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Tripodal organophosphorus ligands as synergistic agents in the solvent extraction of lanthanides(III). Structure of mixed complexes and effect of diluents

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ABSTRACT

The solvent extraction of lanthanides (III) (except for Pm) from chloride medium (at $\mu = 0.1$) into an organic phase containing 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (**HPy**) and neutral tripodal ligands on the triphenylphosphine oxide platform with anchored carbamoyl side arms (2-$R_2NC(O)CH_2OC_6H_4)_3PO$, where R = Bu (**L1**) and *cyclo*-Hex (**L2**) has been studied. A considerable synergistic effect (up to 10^7) has been observed in the presence of neutral ligands **L1** or **L2** in the organic phase containing **HPy**. The stoichiometry of the Ln(III) extracted species has been determined by slope analysis and the equilibrium constants have been calculated. It has been found that the lanthanides(III) ions are extracted with mixtures of **HPy** and neutral ligands **L1** or **L2** in toluene as Ln**Py**$_3$**L** species. The [La**Py**$_3$(H_2O)$_2$], and new [La**Py**$_3$(**L1**)] and [La**Py**$_3$(**L2**)] complexes have been synthesized and characterized *via* elemental analysis and IR spectroscopy. Solution structure of the above complexes has been examined by IR and multinuclear (^{1}H, ^{13}C, and ^{31}P) NMR spectroscopy in toluene-d_8 and $CDCl_3$. The effect of diluents on synergistic extraction and the solution structure of mixed complexes are discussed.

1. Introduction

Solvent extraction is a widely used technique for the separation and preconcentration of lanthanides(III) ions. A synergistic effect is often used to increase extraction efficiency of the metal ions [1–3]. An explanation of synergistic effect in solvent extraction systems is connected with an increase in hydrophobicity of extracted species by a replacement of water molecules bounded to the metal ion by molecules of synergistic compound [3]. The application of mixtures of acidic chelating extactant and neutral donor is the most studied synergistic extraction processes. During the last few decades, the synergistic extraction of lanthanides(III) with mixtures of acidic chelating extractants such as β-diketones, LIX 54 (commercial extractant, highmolecular weight β-diketone, major part 1-phenyl-3-isoheptyl-1,3-propanedion), 4-acylpyrazolones, 4-acylbis (pyrazolones), 4-benzoyl-3-phenyl-5-izoxazolone, *etc.* and neutral donor extractants (*e.g.* nitrogen-containing compounds [4,5], sulfoxides [6–8], crown ethers [3,9,10], diglycolamides [11,12], neutral monodentate organophosphorus compounds [13–16], (alkyl) arylsubstituted methylene diphosphine dioxides [17], diaryl- or alkyl(aryl)[dialkylcarbamoylmethyl]phosphine oxides [14,18], 2,6-bis((diphenylphosphino)methyl)pyridine *N,P,P*-trioxide [18], carbamoyl- and phosphorylmethoxymethylphosphine oxides [19] *etc.*) has been studied. Many studies have been carried out using phosphorus-containing calix[*n*]arenes as a synergistic agent in the Ln(III) extraction with various acidic chelating extractants of β-diketone type [20–25]. The introduction of P(O) functional groups in the calixarene architecture leads to a significant increase in the extraction efficiency [25]. The addition of phosphorus-containing calix[6]arene to the chelating extractant, 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone, improves the Ln(III) extraction and produces very large synergetistic effects (more than five orders of magnitude) [24].

Recently, novel neutral tripodal ligands on the triphenylphosphine oxide platform with anchored carbamoyl side arms (2-$R_2NC(O)CH_2OC_6H_4)_3PO$, where R = Bu (**L1**) and *cyclo*-Hex (**L2**) were synthesized and their coordination and extraction properties

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toward Ln(III) ions were studied [26,27]. Polytopic neutral ligands **L1** and **L2** extract Ln(III) ions from neutral nitrate solutions into 1,2-dichloroethane much more effectively than their mono analog [2-($Oct_2NC(O)CH_2O$)-5-Et-C_6H_3]$P(O)Ph_2$ and known extractant, diphenyl-*N*,*N*-dibutylcarbamoylmethylphosphine oxide **L3** [27].

In this paper, we report the study of synergistic effect of new tripodal ligands **L1** and **L2** on the extraction of Ln(III) ions with 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (**HPy**) in toluene. Furthermore, we determined the composition of the extracted species of Ln(III). The structure and composition of model La(III) complexes with **HPy** and mixed La(III) complexes with **HPy** and **L1** or **L2** in solid state and solutions (toluene-d_8, $CDCl_3$) were studied by IR, NMR (^1H, ^{13}C, ^{31}P) spectroscopy and characterized by elemental analysis. Lanthanum cation was used as a lanthanide model because it is not paramagnetic, that makes it possible to use NMR spectroscopy. The effect of diluents—cyclohexane, CCl_4, toluene, 1,2-dichloroethane, $CHCl_3$—on the extraction of Eu(III) with a mixture of a chelating extractant **HPy** and neutral ligand **L1** was studied and compared with solvent properties and solution structure of mixed complexes. Synergistic effect of the above ligands **L1** and **L2** is compared with that of known organophosphorus extractant $Ph_2P(O)CH_2C(O)NBu_2$ (**L3**). The structural formulae of the extractants studied are given below (Scheme 1).

2. Experimental

2.1. Reagents

The synthesis of *tris*[2-(*N*,*N*-dibutylcarbamoylmethoxy)phenyl] phosphine oxide (**L1**) [26] and *tris*[2-(*N*,*N*-dicyclohexylcarbamoylmethoxy)phenyl]phosphine oxide (**L2**) [27] was described in the previous works. Diphenyl-*N*,*N*-dibutylcarbamoylmethylphosphine oxide (**L3**) was synthesized according to the known synthesis procedure [28]. The commercial product 4-benzoyl-3-methyl-1-phenylpyrazol-5-one (purity > 99%, Vekton) was recrystallized from absolute ethanol, mp 87–88 °C (mixture of enol and keto forms [29]) (lit. [30]: mp = 92 ± 1 °C (5-OH enol form); mp = 118 ± 1 °C (2-NH-keto form).

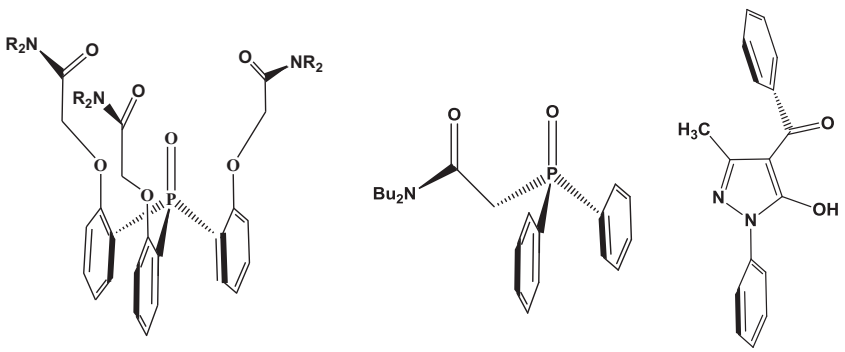
Chemical- and analytical-grade cyclohexane, carbon tetrachloride, chloroform, 1,2-dichloroethane and toluene were used as diluents. Deionized water, HCl (37%, high purity grade) and NaCl (high purity grade) were used for the preparation of solutions in the extraction study. Extractant solutions in the organic diluents were prepared from precisely weighed amounts of the reagents. Stock solutions of the lanthanide(III) ions were prepared from their oxides (reagent grade) by dissolving in concentrated hydrochloric acids and diluting with deinonized water to required volume. Salt $LaCl_3$ (Sigma–Aldrich), deuterated solvents, $CD_3C_6D_5$ (99.8% D, Sigma–Aldrich) and $CDCl_3$ (99.8% D, Sigma–Aldrich), were used as received. Solutions for spectral studies were prepared by volumetric/gravimetric method.

2.2. Apparatus

Multinuclear ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance 500 spectrometer (operating at 500.15, 202.46 and 125.75 MHz, respectively) at 25 °C using $CD_3C_6D_5$ or $CDCl_3$ (c = 0.02 M) solution. Chemical shifts (ppm) refer to the residual protic solvent peaks (for ^1H and ^{13}C), and 85% H_3PO_4 (for ^{31}P) as external standards and coupling constants are expressed in hertz (Hz), the band width at half-height ($W_{1/2}$) is given in ppm (for $^{31}P\{^1H\}$ NMR spectra). IR spectra in the region 400–4000 cm^{-1} for solid samples and 900–4000 cm^{-1} for solutions were obtained on a Bruker Tensor 37 FTIR spectrometer. The samples were KBr pellets and mulls in nujol as well as 0.01, 0.02 and 0.1 M solutions in $CD_3C_6D_5$ and $CDCl_3$, respectively, in CaF_2 cuvettes (0.06 and 0.22 mm). For spectra interpretation, we used band decomposition and abstraction of solution spectra of ligands **L1**, **L2** and complex **1** from the spectra of the corresponding solutions of mixed complexes **2** and **3**. The content of C, H, and N was determined on a Carlo Erba 1106 instrument. The content of P was determined according to the published procedures [31]. Melting points were determined in open capillary tubes on a Stanford Research Systems MPA120 EZ-melt automated melting point apparatus and were not corrected. An X-7 mass spectrometer with a quadrupole mass analyzer (Thermo Electron, USA) was used for measurement of lanthanides concentration and pH-150 digital pH meter was used for pH measurements.

