Ln(III) and Am(III) extraction with CMPO in the presence of hydrophobic picrate [38] or chlorinated cobalt dicarbollide [44] anions.

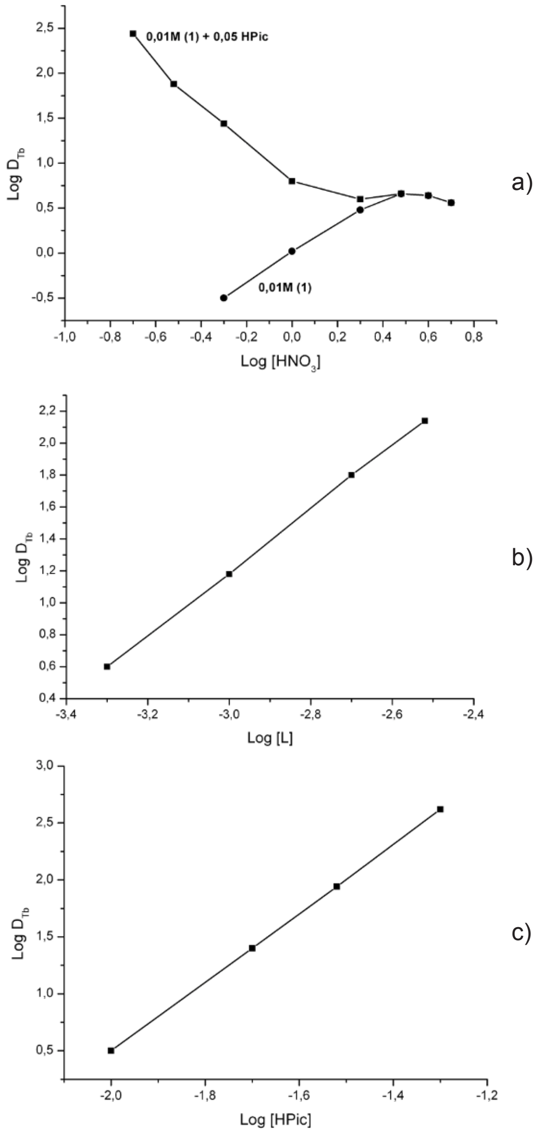


Figure 5. a) The effect of HNO_3 concentration in the aqueous phase on the extraction of Tb(III) by 0.01 M solutions of **1** in 1,2-dichloroethane and in the presence 0.05 M Hpic; b) The effect of extractant **1** concentrations in 1,2-dichloroethane on the extraction of Tb(III) from 0.1 M HNO_3 solutions ([HPic] = 0.05 M); c) The effect of HPic concentrations in 1,2-dichloroethane on the extraction of Tb(III) from 0.1 M HNO_3 solutions ([1]= 0.005 M).

Table 1. Extraction of some metal ions from 0.001 M HNO_3 solution by tris-CMPO **1** in the presence of picric acid in 1,2-dichloroethane[a].

Cation	logD	Cation	logD
Fe^{3+}	1.65	Zn^{2+}	0.11
Al^{3+}	< -1.50	Cd^{2+}	0.32
Mn^{2+}	0.56	Pb^{2+}	2.03
Co^{2+}	0.37	Ca^{2+}	0.62
Ni^{2+}	0.23	Sr^{2+}	1.09
Cu^{2+}	0.16	Ba^{2+}	2.15

[a]*Concentration of 1 and HPic 0.025 M.*

Table 2. Extraction of Ca^{2+}, Sr^{2+} and Ba^{2+} from 0.001 M HNO_3 solutions by the ligand **1-3** in 1,2-dichloroethane in the presence of 0.05 M HPic [a].

Cation	log D		
	1	**2**	**3**
Ca^{2+}	0.90	0.85	-0.40
Sr^{2+}	1.35	0.62	-0.85
Ba^{2+}	2.35	0.52	-0.97

[a]*Concentrations were 0.005 M, 0.005 M, and 0.01 M, respectively, for the ligands **1**, **2**, and **3***

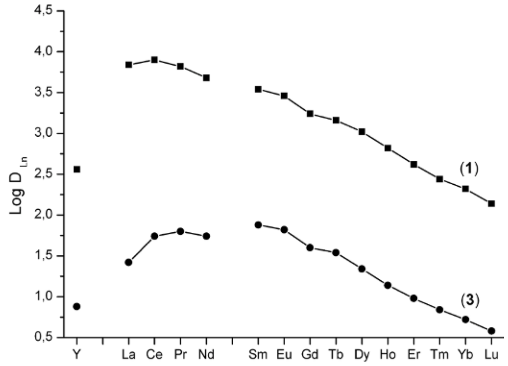


Figure 6. The extraction of lanthanides(III) from 0.1 M HNO_3 solutions with 0.01 M solutions of compounds **1** and **3** in 1,2-dichloroethane in the presence 0.05 M HPic.