2.3. Solvent extraction procedure

All lanthanides (III) (except for Pm) were present in the initial aqueous phase when simultaneous extraction of Ln(III) was studied. The ionic strength was maintained at 0.1 M with (Na, H)Cl. The initial lanthanides ions concentration was 2×10^{-6} M for each element. Equal volumes (2 mL) of the aqueous and organic phases were shaken mechanically for 60 min at room temperature, this time was sufficient to reach equilibrium. After phase separation, 1 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 1 M HCl solution was added. The mixture was shaken for 30 min and Ln(III) in the organic phase were back-



Scheme 1. Chemical structure of tripodal ligands **L1**, **L2**, reference extractant **L3**, and ligand **HPy**.

extracted into the aqueous phase. Metal concentrations in the initial and equilibrium aqueous solutions after extraction and back-extraction were determinated by inductively coupled plasma mass-spectrometry (ICP-MS). The sum of the metal ions concentrations in the two phases agreed well with the initial concentration. The distribution ratios of lanthanides were calculated as the ratio of concentrations in the equilibrium organic and aqueous phases ($D_{Ln} = [Ln_{org}]/[Ln_{aq}]$). Triplicate experiments showed that the reproducibility of the D_{Ln} measurements was generally within 5%. The acidity of the aqueous phase was measured by a pH-meter with an accuracy of 0.01 pH units.

2.4. Preparation of lanthanum(III) complexes

2.4.1. $[LaPy_3(H_2O)_2]$, **1**

A solution of 0.0267 g (0. 1088 mmol) of $LaCl_3$·in 1 mL of absolute ethanol was added with stirring to a solution of 0.0907 g (0.326 mmol) of ligand **HPy** in 10 mL of absolute ethanol. The reaction mixture was stirred for 5 h at room temperature. The transparent solution was evaporated to dryness under reduced pressure twice to give 0.0902 g of solid. The residue was dissolved in 4 ml of absolute ethanol. The product was precipitated *via* addition of ~0.5–1 ml water dropwise. The solution above the precipitate had neutral pH. The precipitate was separated by filtration, washed with water and dry ether, and dried in vacuo (~1 Torr) at 62 °C to give 0.083 g (81%). Mp (with decomp.) 156 °C (lit. [32]: mp (with decomp.) 151 °C). *Anal.* Calc. for $C_{51}H_{43}N_6LaO_8$: C, 60.84; H, 4.30; N, 8.35. Found: C, 61.01; H, 4.42; N, 8.21%. IR (KBr disk): ν_{max}/cm^{-1} 3428br (νH_2O), 3050vw, 2550br, 1640sh (δH_2O), 1620sh, 1609vs, 1593sh (Ph), 1583sh, 1575m, 1498s, 1477vs, 1458sh, 1432s, 1411sh, 1398sh, 1367m, 1357sh, 1230vw, 1205w, 1177w, 1152w, 1072w, 1058w, 1025w, 999vw, 946m, 835m, 762m, 729w, 702sh, 692m, 657w, 611 m. ^{1}H NMR (500.13 MHz, $CDCl_3$, 0.02 M): δ 1.5 (9H, br s, 3-CH_3), ~ 4.5 (~4H, v br s, H_2O), 6.97–7.40 (24H, br m, Ph-H), 7.73 (6H, br s, Ph-H). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, 0.02 M): 15.70 (br s, 3-CH_3), 106.54 (br s,C-4), 120.53 (br s, Ph-C), 125.22 (br s, Ph-C), 127.83 (br s, Ph-C), 128.16 (br s, Ph-C), 128.55 (br s, Ph-C), 130.91 (br s, Ph-C), 137.72 (br s, Ph-C), 139.07 (br s, Ph-C), 148.66 (br s, C-3), 162.96 (br s, C-5), 190.81 (br s, C-6).

2.4.2. $[LaPy_3(L1)]$, **2**

A solution of 0.0462 g (0.0554 mmol) of ligand **L1** in 1 ml of absolute ethanol and a solution of 0.0136 g (0.0555 mmol) of $LaCl_3$·in 1 mL of absolute ethanol was added with stirring to a solution of 0.0462 g (0.1662 mmol) of ligand **HPy** in 4 mL of absolute ethanol. The reaction mixture was stirred for 5 h at room temperature. The product was precipitated *via* addition of ~1.5–2 ml water dropwise. The precipitate was separated by filtration, washed with water, dissolved in 1.2 mL of absolute ethanol, evaporated to dryness, and dried in vacuo (~1 Torr) over P_2O_5 at 62 °C to give 0.083 g (83%). Mp 97–98 °C. *Anal.* Calc. for $C_{99}H_{111}N_9LaO_{13}P$: C, 65.88; H, 6.20; N, 6.98; P, 1.72. Found: C, 65.86; H, 6.19; N, 6.95; P, 1.70%. IR (KBr disk): ν_{max}/cm^{-1} 3450br, 3280br, 3060vw, 2958w, 2930w, 2872w, 1660sh, 1621vs, 1614sh, 1594s, 1578m, 1499s, 1482s, br, 1459sh, 1436m, 1396w, 1364w, 1239w, 1215w, 1151m, 1060m, 947m, 835w, 763m, 704w, 657w, 612w, 544vw, 511vw. ^{1}H NMR (500.13 MHz, $CD_3C_6D_5$, 0.02 M): δ 0.68–0.75 (9H, br m, 3-CH_3(**Py**)), 0.82–0.95 (18H, br t, CH_3 (**L1**)), 1.05–1.20 (6H, br m, CH_2 (**L1**)), 1.25–1.42 (6H, br m, CH_2 (**L1**)), 2.30–2.50 (6H, v br s, CH_2 (**L1**)), 2.90–3.25 (6H, v br s, CH_2 (**L1**)), 4.0–4.5 (~6H, v br s, CH_2O), 6.50–6.80 (~6H, v br m, Ar-H), 6.87–6.97 (3H, br m, Ar-H), 7.25–7.45 (~6H, v br s, Ar-H), 8.68–8.90 (~6H, v br s, Ar-H). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CD_3C_6D_5$, 0.02 M): δ 13.70 (s, CH_3 (**L1**)), 13.77 (s, CH_3 (**L1**)), 16.74 (br s, 3-Me), 29.81 (s, N–CH_2–CH_2), 30.35 (s, N–CH_2–CH_2), 45.68 (s, N–CH_2), 45.95 (s, N–CH_2), ~67.0 (v br s, CH_2O), 106.39 (s, C-4), ~113.0–115.0 (vv br s, Ar-C), 119.46 (s, Ph-C), 121.27 (d, J = 12.5, Ar-C (**L1**)), 123.00 (s, Ar-C (**L1**)), 127.80 (s, Ar-C),128.8 (s, Ar-C), (129.16 (s, Ar-C), 133.0 (v br s, Ar-C), ~134.5–136.2 (vv br s, Ar-C), 140.65 (s, Ph-C), 141.75 (s, Ph-C), 147.77 (s, C-3), ~160.9 (v br s C-2′ (**L1**)), 165.50 (s, C-5), ~166.9 (v br s, C=O (**L1**)), 188.71 (s, C-6). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CD_3C_6D_5$, 0.02 M): δ 29.0(s, $W_{1/2}$ = 0.2).

2.4.3. $[LaPy_3(L2)]$, **3**

A solution of 0.0970 g (0.0980 mmol) of ligand **L2** in 1 ml of absolute ethanol and a solution of 0.0238 g (0.0980 mmol) of $LaCl_3$·in 1 mL of absolute ethanol was added with stirring to a solution of 0.0817 g (0.294 mmol) of ligand **HPy** in 11 mL of absolute ethanol. The reaction mixture was stirred for 5 h at room temperature. The product was precipitated *via* addition of ~0.5–1 ml water dropwise. The precipitate was separated by filtration, washed with water and dry ether, and dried in vacuo (~1 Torr) over P_2O_5 at 62 °C to give 0.173 g (90%). Mp (with decomp.) >170 °C. *Anal.* Calc. for $C_{111}H_{123}N_9LaO_{13}P$: C, 67.98; H, 6.32; N, 6.43; P, 1.58. Found: C, 67.98; H, 6.29; N, 6.27; P, 1.49%. IR (nujol): ν_{max}/cm^{-1} 1661m, 1651sh, 1620s, 1615s, 1612s, 1592m, 1577m, 1498m, 1311m, 1290sh, 1267w, 1228m, 1180vw, 1164sh, 1150sh, 1142m, 1125m, 1091w, 1071m, 1059sh, 1025m, 997w, 916m, 894w, 835w, 813w, 755m, 729s, 719m, 657w, 611w. ^{1}H NMR (500.13 MHz, $CD_3C_6D_5$, 0.02 M): All signals are very broadened and could not be interpreted. $^{13}C\{^1H\}$ NMR (125.76 MHz, $CD_3C_6D_5$, 0.02 M): δ 15.58*[1] (br s, 3-CH_3), 16.09* (s, 3-CH_3), 16.60 (br s, 3-CH_3), 25.4 (v br s, CH_2 (cyclo-Hex)), 26.6 (v br s, CH_2 (cyclo-Hex)), ~30.0 (v br s, CH_2 (cyclo-Hex)), ~30.8 (v br s, CH_2 (cyclo-Hex)), 55.67 (s, N–CH), 56.0 (v br s, N–CH), 56.89 (s, N–CH), 66.5 (br s, CH_2O), 68.7 (v br s, CH_2O), 103.7* (s, C-4), 106.54 (s,C-4), ~111.0–112.5 (v br s, Ar-C), 113.86* (s, Ar-C), ~115.0–116.5 (v br s, Ar-C), 119.05* (s, Ph-C), 119.0 (br s, Ph-C), 120.7* (br s, Ar-C), 121.0–122.5 (v br s, Ar-C), 123.2 (br s, Ar-C), 131.2 (s, Ar-C), 132.5 (br s, Ar-C), 133.4 (s, Ar-C), 138.1 (s, Ar-C), 140.51 (s, Ph-C), 141.7 (br s, Ph-C), 142.38 (s, Ph-C), 147.07* (s, C-3), 147.8 (br s, C-3), 149.28* (s, C-3), ~159.5 (v br s, C-2′), 163.0 (br s C-2′), 164.73* (s, C-5), 165.26 (s, C-5), 167.0 (v br s, C=O (**L2**)), 188.5 (v br s, C-6), 189.4* (s, C-6), 190.4* (s, C-6). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CD_3C_6D_5$, 0.02 M): δ 26.7 (s, $W_{1/2}$ = 0.05), 29.4 (br s, $W_{1/2}$ = 0.2), 32.0 (s, $W_{1/2}$ = 0.05); (integral intensity ratio 0.03:1.00:0.21).

3. Results and discussion

3.1. Extraction of lanthanide(III) ions with mixtures of **HPy** and neutral ligands **L**

The solvent extraction of lanthanide(III) ions with 4-acylpyrazolones is well documented [33].The lanthanide(III) extraction with a solution of **HPy** alone in benzene [34], chloroform [35], carbon tetrachloride [35], cyclohexane [35], and in toluene [19] was studied previously. The metal extraction can be represented by the equation

$$Ln^{3+}_{aq} + 4\mathbf{HPy}_{org} \rightleftharpoons Ln\mathbf{Py}_3\mathbf{HPy}_{org} + 3H^+_{aq} \quad (1)$$

where Ln^{3+} denotes lanthanides and the subscripts "aq" and "org" denote aqueous and organic phases, respectively, and $D_{Ln(Py)} = [Ln_{org}]/[Ln_{aq}]$ ($D_{Ln(Py)}$ is distribution ratio for extraction with **HPy** alone).

The corresponding extraction constant $K_{\mathbf{Py}}$ is

$$K_{Py} = D_{Ln(Py)}\left[H^+\right]^3_{aq}[\mathbf{HPy}]^{-4}_{org} \quad (2)$$

[1] *Signals of low intensity.

Preliminary experiments showed that the lanthanides(III) extraction with compounds **L1**, **L2**, and **HPy** alone is negligible ($D_{Ln} < 10^{-2}$) under the experimental conditions of the present study. However, a considerable enhancement of the Ln(III) extraction with **HPy** in the presence of compounds **L** in the organic phase is observed.

The synergistic solvent extraction of lanthanides was studied using traditional and effective approaches to obtain stoichiometric coefficients. The composition of the extracted species in the organic phase and equilibrium constants information were determined by slope analysis. It is based on an examination of the variation of $D_{Ln(\mathbf{Py,L})}$ ($D_{Ln(\mathbf{Py,L})}$ is the distribution ratio due to the synergistic effect with mixture of **HPy**–**L**) as a function of the relevant experimental variables. The experimental data for the extraction of the Ln(III) ions with mixture of **HPy** with **L1** or **L2** are given in Figs. 1–3.

The plots of $\log D_{Ln(\mathbf{Py,L})}$ *vs.* pH and log[**HPy**] are linear with slope close to three, and the plots of $\log D_{Ln(\mathbf{Py,L})}$ *vs.* log[**L**] with a slope close to one. Therefore, the lanthanides extraction with **HPy**–**L** mixture can be expressed by the following equations:

$$Ln^{3+}_{aq} + 3\mathbf{HPy}_{org} + \mathbf{L}_{org} \rightleftharpoons Ln\mathbf{Py}_3\mathbf{L}_{org} + 3H^{+}_{aq} \quad (3)$$

As the Ln(III) extraction from aqueous solutions with compounds **L1**, **L2** and **HPy** alone is negligible ($\log D_{Ln(\mathbf{Py})} < -2$, and $\log D_{Ln(\mathbf{L})} < -2$) at pH = 2, the values of $D_{Ln(\mathbf{Py,L})}$ obtained experimentally are equal to the distribution ratios due to the synergistic effect and the overall equilibrium constant values $K_{\mathbf{Py,L}}$ can be determined by the equation:

$$\log K_{Py,L} = \log D_{Ln(Py,L)} - 3\log[\mathbf{HPy}]_{org} - \log[\mathbf{L}]_{org} - 3\mathrm{pH} \quad (4)$$

The formation of synergistic adducts in the organic phase can be described by the equation:

$$Ln\mathbf{Py}_3\mathbf{HPy}_{org} + L_{org} \rightleftharpoons Ln\mathbf{Py}_3\mathbf{L}_{org} + \mathbf{HPy}_{org} \quad (5)$$

The equilibrium constant $\beta_{\mathbf{Py,L}}$ for the adducts formation in the organic phase can calculated using the expression

$$\log \beta_{Py,L} = \log K_{Py,L} - \log K_{Py} \quad (6)$$

The values of the equilibrium constants $K_{\mathbf{Py,L}}$ and $\beta_{\mathbf{Py,L}}$ were calculated from the experimental data are and are presented in Table 1. Note that these constants are concentration only, because they were calculated on the assumption that the activity coefficients of the involved species do not change significantly under the experimental conditions of the present work.

The data presented in Table 1 show that the addition of neutral donor ligands **L1** and **L2** to the system Ln(III)–**HPy** leads to a very large increase of the efficiency of Ln(III) extraction. The synergistic enhancement produced by mixtures of **HPy** and the studied neutral donor extractants can be determined using a synergistic coefficient $SC = D_{Ln(\mathbf{Py,L})}/(D_{Ln(\mathbf{Py})} + D_{Ln(\mathbf{L})})$, where $D_{Ln(\mathbf{L})}$, $D_{Ln(\mathbf{Py})}$ and

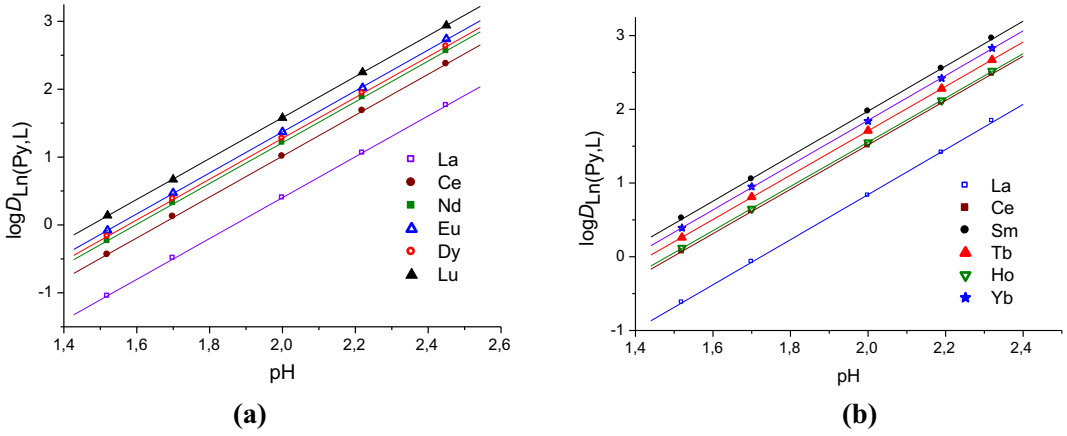


Fig. 1. $\log D_{Ln(\mathbf{Py,L})}$ *vs.* pH for extraction of Ln(III) with mixtures of **HPy**–**L1** (**a**) and **HPy**–**L2** (**b**) in toluene. [**HPy**] = 0.02 M, [**L**] = 0.003. Slope (**a**): 3.01 ± 0.01 (La); 3.02 ± 0.01 (Ce); 3.01 ± 0.01 (Nd); 3.02 ± 0.01 (Eu); 3.01 ± 0.01 (Dy); 3.01 ± 0.01 (Lu). Slope (**b**): 3.06 ± 0.02 (La); 3.00 ± 0.02 (Ce); 3.05 ± 0.02 (Sm); 3.01 ± 0.01 (Tb); 3.00 ± 0.01 (Ho); 3.03 ± 0.02 (Yb).

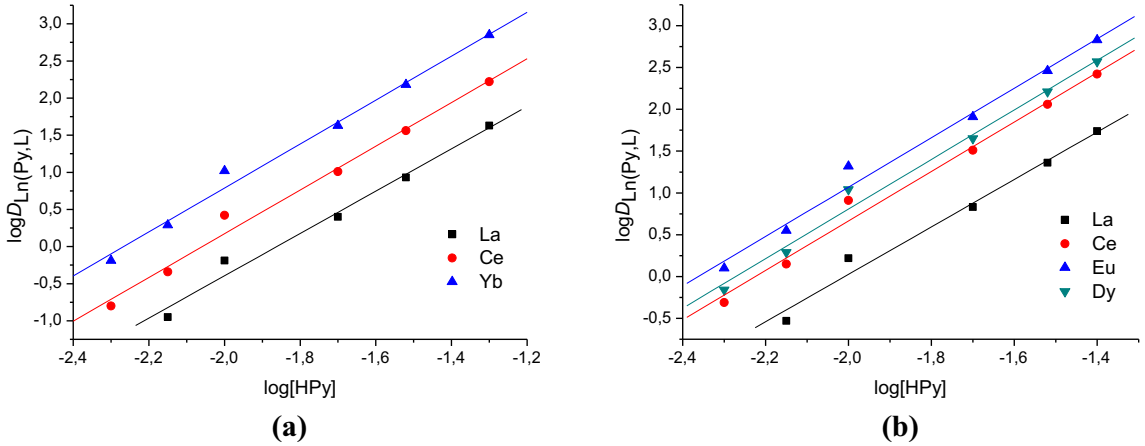


Fig. 2. $\log D_{Ln(\mathbf{Py,L})}$ *vs.* log[**HPy**] for extraction of Ln(III) with mixtures of **HPy**–**L1** (**a**) and **HPy**–**L2** (**b**) in toluene. [**L**] = 0.003, pH = 2.0. Slope (**a**): 2.85 ± 0.21 (La); 2.95 ± 0.16 (Ce); 2.96 ± 0.15 (Yb). Slope (**b**): 2.83 ± 0.22 (La); 2.96 ± 0.17 (Ce); 2.96 ± 0.17 (Eu); 2.97 ± 0.16 (Dy).