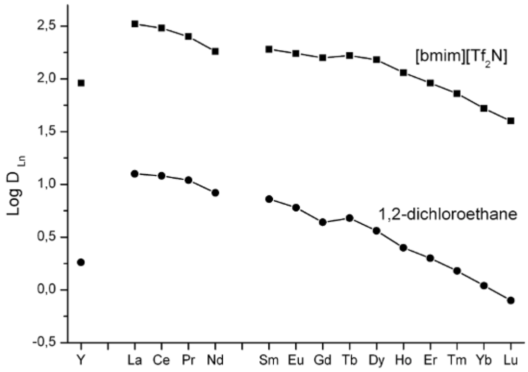


Figure 7. The extraction of lanthanides(III) from 3 M HNO_3 solutions with 0.01 M solutions of compound **1** in 1,2-dichloroethane and [bmim][Tf_2N].

3.2.5. Extraction of ReO_4^- from acidic solutions

A sufficiently easy protonation of the central amine nitrogen atom of the ligand **1** molecule in the acidic media provides also the possibility of extraction of the anionic complexes, *e.g.* ReO_4^- , to the organic phase in the form of ionic pairs. Fig. 8 shows the effect of HNO_3 concentration in the aqueous phase on the extraction of ReO_4^- by solutions of compound **1** in 1,2-dichloroethane. The curve, log D_{Re} *vs.* log [HNO_3], exhibits maximum at [HNO_3] = 0.003 M. This maximum is explained by combined effect of [H^+] on the formation of LH^+ cation and competition for the extractant molecule by the co-extraction of HNO_3. The variations in D_{Ln} as a function of the extractant **1** concentration in 1,2-dichloroethane solution for 0.1 M HNO_3, 0.1 M HCl, 0.1 M $HClO_4$ and 0.1 M H_2SO_4 systems are shown in Fig. 9. The first power dependence of D_{Re} on [L] points out that ReO_4^- is extracted from acidic solutions by compound **1** as $HLReO_4$ complexes. As one may see Re(VII) extraction by solution of compound **1** in 1,2-dichloroethane increases in the order H_2SO_4 < HCl < HNO_3 < $HClO_4$ in parallel with increasing hydration energies of the relevant anions [40], that is, with the increase of hydrophobicity of co-extracted HLA complexes. Furthermore, the extraction ability of the tris-CMPO ligand **1** towards Re(VII) is significantly higher compared withthe related bis-CMPO **2** and especially mono-CMPO **3** ligands.

Therefore, the novel tripodal CMPO ligand **1** with tris-N-[(2-aminoethyl)] scaffold possess higher extraction efficiency towards Ln(III) both from neutral and acidic media than the corresponding mono and di-CMPO compounds as well as the related tripodand with the core carbon atom. Moreover, the presence of the basic nitrogen atom makes this ligand a a promising system for Re(VII) extraction.

3.3. Luminescent properties

Nowadays, *f*-element complexes are in focus in material science and attract growing attention due to their unique luminescent properties defining their relevance to luminescent systems with long lifetimes, photostability, and line-like emission bands [45-53]. The ability of neutral organophosphorus ligands to form strong complexes with Ln(III) is not only of interest for practical processing on nuclear wastes but these complexes may subsequently find self-dependent application for the development of novel luminescent materials. Thus, reported are photophysical properties of complexes of lanthanide ions, Ln(III), with a range of phosphonates [54] including those bearing additional functionalities such as crown ether, phthalimidomethycarboxylate, hydroxyl, carbonyl, and amine groups attached to phosphonic acid [55-59].

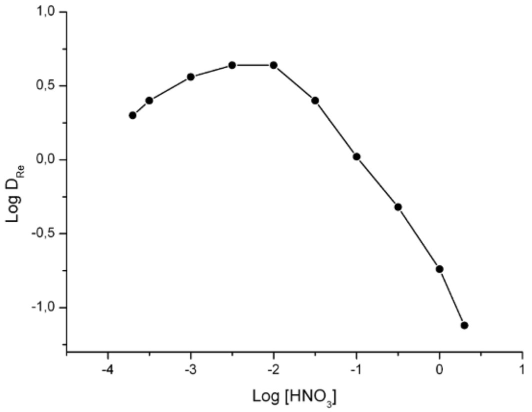


Figure 8. The effect of HNO_3 concentration in the aqueous phase on the extraction of Re(VII) by 2×10^{-4} M solution of compound **1** in 1,2-dichloroethane.