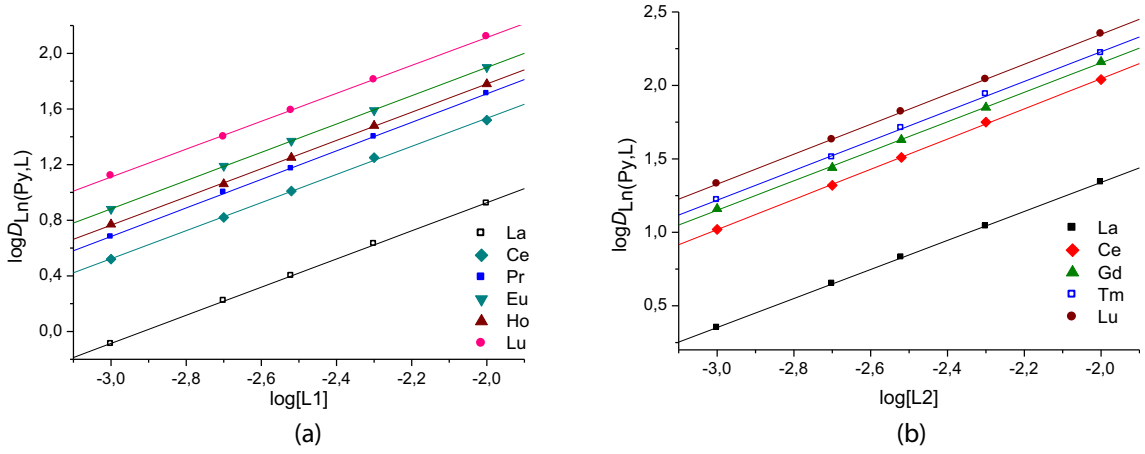


Fig. 3. log$D_{Ln(\mathbf{Py,L})}$ *vs.* log[**L**] for extraction of Ln(III) with mixtures of **HPy**–**L1** (**a**) and **HPy**–**L2** (**b**) in toluene. [**HPy**] = 0.02 M; pH = 2.0. Slope (**a**): 1.01 ± 0.01 (La); 1.01 ± 0.02 (Ce); 1.02 ± 0.01 (Pr); 1.010 ± 0.004 (Eu); 1.02 ± 0.01 (Ho); 1.00 ± 0.01 (Lu). Slope (**b**): 0.99 ± 0.01 (La); 1.02 ± 0.01 (Ce); 1.00 ± 0.01 (Gd); 1.01 ± 0.01 (Tm); 1.02 ± 0.004 (Lu).

Table 1
Values of equilibrium constants K_{Py}, $K_{Py,L}$, $\beta_{Py,L}$ as well as values of the synergistic coefficients SC for Ln(III) extraction with **HPy**–**L** mixtures in toluene ([**HPy**] = 0.02 M, [**L**] = 0.003 M, pH = 2.0).

Ln	logK_{Py} [19]	log$K_{Py,L}$(**L1**)	log $\beta_{Py,L}$(**L1**)	logSC(**L1**)	log$K_{Py,L}$(**L2**)	log$\beta_{Py,L}$(**L2**)	logSC(**L2**)
La	−5.56	2.02	7.58	6.76	2.45	8.01	7.19
Ce	−4.83	2.62	7.46	6.64	3.13	7.96	7.14
Pr	−4.36	2.79	7.15	6.33	3.34	7.70	6.88
Nd	−4.08	2.83	6.91	6.09	3.39	7.47	6.65
Sm	−3.48	3.05	6.53	5.71	3.59	7.07	6.25
Eu	−3.35	2.99	6.34	5.52	3.53	6.88	6.06
Gd	−3.44	2.79	6.23	5.41	3.25	6.69	5.87
Tb	−3.17	2.88	6.05	5.23	3.32	6.49	5.67
Dy	−3.06	2.89	5.95	5.13	3.27	6.33	5.51
Ho	−3.07	2.87	5.94	5.12	3.17	6.24	5.42
Er	−2.94	2.95	5.89	5.07	3.18	6.12	5.30
Tm	−2.67	3.13	5.80	4.98	3.33	6.00	5.18
Yb	−2.43	3.25	5.68	4.86	3.46	5.89	5.07
Lu	−2.46	3.21	5.67	4.85	3.44	5.90	5.08

$D_{Ln(\mathbf{Py,L})}$ are the distribution ratios of the metal ion upon extraction with the two extractants taken separately and with their mixture, respectively.

The addition of **L** to the chelating extractant **HPy** improves the extraction efficiency of the lanthanides ions and produces very large synergistic effects (up to 10^7). The synergistic enhancement established in the present study is higher (up to 10^3–10^4) as compared to those found in some of investigations dealing with lanthanides extraction with the same acidic chelating extractant (**HPy**) and various synergistic agents, *e.g.* phosphoryl-containing compounds [27], phosphorus-containing calixarenes––calix[8]arene [22], calix[4]arene [20], ––calix[4]arene [23], 1-(2-pyridylazo)-2-naphthol [36], dibenzo-18-crown-6 or dibenzo-24-crown-8 [37]. Synergistic effects, close to that found in this work, was revealed only for phosphorus-containing calix[6]arene [24]. Let us note that the values of SC for Ln(III) extraction with **HPy**–**L2** mixture are higher as compared with **HPy**–**L1** mixture (Table 1), although ligand **L1** is more lipophilic than ligand **L2** [27].

The data presented in Table 1 show that the values of $\beta_{Py,L}$, $K_{Py,L}$ as well as SC decrease from La(III) to Lu(III). A similar tendency was observed previously for synergistic extraction of Ln(III) using **HPy** mixtures with trioctylphospine oxide [13], phosphorus-containing calix[6]arene [24] and dibutyl-(N,N-dibutylcarbamoylmethoxy) phosphine oxide [19].

3.2. Effect of structure of synergistic agent **L** on the extraction efficacy

To compare the extraction efficiency of neutral donor compounds with different number of coordinating groups, the extraction of Ln(III) ions from aqueous solutions with mixtures of **HPy** and compounds **L1**, or **L2**, or **L3** in toluene was studied. At the same experimental conditions, the extraction ability of compounds **L1** and **L2** as a sinergist is higher than that of reference extractant **L3** (Fig. 4).

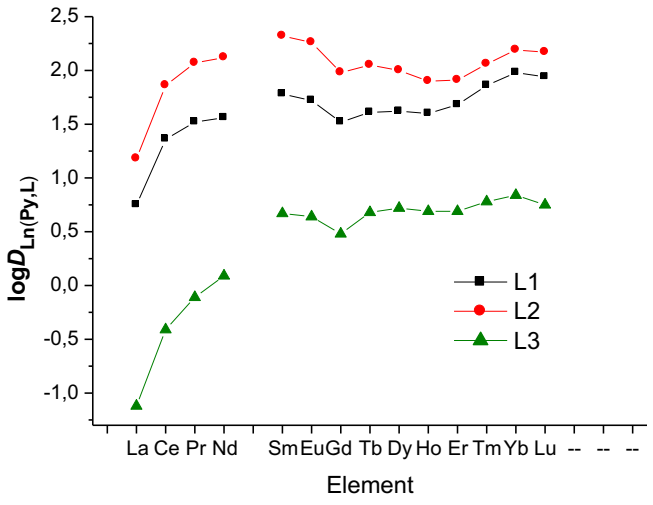


Fig. 4. Extraction of Ln(III) from aqueous chloride solutions with mixtures of **HPy** with ligand **L1**, or **L2**, or **L3** in toluene. [HPy] = 0.03 M; [L] = 0.002 M; pH = 2.0. Dots are connected with lines to provide better readability.

Thus, tripodal ligands **L1** and **L2** containing the same P═O and C(O)NAlk$_2$ groups as in reference extractant **L3** provide considerably higher synergistic effect.

Fig. 4 shows that the efficiency of Ln(III) extraction with **HPy**–**L2** mixture is higher than that with **HPy**–**L1** mixture. At the same time, ligand **L1** is known to be slightly more lipophilic than **L2** [27]. To elucidate the reasons and features of synergistic efficacy of compounds **L1** and **L2** in toluene, we prepared new mixed complexes of composition La:**Py**:**L** = 1:3:1, corresponding to the composition of extracted species, and studied their structure in solid state and solutions in this solvent (see Sections 3.4, 3.5.1, and 3.6.1.)

3.3. Diluent effect on the synergistic extraction

The effect of organic diluent on the synergistic extraction of Ln(III) ions was studied by the example of extraction of Eu(III) with mixtures of **HPy** and compound **L1**. The data in Table 2 show that the extraction efficiency increases in the order: chloroform ≪ 1,2-dichloroethane < toluene < carbon tetrachloride < cyclohexane.

In the first approximation, when chloroform being excluded, extraction efficiency increases when dielectric constant and dipole moment of solvent decrease (Table 2). The same tendency was observed for the Ln(III) ions extraction with mixtures of **HPy** (or other acidic chelating extractants) and neutral donor compounds [39–43].

As shown above in this paper (see Section 3.1), extracted species are neutral complexes of composition [Ln**Py**$_3$**L**]. Therefore, the most efficient extraction will be achieved into nonpolar solutions. However, the extraction into chloroform, which is nonpolar solvent (ε = 4.79), is considerably lower than into other solvents with close dielectric constant (*e.g.*, more polar dichloroethane (ε = 10.4), Table 2). We studied the structure of species involved in extraction equilibria (**HPy**, **L**, and mixed lanthanum complexes) in more detail by the example of two solvents––toluene and chloroform (vide infra Section 3.6.2).