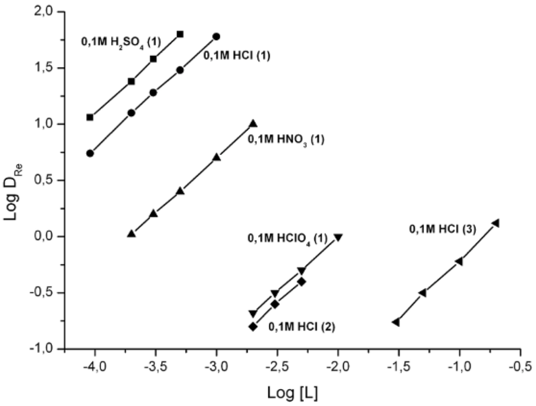


Figure 9. The effect of the concentration of extractants **1-3** in 1,2-dichloroethane on the extraction of Re(VII) from 0.1 HCl, 0.1 M HNO_3, 0.1 M $HClO_4$, and 0.1 M H_2SO_4 solutions.

Nevertheless, despite variety of *f*-element complexes with known CMPO derivatives have been examined by a number of researchers and reported in the literature [29], the data concerning their luminescent properties, to the best of our knowledge, are absent in the literature. Therefore, we have investigated the luminescent behaviour in solid (Eu) and in solutions (Eu and Tb) of some complexes formed by tripodal ligand **1** or the related mono-CMPO ligands **4**, **5** differing in the presence or absence of hydrophilic hydrogen at the nitrogen atom of CMPO moiety. Complexation properties towards *f*-elements for the ligands **4** and **5** were reported by us previously [22]. According to the IR, multinuclear NMR data and X-ray diffraction studies, ligand **4** forms complexes with europium nitrate of different composition having either three or two ligand molecules in Eu coordination sphere, namely, $Eu(NO_3)_3(\mathbf{L^4})_3$ and $Eu(NO_3)_3(\mathbf{L^4})_2$ while ligand **5**, independently on reaction conditions, form only complex $Eu(NO_3)_3(\mathbf{L^5})_2$ of ML_2 composition.

The tris-CMPO ligand **1** also forms strong Eu(III) complex of 1:1 composition**,** $Eu(\mathbf{L^1})Cl_3$, which was obtained using the reaction of the ligand with europium trichloride in ethanol solution (see experimental). In this complex europium coordinates three complexing arms *via* O,O-bidentate coordination mode with participation of all oxygen atoms of the phosphoryl and carbonyl groups. Indeed, in the ^{31}P NMR spectrum the complex demonstrated a singlet upfield shifted (up to 0.7 ppm) compared to the resonance of the free ligand observed at ca. 30 ppm. It should be noted that, in contrast to the phosphonate analogs [58,59], europium complexes of CMPO ligands bearing diphenylphosphoryl group usually display a large upfield coordination shift in the phosphorus spectra with Δδ in the range of 12-45 ppm depending on metal:ligand ratio [29]. This fact may be explained by formation of more strong complexes due to the so called effect of 'anomalous aryl strengthening' [60] as a coordination shift is a measure of the coordination bond strength. The IR spectrum (KBr) of the complex showed no absorption bands of the free P=O and C=O groups while the intensive bands of the metal coordinated phosphoryl and carbonyl group were observed at 1160 cm^{-1} and 1625 cm^{-1}, respectively.

First of all we estimated the luminescent properties in a solid state of the above complexes at 300 K. All complexes show an intensive red luminescence characteristic for the Eu(III) ions in the coordination compounds. The values of the luminescence intensity (I_{lum}, rel. units) at the maximum of the most intensive band at 613 nm which corresponds the supersensitive $^5D_0 \rightarrow {}^7F_2$ transition, are presented in the Table 3. Comparing the I_{lum} values one may note that the value for the complex $Eu(NO_3)_3(\mathbf{L^5})_2$ is higher than that for its analogs formed with ligand **4** with the secondary amide group. Indeed, high-frequency oscillations of the N-H groups (ν=3300 sm^{-1}) are known to be quenchers of lanthanide ion luminescence, particularly when these groups are located close to the coordination unit. In the case of complex $Eu(\mathbf{L^1})Cl_3$, in which the ligand also possess N-H groups, the higher luminescence may be connected with the disposition of the metal ion in the cavity of the tripodal ligand. In such case phenyl groups being the good photoantenna absorbing the UV-radiation, are apparently more close to the coordination unit. Moreover, the influence of different anions (Cl^- and NO_3^-) presenting in the complexes could not be completely excluded.