3.4. Synthesis and solid state characterization of the La(III)complexes with *HPy* and *L*

The majority of described crystalline lanthanide complexes of pyrasolone **HPy** has composition [Ln**Py**$_3$Solv$_2$] (Solv is a molecule of water or other solvent) [44]. Common coordination number (CN) of lanthanide cations is eight. Lanthanide has CN = 7 only in complexes of acylpyrazolones with bulky substituents, whose structures include one solvent molecule. In all lanthanide complexes of pyrazolones known to date, pyrazolonate ions behave as O,O-bidentate ligands. The two oxygen atoms and Ln–O bond distances are nonequivalent [44]. We prepared complex [La**Py**$_3$(H$_2$O)$_2$] (**1**) of known structure [32,45] to provide correct comparison of mixed complexes structure.

Compounds **L1** and **L2** are tripodal polytopic ligands, whose molecules include strong donor P═O and C═O groups and weaker ether oxygen atoms of C—O—C groups, which also can participate in coordination to lanthanide cations [27]. In lanthanide nitrate complexes, the tripodal ligands have variable denticity with different donor center combination [27].

The mixed complexes **2** and **3** were prepared by the reaction of stoichiometric amounts of pyrazolone **HPy** and ligands **L1** or **L2** with lanthanum(III) chloride in absolute ethanol. The composition and structures of the complexes in the solid state were studied using elemental analysis, and IR spectroscopy. Complexes **2** and **3** are white solids stable in air and well soluble in alcohol and nonpolar solvents. Complex **2** is less lipophilic than complex **3**. Spectral data were analyzed with the use of characteristics of previously obtained complexes [La(**L1**)(NO$_3$)$_3$] (**4**), [La(**L1**)$_2$(NO$_3$)$_2$](NO$_3$) (**5**), [La(**L2**)(NO$_3$)$_3$] (**6**), and [La(**L2**)$_2$(NO$_3$)$_2$](NO$_3$) (**7**) [27].

Table 3 displays vibrational frequencies of functional groups of ligands **L1** and **Py**$^-$ in solid complex **2** and the corresponding frequencies used for the comparison of compounds **HPy** and **4**. The spectrum of complex **3** in general is similar to the spectrum of complex **2**, while the spectra of their solutions are similar to the spectra of solids. Revealed differences and features are discussed in the text.

The spectrum of solid pyrazolone **HPy** exhibits bands typical for the enol form of **HPy** with hydrogen bond C–OH···O═C: at 1604 and 1560 cm^{-1} referred to the mixed vibrations of double bonds ν(C═O) and ν(C═C)), 1285 cm^{-1} related to ν(C–OH) vibration, and a wide band with maximum at about 3100 cm^{-1} (ν(O—H)) [46]. The main changes in the spectrum of complex **1** as compared with the spectrum of **HPy** is the disappearance of bands at 1560 and 1285 cm^{-1} and emergence of absorption at 1477 cm^{-1}, as well as a slight shift of band about 1600 cm^{-1} to the high-frequency region (Table 3). Similar spectral data were obtained for complexes Ln**Py**$_3$X$_n$ (where X is molecule of solvent or neutral donor ligand) with established bidentate coordination of pyrazolonate ions, it should be noted that the value of shift of the band about 1600 cm^{-1} depends on metal [32,47–49]. Consequently, the couple of bands at 1609 and 1477 cm^{-1} in complex **1** can be related to C—O bond vibrations, whose frequencies altered on deprotonation and replacement of hydrogen bond by coordination bond. The spectrum of the complex shows the absorption bands of water molecules at 3428 and 2550 cm^{-1} (ν(OH)) and at 1640 cm^{-1} (δ(OH)). Thus, pyrazolonate ions in complex **1** are coodrinated in bidentate mode.

The analysis of spactrum of mixed complex **2** is complicated by band overlapping. For example, pyrazolonate ions show absorption (1620, 1610 cm^{-1}) in the region of vibrations of coordinated C═O bonds of ligand **L1** (1610 cm^{-1} in complex **4**), while a strong band of ligand **L1** (1475 cm^{-1}) is in the region of C—O bond vibrations of coordinated pyrazolonate ions (1477 cm^{-1} in complex **1**). The same situation is observed for the spectra of **L2** complexes. Nonetheless, we can note that vibration frequencies of pyrazolonate ions in mixed complex **2** are close to those in complex **1**, except for the band at 1488 cm^{-1} apperared in the spectrum of

Table 2
Solvent properties [dielectric constant (ε), dipole moment (μ)] and values of equilibrium constants $K_{Py,L}$ for Eu(III) extraction with **HPy**-**L1** mixture in organic diluents.

Diluent/solvent	ε [38]	μ [38]	log$K_{Py,L}$(**L1**)
Cyclohexane	2.02	0	6.25
Carbon tetrachloride	2.23	0	3.74
Toluene	2.38	0.36	2.99
1,2-Dichloroethane	10.4	1.44	2.09
Chloroform	4.79	1.87	0.77

Table 3
Selected IR (ν, cm^{-1}) spectroscopic data for the ligand **L1**, **HPy** and complexes **1**, **2**, and **4** in the solid state.

Compound	**L1** vibrations		**Py** vibrations
	ν(P═O)	ν(C═O)	ν(C—O, C—C, C═N) + δ(CH)
L1 [27]	1181	1669, 1654, 1648	
4 [27]	1121	1665, 1630, 1610	
HPy			1620, 1604, 1587, 1574, 1560, 1498
1			1620, 1609, 1583, 1575, 1498, 1477
2	1151	1664, 1655, ~1613	1621, 1610, 1577, 1498, 1488, 1482, 1477

complex **2** along with the band at 1477 cm^{-1}. Pyrazolonate ions seem to be coordinated differently. We showed [27] that phosphoryl and two carbonyl groups are coordinated in complex **4**, its spectrum contains ν(P=O) and ν(C=O) bands shifted to the low-frequency region with respect to those of free ligand **L1** (Table 3). The band of ν(P=O) in the spectrum of mixed complex **2** is shifted in a lesser extent to1150 cm^{-1}, *i.e.*, the phosphoryl grup is coordinated weaker than in complex **4**. The spectrum of complex **2** exhibits a split band of medium intensity with maxima at 1660 and 1651 cm^{-1} in the region of vibrations of free C=O groups, the spectrum of complex **3** displays a similar band. It is impossible to determine the strict vibration frequency of coordinated C=O groups because of band overlapping. Using spectrum decomposition, we determined absorption about 1613–1615 cm^{-1} (about 1609–1615 cm^{-1} for similar complex **3**), which can be referred to the ν(C=O) vibrationof coordinated group. For the same reason, it is impossibe to determine from the intensity ratio of ν(C=O) whether one or two C=O groups are coordinated. Let us note that the spectral appearance of coordination of C—O—C groups could not be determined unambiguously because, according to quantum chemical calculations [26], the bands in the region 1260–1210 cm^{-1} are related to mixed modes and include contribution of both C_{Ar}–O and ν(P=O) bond vibrations [27]. Since CN of lanthanides in pyrazolonate complexes as a rule is eight, one can suppose that tripodal ligand **L1** will be coordinated in P(O),C(O)-bidentate mode.

Thus, pyrazolonate ions in solid mixed complexes **2** and **3** are coordinated in O,O-bidentate nonequivalent mode, whereas ligands **L1** and **L2** display P(O),C(O)-coordination. Lanthanum coordination number is eight.

3.5. Solution-state characterization of the complexes

Solution structure of complexes **1**–**3** was examined by IR and multinuclear (^{1}H, ^{13}C, and ^{31}P) NMR spectroscopy. Solvents used were toluene and chloroform because these diluents show dramatically different effect on the synergistic extraction. Along with complexes in these solvents, we also studied the structure of pyrazolone **HPy** and ligands **L1** and **L2** (see Section 3.6).

The selected suitable for analysis parameters of and ^{31}P, and ^{13}C NMR spectra for the solutions of mixed complexes **2** and **3** in comparison with the data for the free ligands **HPy**, **L1**, and **L2** are given in Tables 4 and 5.

The tables also include the data for lanthanum complexes **1** and **4**–**7** used for comparison. The signals in ^{1}H NMR spectra of both mixed complexes **2**, **3** are considerbly broadened and could not be integrated, therefore these spectra are excluded from discussion below. The sole exclusion is the ^{1}H NMR spectrum of complex **2** in toluene-d_8. No fine structure is observable; however, the signals show expected shifts, which are in line with the complex structure assumed on the basis of other spectral data (Fig. S1).

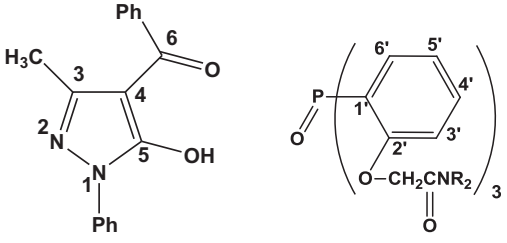
The chelate O,O-coordination of pyrazolonate ions is reliably determined by the data of IR, ^{1}H and ^{13}C NMR spectra [32,48]. Signal broadening in the spectra agrees well with nonequivalent coordination of pyrazolonate ions (Table 4).

The coordination of the P=O group of ligands **L** can be reliably determined from the NMR spectra of complexes. The signals of the phosphorus nuclei exhibit corresponding downfield shifts (Table 5) close to those for the known complexes of tripodal ligands [27]. The participation of the C=O group of ligands **L** in coordination appears in the ^{13}C NMR spectra as a downfield shift of the carbon signals of the C=O group relative to the free ligand signals [27]. The carbon resonances of neighboring CH_2 groups also display the corresponding shifts (Table 5). The participation of C—O—C ethereal oxygen atoms in coordination should result in the shift of resonances for neighboring C-2′ and OCH_2 groups. The shift of C-2′ nucleus is more reliable indicator of ethereal oxygen coordination, because the signal of –OCH_2– group will respond to coordination of both carbonyl and ethereal oxygen atoms. IR spectra proved to be less informative that NMR spectra and more complex for assignement because of overlapping of absorption bands of ligands **L1** and **L2** and pyrazolonate ions (see Section 3.4).

3.5.1. Toluene solutions

^{13}C NMR spectral data of complex **2** in toluene-d_8 are similar to the data for model complex **1** and indicate the O,O-coordination of all three pyrazolonate ions (Table 4). The IR spectrum of solution of mixed complex **2** shows ν(C—O) band of pyrazolonate ions shifted

Table 4
Selected ^{13}C NMR spectroscopic data (δ_C, ppm) for ligand **HPy** and its lanthanum complexes **1**–**3** in toluene-d_8 and $CDCl_3$ (0.02 M) at 25 °C.



Com-pound	Solvent	δ_C(C-4)	δ_C(C-3)	δ_C(C-5)	δ_C(C-6)	δ_C(3-CH_3)
HPy	Toluene-d_8	103.66 s	147.02 s	162.59 s	190.36 s	15.54 s
	$CDCl_3$[a]	103.60 s	148.00 s	161.44 s	192.13 s	15.83 s
1	Toluene-d_8[b]	106.53 s	147.79 br s	162.96 s	190.35 br s	15.67 br s
	$CDCl_3$	106.54 br s	148.66 br s	162.96 br s	190.81 br s	15.70 br s
2	Toluene-d_8	106.39 s	147.77 s	165.50 s	188.71 s	16.74 s
	$CDCl_3$[c]	106.15 br s	148.54 br s	164.58 br s	189.2 br s	16.46 s
3	Toluene-d_8[d]	106.54 s	147.8 br s	165.26 s	188.5 br s	16.60 s
		(103.70 s)	(147.07 s)	(164.73 s)	(190.4 br s)	(15.58 br s)
	$CDCl_3$[c]	106.18 s	148.5 br s	164.25 s	189.1 br s	16.1 v br s

[a] Major component (5-OH enol form).
[b] Saturated solution, c ~ 0.005 M.
[c] Major component. Spectrum shows two additional sets of minor signals (see Section 3.5.2).
[d] Spectrum shows two sets of signals (see Section 3.5.1). Values for minor component are in brackets.

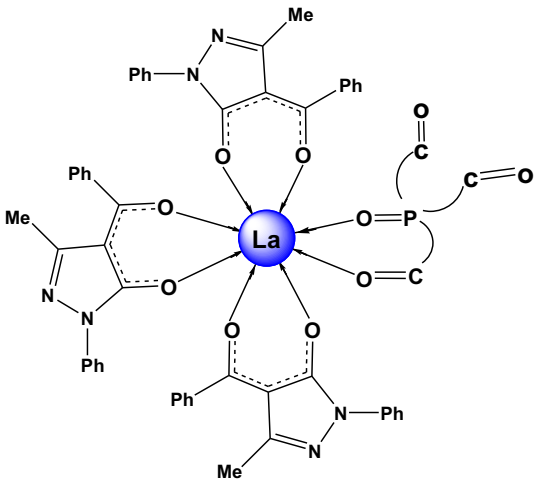
Table 5
Selected $^{31}P\{^1H\}$ and ^{13}C NMR spectroscopic data (δ, ppm) for ligands **L1**, **L2** and their lanthanum complexes **1**–**3** and **4**–**7** in toluene-d_8 and $CDCl_3$ (0.02 M) at 25 °C.

Compound	Solvent	$\delta_P(W_{½})$[a]	δ_C(C═O)	δ_C(O$\underline{C}H_2$)	δ_C(C-2′)
L1	Toluene-d_8	20.3 s (0.04)	167.11 s	69.00 s	161.16 d
	$CDCl_3$ [27]	24.4 s (0.01)	167.34 s	68.71 s	160.67 d
2	Toluene-d_8	29.0 (0.2)	166.9 v br s	67.0 br s	160.9 v br s
	$CDCl_3$	31.5 (0.6), 29.2 (0.2), 27.1(0.01)[b]	167.3 v br s[c]	67.3 br s[c]	160.4 v br s[c]
4 [27]	$CDCl_3$	31.4 s (0.4)	167.34 s	65.97 s	160.04 s
5 [27]	$CDCl_3$	30.0 s (0.5)[d]	167.7 v br s	66.5 br s	160.17 s
L2	Toluene-d_8	20.6 (0.05)	166.68 s	70.48 s	161.43 s
	$CDCl_3$ [27]	24.8 (0.01)	166.81 s	70.33 s	161.24 s
3	Toluene-d_8	32.2, 29.4 (0.2) 26.7 (0.05)[e]	~167.0 v br s	68.7 br s, 66.5 br s	159.5 br s, 163.0 br s
	$CDCl_3$	31.4 (0.3), 29.9 (0.3), 26.2 (0.05)[f]	167.1 v br s	69.2 v br s, 66.4 br s, 64.4 s	~160.0 v br s, 161.6 br s
6 [27]	$CDCl_3$	31.4 (0.5)	167.3 br s	69.0 v br s	159.97 s
7 [27]	$CDCl_3$	31.2 (1.1)[g]	~167.8 br s	70.0 v br s, 66.1 br s	160.0 br s, 165.0 br s

[a] The band width at half-height (in ppm).
[b] Integral intensity ratio 0.23:1.00:0.15.
[c] Major component. Spectrum shows two additional sets of minor signals (see Section 3.5.2).
[d] Minor signal (~2%) at 31.1 [27].
[e] Integral intensity ratio 0.03:1.00:0.21.
[f] Integral intensity ratio 0.34:1:0.27.
[g] Minor signals at 36.5 and 45.4 ppm [27].

to the high-frequency region (1488 cm^{-1}) as compared with the similar band in the spectrum of complex **1** (1476 cm^{-1}). These observations correspond to the weaker coordination of **Py**$^-$ ions and agree well with the data of ^{13}C NMR spectra (Table 4).

The $^{31}P\{^1H\}$ NMR spectrum of solution of complex **2** in toluene-d_8 (Fig. S2) shows one broadened ($W_{½}$ = 0.2 ppm) singlet at 29.0 ppm shifted downfield toward the signal of the free ligand **L1** (Table 5). The participation of the N—C═O groups in coordination appears in the ^{13}C NMR spectrum as a downfield shift of the carbon signals of the C═O groups. Signal change for neighboring groups (OCH_2, C-2′, etc.) in ^1H and ^{13}C NMR spectra (Table 5, Figs. S1 and S3) confirms the conclusion on the coordination of P═O and two or one C═O groups, like lanthanum nitrate complexes with the same ligand **L1** – **4** and **5** (Table 5). Lanthanide cation in nitrate complexes of ligand **L1** has CN = 9 [27], but lanthanide CN in complexes with bulkier pyrazolonate ions as a rule is not larger than 8 [50]. One can suppose that the ligand **L1** is coordinated in a P(O),C(O)-bidentate mode and compound **2** in toluene-d_8 solution is present as mononuclear neutral complex [La{P(O),C(O)-**L1**}(OO-**Py**)$_3$]^0 (Scheme 2).

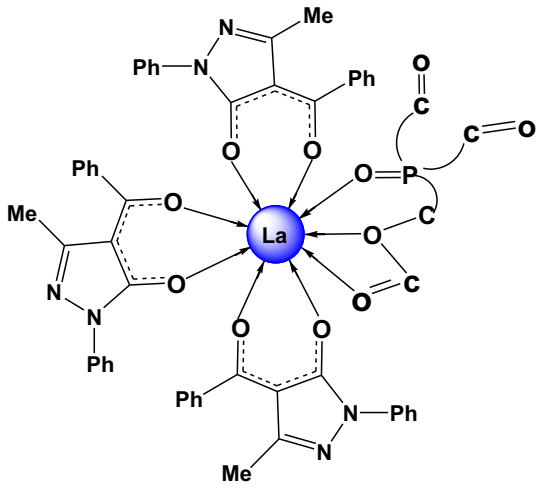


Scheme 2. Complex **2** in $CD_3C_6D_5$ as well as major component (~73%) of equilibrium of complex **2** in $CDCl_3$ solution.

The data of IR spectra are in line with NMR spectral data. Thus, the IR spectrum of solution of complex **2** contains no band of free P═O group (1185 cm^{-1} in the spectrum of solution of free ligand **L1**) and shows ν(P═O) band of coordinated group at 1152 cm^{-1}. The ν(C═O) band of coordinated carbonyl groups is observed at ~1615 cm^{-1} (a shoulder of strong band at 1620 cm^{-1} related to vibrations of pyrazolonate ion). In the region of vibrations of C═O groups, the spectra exhibit a split band with maxima at 1655 and 1666 cm^{-1}, which may be related to ν(C═O) vibrations of two free C═O groups.

The IR spectrum of complex **3** solution in the region of vibrations of pyrazolonate ions are close to that of complex **2**, which indicates similar O,O-coordination of **Py**$^-$ ions in these compounds. The ^{13}C NMR spectrum shows the main set of signals of pyrazolonate ions, whose values are given in Table 4, and supplementary narrow minor signals. The signals of the main set are broadened; their chemical shifts are close to the corresponding values in the spectra of complexes **1** and **2**, which conforms to the conclusion on the O,O-bidentate coordination of **Py**$^-$ ions.