As one may expect, the luminescence of these Eu(III) complexes is 6-16 fold weaker in ethanol solutions (concentration 1×10^{-3}M) than that observed for the solid samples. In this case, complexes with the ligand

Table 3. Luminescence intensity (I_{lum}) of the europium complexes in the solid state and in solution in the abs. EtOH (c= 1×10^{-3} M).

Eu complex	**I_{lum},* rel. units**		**The luminescence color visually**	
	Solid	**Solution**	**Solid**	**Solution**
$Eu(NO_3)_3(4)_3$	136	21	red	sky-blue
$Eu(NO_3)_3(5)_2$	215	13	red	sky-blue
$Eu(NO_3)_3(4)_2$	184	17	red	sky-blue
$EuCl_3(1)$	217	14	red	red

** I_{lum} values are reduced to the unified experiment condition*

Table 4. Luminescence of europium and terbium complexes in solutions with 1:10 Ln(III):L ratio ($C_{Eu,Tb}$ = 5×10^{-5} M, C_{Lig} = 5×10^{-4} M).

Solutions[a] Tb(III)	**I_{lum},[b] rel. units**	**Solutions[a] Eu(III)**	**I_{lum},[b] rel. units**
$TbCl_3$ + 1	100	**$EuCl_3$ + 1**	30
$TbCl_3$ + 4	107	**$EuCl_3$ + 4**	3
$TbCl_3$ + 5	116	**$EuCl_3$ + 5**	5

[a] Ethanol in the case of ligands 4,5, and 1:1 acetonitrile-ethanol mixture for the ligand 1.
[b] I_{lum} is reduced to the unified experiment conditions.

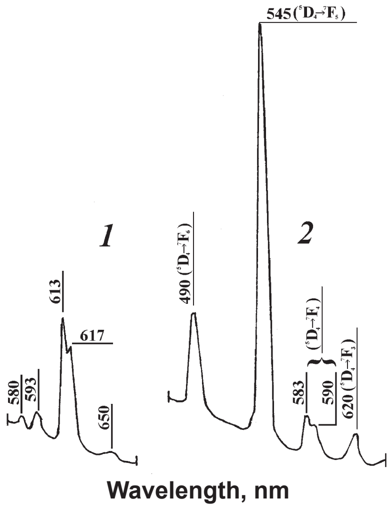


Figure 10. Luminescence spectra of Eu(III) (**1**) and Tb(III) (**2**) complexes with tripodal ligand 1 in acetonitrile solution ($C_{Eu,\ Tb}$=5×10^{-5} M, C_{Lig}=5×10^{-4} M).

4 displayed slightly higher luminescence than those formed by ligands **1** and **5**. Note, that excluding the complex Eu(**L**^{1})Cl_3, visually the sky-blue luminescence was observed in solutions of the complexes with mono-CMPO ligands.

Furthermore, we investigated the luminescent properties of solutions of the complexes obtained by mixing of the lanthanide (Tb(III) and Eu(III)) chloride with the corresponding ligand in different ratio (six series, the ratio M:L was equal to 1:1, 1:2, 1:3, 1:5, and 1:10). In general, the intensity of luminescence increased with the increase of the ligand concentration and achieved the maxima when 10-fold excess of the ligand was used (Table 4). For the complexes formed by the same mono-CMPO ligands **4** and **5**, the intensity of Tb(III) radiation is 20-40 times higher than for the corresponding Eu(III) ones and the luminescence was slightly more intensive when the ligand had no hydrophilic NH-group. For the complex of tris-CMPO **1**, the difference in Tb(III) and Eu(III) luminescence was significantly less (3.3 times) (Fig. 10). It should be noted that in the related studies on photoptical properties complexes of lanthanide ions, Ln(III), formed in solutions by phosphonate analogs of acetylacetonate ligands $RC(O)CH_2P(O)(OEt)_2$ (R= CH_3, Ph) [58] and diethyl(phthalimidomethyl)phosphonate ligand [59] the more intensive luminescence was observed in the case of the Tb-based systems.

4. Conclusions

The novel tripodal CMPO ligand - N-tris[(2-aminoethyl)-2-(diphenylphosphoryl)acetamide)] was synthesized and studied as extractant for Ln(III), alkaline-earth cations and perrenate anion from neutral and acidic media in comparison with the related mono- and bis-CMPO derivatives. The effect of different additives in the aqueous phase and that of the extractant concentration in the organic phase on the extraction of metal ions was considered. The stoichiometry of the extracted complexes has been determined. The Eu(III) and Tb(III) *O,O*-bidentate complexes with carbamoylmethylphosphoryl compounds possess intensive luminescence both in a solid state and in solutions and some insight on the relationship structure-luminescence properties may be of interest for further development of luminescent materials on the base of such compounds.

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