The $^{31}P\{^1H\}$ and ^{13}C NMR spectra of complex **3** in the region of signals of ligand **L2** considerbly differ from those of complex **2** (Table 5). Thus, the $^{31}P\{^1H\}$ NMR spectrum, along with expected signal (about 81%) of coordinated phosphoryl group at 29.4 ppm, exhibit additional signal (about 17%) of uncoordinated phosphoryl group at 26.7 ppm and a trace signal (~2%) at 32.2 ppm (Fig. S4). Analytically valuable signals in the ^{13}C NMR spectrum of the main component in solution represented in Table 5 are broadened. The shift of the signal of C═O groups is small ($\Delta\delta_C$(C═O) ~ 0.3 ppm) but the signal is considerably broadened, which indicates that a part of C═O groups are involved in coordination. The major feature of ^{13}C NMR spectrum is the emergence of a broadened signal of C-2′ at ~163.0 ppm along with a signal at 159.5 ppm (Table 5). We believe the first signal, shifted downfield relative to the signal of free lugand (161.43 ppm) provides evidence on the participarion of ethereal oxygen atom in coordination, whereas the second upfield signal indicates that the phosphoryl and carbonyl groups are involved in coordination. The shifts of signals of O$\underline{C}H_2$ groups (Table 5) agree well with this assumption. Similar spectral features were described in detail for the complexes of ligand **L2** with lanthanide nitrates [27]. Table 5 provides comparison of the corresponding data for lanthanum complex **7**. Thus, we assume that mononuclear neutral complex [La{P(O),C(O),O_{eth}-**L2**}(OO-**Py**)$_3$]^0



Scheme 3. Major component (~81%) of equilibrium of complex **3** in toluene-d_8 solution.

(Scheme 3) is the main component (81%) of equilibrium complex **3** in toluene solution, while CN of lanthanum cation is nine.

Let us note that the occupied space of ligand **L2** in the coordination sphere of lanthanum upon tridentate P(O),C(O),O_{eth}-coordination (Fig. 5) is smaller than that upon bidentate P(O),C(O)- or C(O),C(O)-coordination (X-ray diffraction data for the akin complex of ligand **L2** with P(O),C(O),O_{eth}-coordination of the ligand will be published elsewhere).

The main complex is in equilibrium with complex species (~18%) where phosphoryl group is not coordinated (δ_P = 26.7). The ^{13}C NMR spectrum in the region of **Py**$^-$ signals displays a set of supplementary narrow signals of low intensity (Fig. S5). The chemical shifts of these analytically valuable nuclei (C-4, C-3, C-6, 3-Me) are close to those of free ligand (see Table 4) except for the signal of C-5 (164.73 ppm), which is shifted downfield relative to the signal of free ligand (162.59 ppm) similarly to the signal of this nucleus in the complexes with chelate coordination of pyrazolonate ion (see Table 4). One can suppose that this set of signals corresponds to the **Py**$^-$ anion coordinated in monodentate mode. The broadened signals of analytically valuable nuclei of ligand **L2** allow one to suppose that supplementary species is the neutral mononuclear complex [La{C(O),C(O)-**L2**}(OO-**Py**)$_2$(O-**Py**)]^0 (Scheme 4).

The data of IR spectra agree well with the data of NMR spectra. Thus, the spectra of solutions of complexes **3** and **2** display a band at 1151 cm^{-1} related to the ν(P=O) vibrations of coordinated phosphoryl group. A weak band at 1185 cm^{-1} also remains but it could not be unambiguously associated with vibrations of free P=O group because this spectral region contains also a band of another vibration of ligand **L2**. The ν(C=O) vibration of coordinated carbonyl group appears at ~ 1615 cm^{-1} like in spectrum of complex **2**. The bands at 1661 and 1653 cm^{-1} refer to free C=O groups. The coordination of the ethereal oxygen atom was not detected (see Section 3.4).

The traces of complex with δ_P = 32.2 ppm are most likely refer to cationic complex, compounds with similar chemical shift are considered below (see Section 3.5.2.).

Thus, the mixed complexes [LaPy$_3$**L**] of both ligands in toluene are neutral mononuclear complexes, whose structure differs mainly by coordination mode of tripodal ligand **L**. Ligand **L1** in complex **2** exhibits P(O),C(O)-coordination and solution contains species of the same structure, whereas solution of complex **3** includes equilibrium of neutral complexes of different structure, the main species contains **L2** ligand coordinated in P(O),C(O),O_{eth}-tridentate mode.

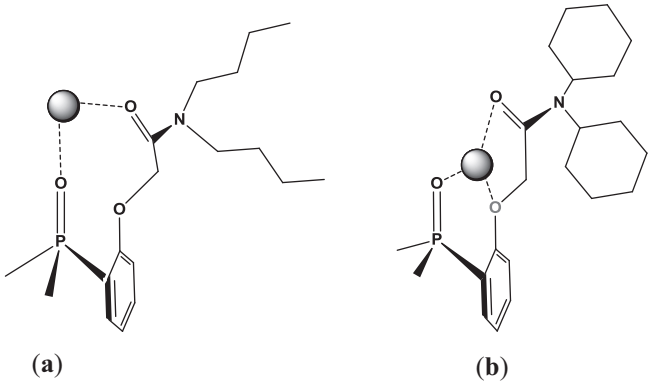


Fig. 5. Visualization for the portion of the spatial structure of P(O),C(O)-coordinated ligand **L1** (**a**) and of P(O),C(O),O_{eth}-coordinated ligand **L2** (**b**) in complexes with La (III).

3.5.2. Chloroform solutions

According to IR and NMR spectral data (Table 4), the structure of complex **1** is not changed on the change of solvent.

NMR spectra of both mixed complexes **2** and **3** in $CDCl_3$ are considerably complicated as compared with spectra in toluene-d_8. Specific solvation due to hydrogen bonding seems to be the main reason of change in the structure of complex species involved in equilibria on passing from toluene to chloroform.

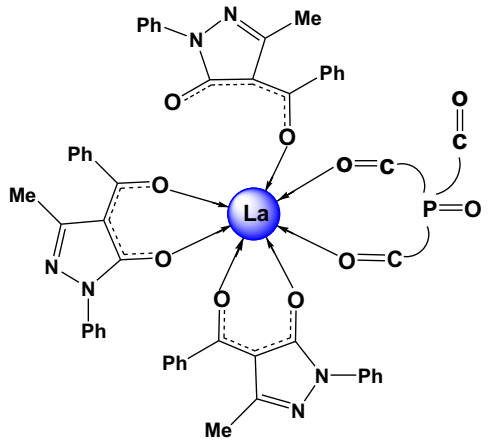
Thus, the $^{31}P\{^1H\}$ NMR spectrum of complex **2** displays three signals of different integral intensity (Table 5). Along with the main (73%) expected signal at 29.2 ppm, the spectrum shows two additional signals: a broadened (17%) at 31.5 ppm and a narrow signal (11%) at 27.1 ppm corresponding to compound with uncoordinated phosphoryl group (Fig. S6). The positions of signals of the main component in the ^{13}C NMR spectrum of chloroform solution are close to that of toluene solution (Tables 4 and 5), many of them (C-4, C-6, NC = O, C-2′) are broadened considerably larger than the similar signals in the spectra of toluene solution (Fig. S7).

The IR spectrum of complex **2** in $CDCl_3$ differs from the spectrum of solution in toluene-d_8 by redistribution of intensities of certain bands. First, the intensity of a shoulder at ~1615 cm^{-1} referred to the ν(C=O) vibration of coordinated carbonyl groups slightly increases, while the intensity of one of bands of free C=O groups at 1666 sm^{-1} decreases. Second, the intensity of ν(C=O) band of pyrazolonate ions at 1487 cm^{-1} slightly decreases and a shoulder at ~1478 cm^{-1} appears. These differences can be explained by the emergence in chloroform solution of complex species of another structure. At the same time, no difference in P=O bands was observed.

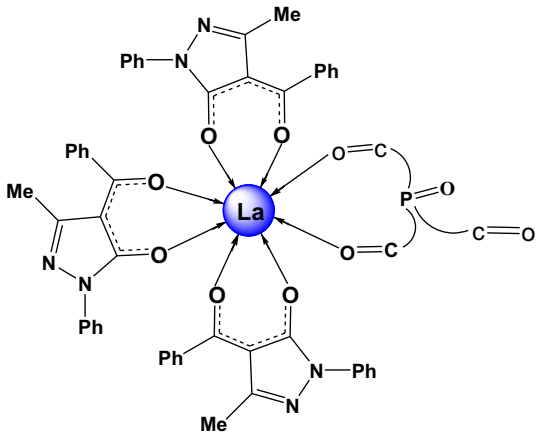
The body of data allows us to consider the structure of the main components in solutions of complex **2** in both solvents to be identical (Scheme 2). Two kinds of complex species appear in equilibrium with the main component in solution. Compound with uncoordinated phosphoryl group seems to be neutral mononuclear complex [La{C(O),C(O)-**L1**}(OO-**Py**)$_3$]^0 where CN of the lanthanum cation is eight (Scheme 5). The data of the ^{13}C NMR spectrum conform to this assumption.

The second additional component (17%) with δ_P = 31.5 ppm is likely to be a cationic complex that exists in solution as a contact or solvent-separated ion pair [La{P(O),C(O),C(O)-**L1**}(OO-**Py**)$_2$]$^+$ (**Py**)$^-$ where CN of lanthanum is seven (Scheme 6). Such complexes typically have larger shift of δ_P value than neutral ones [27,51].

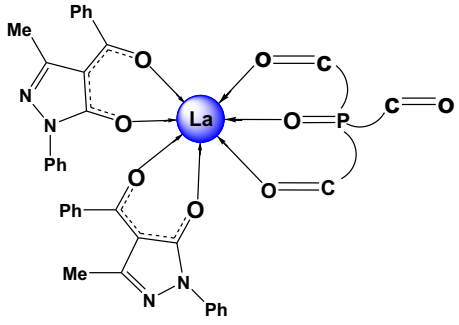
We studied in detail similar equilibria of molecular and ionic complexes of organophosphorus compounds with lanthanide



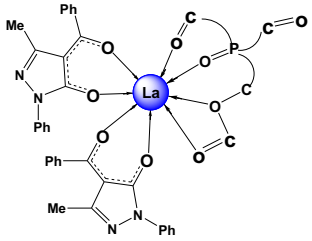
Scheme 4. Minor component (~17%) of equilibrium of complex **3** in toluene-d_8 solution.



Scheme 5. Minor component (~11%) of equilibrium of complex **2** in $CDCl_3$ solution.



Scheme 6. Cation of minor component (~17%) of equilibrium of complex **2** in $CDCl_3$ solution (as well as for complex **3**).



Scheme 7. Cation of the minor component (~21%) of equilibrium of complex **3** in $CDCl_3$ solution.

nitrates earlier [51]. Additional minor signals in the ^{13}C NMR spectrum agree well with these assumptions.

The $^{31}P\{^1H\}$ NMR spectrum of solution of complex **3** in chloroform, like in the spectrum of toluene solution, displays three signals (Fig. S8). Their positions in both spectra are close but integral intensities differ considerably (Table 5). One may believe that the structure of the main and additional components in chloroform (δ_P = 29.9 and 26.2 ppm, respectively) is the same as in toluene (Schemes 3 and 4). The data of the ^{13}C NMR spectrum agree well with this assumption. The second additional component (δ_P = 31.4 ppm) seems to be a cationic complex that exists in solution as a contact or solvent-separated ion pair. Ionic complexes of two types—[La{P(O),C(O),C(O)-**L2**}(OO-**Py**)$_2$]$^+$ (**Py**)$^-$ (CN of lanthanum is 7) and [La{P(O),C(O),C(O),O_{eth}-**L2**}(OO-**Py**)$_2$]$^+$ (**Py**)$^-$ (CN of lanthanum is 8)—can coexist in solution in equilibrium or only one of them is present (Schemes 6 and 7).

The IR spectrum of chloroform solution of complex **3** as compared with its toluene solution displays the same redistribution of intensities for ν(C═O) bands of ligand **L2** and ν(C—O) bands of pyrazolonate ions as in the case of complex **2**. The presence of uncoordinated **Py**$^-$ ion within ionic complex was not detected because of its low concentration or symmetry violation in ion pair.

Thus, the mixed complexes of both ligands [La**Py**$_3$**L**] in chloroform show equilibrium with participation of ionic and two types of neutral complexes: with coordinated and uncoordinated phosphoryl group. The coordination mode of the tripodal ligands **L1** and **L2** in neutral complexes in toluene and chloroform is the same. The content of ionic complexes in chloroform under used experimental conditions is rather high (up to ~20%, Table 6).

The emergence of ionic complexes in equilibrium in chloroform seems to be due to the possibility of specific solvation owing to hydrogen bonding in this solvent. The stabilization of ion pair [La(**L2**)(OO-**Py**)$_2$]$^+$ (**Py**)$^-$ seems to be possible mainly due to solvation of anion (**Py**)$^-$. It is known, for example, that in crystals of complexes pyrazolonate ions produce strong H-bonds with participation of N-2 atom of the pyrazolone ring [44]. The solvation in chloroform in more detail see in Section 3.6.2.

3.6. Synergistic effect and solution structure of extracted species

The structure of complexes formed under liquid extraction processes can differ from the structure of model systems, however, the information on the coordination chemistry of ligands facilitates both search for efficient extractants and the selection of optimal conditions of metal recovery and allows one to predict the results of experiments.

Extraction efficiency is known to be dependent in complicated manner on numerous factors, including the strength and structure of extracted complexes, hydrophilicity/lipophilicity balance of a ligand and its complexes *etc*. Synergistic effect in solvent extraction systems **HPy**–**L** is caused by the replacement of **HPy** molecule in self-adducts Ln**Py**$_3$ **HPy** by molecule of synergistic compound **L** (organophosphorus ligands **L1** and **L2**), which seem to result in increase of hydrophobicity of extracted species and, as shown above, in the growth of efficiency of Ln(III) recovery.

3.6.1. Toluene solutions

The model complexes [La**Py**$_3$**L**] of both ligands with the same stoichiometry (1:3:1) like those of the extracted mixed complexes in toluene were neutral mononuclear complexes, whose main structural difference is the coordination mode of the tripodal

Table 6
Content (%)[a] of equilibrium components of complexes **2**, **3** in toluene-d_8 and $CDCl_3$ solutions.

Complex	Solvent	Ionic complex	Neutral complex (with coord. P=O)	Neutral complex (with uncoord. P=O)
2	Toluene-d_8	–	100	–
	$CDCl_3$	17	73	11
3	Toluene-d_8	2	81	17
	$CDCl_3$	21	62	17

[a] According to ^{31}P NMR data.

ligand **L**. Ligand **L1** in complex [La**Py**$_3$**L1**] demostrates bidentate P(O),C(O)-coordination and solution contains only one type of species. At the same time, equilibrium of neutral complexes of different structure is observed in a solution of complex [La**Py**$_3$**L2**]: ligand **L2** in one complex (81%) is coordinated in P(O),C(O),O_{eth}-tridentate mode but the ligand in another complex (17%) is coordinated in C(O),C(O)-bidentate mode. Such a structural difference should affect the strength and lipophilicity of extracted complexes. The synergistic effect in lanthanide extraction with **HPy**–**L2** mixtures is higher than that with **HPy**–**L1** mixtures (Fig. 4), although ligand **L1** shows slightly higher lipophilicity, than ligand **L2** [27]. We suppose that the different structure of their mixed complexes in toluene solution is one of the main reasons of difference in the synergistic effects of related ligands **L1** and **L2**.

3.6.2. Chloroform solutions. Solvation features

The diluent effect in synergistic extraction was studied by the example of Eu(III) extraction with **HPy**–**L1** mixtures (see Section 3.3.). The extraction efficiency increased in the order: chloroform ≪ 1,2-dichloroethane < toluene < carbon tetrachloride < cyclohexane (Table 2). We studied the structure of species involved in extraction equilibria in more detail by the example of toluene and chloroform.

It is known that chloroform in contrast to toluene can solvate due to hydrogen bonding with substrate. However, in certain cases, specific solvation simply increases substrate solubility but, in other cases, dissolved compound can change its structure as compared with solid state or solution in another solvent.

The structure of ligands **L1** and **L2** is the same in different solvents. IR and NMR spectral data indicate only specific solvation due to formation of H-bonds between donor groups of the ligands and chloroform molecules. The signals of the corresponding nuclei in NMR spectra display downfield shift on passing from toluene to chloroform (Table 5). Vibrational bands of donor groups (mainly P=O) show a shift to the low-frequency region. Moreover, IR spectra of solutions of all studied compounds at 2220–2240 cm^{-1} exhibit a band of ν(C–D), which indicates the formation of H-bonds between solvent molecules $CDCl_3$ and the donor groups of the dissolved species.

Pyrazolone **HPy** belongs to the class of 1,3-dicarbonyl compounds, which can exist in pure state and solutions in several tautomeric forms [52]. Several works dealt with the studies of tautomeric equilibria, later works revealed that two forms are observed in crystal state and diluted solutions: 5-OH enol form with intramolecular H-bond and 2-NH keto form [29,46,53]. According to the data of NMR (^1H and ^{13}C) spectroscopy, we established that equilibrium of enol and NH-keto form (~12:1, respectively) is observed in chloroform solution of pyrazolone, whereas only enol form exists in toluene solution under the same conditions (c = 0.01 M) (Figs. S9–S11). Signal assignment in NMR spectra was made on the basis of 2D HMBC correlations. These data conform to the well-known thoroughly studied solvent effect on keto-enol equilibrium [52]. Enol forms stabilized by intramolecular hydrogen bonds have lower polarity than diketone forms, therefore solvent polarity affects keto-enol equilibrium. Enol stabilization due to intramolecular hydrogen bond formation is more efficient in the absence of competitive process, intermolecular hydrogen bonding with solvent molecules. Thus, the content of enol forms in nonpolar H-bond donor solvents capable of specific solvation due to H-bonding is lower than in aprotic nonpolar solvents. In dilute solutions (c = 0.01 M) in nonpolar solvents presented in Table 2, pyrazolone **HPy** is in enol form in CCl_4 [46] and toluene [the present work]. NH-keto form of pyrazolone **HPy** is observed in solvents that solvate due to H-bonding, for example, in MeOH [46]. Both forms are present in equilibrium in chloroform capable of specific solvation due to intermolecular hydrogen bonding. Let us note that the enol form of **HPy** stabilized by intramolecular hydrogen bonds is preorganized for the formation of chelate complex with metal cation, which, in principle, can affect extraction process.

Equilibria with participation of [La**Py**$_3$**L**] complexes in toluene and chloroform also differ substantialy. The main difference is the considerable share (~20%) of ionic-type complexes in chloroform (Table 6). We believe, that the high content of ionic complexes in chloroform is caused by the stabilization of ion pair [La(**L**)(OO-**Py**)$_2$]$^+$ (**Py**)$^-$, which is determined mainly by solvation of (**Py**)$^-$ anion, in particular, due to H-bonding between N-2 atom of the pyrazolonate ring and chloroform molecule. Since ionic complexes, in contrast to neutral ones, are poorly extracted into nonpolar solvents, it is the formation of ionic complexes that causes extremely low synergistic extraction of lanthanides into chloroform as compared with other nonpolar solvents (see Table 7).

It should be also noted that the literature contains data on the formation ionic complexes $[H_3O]^+[LnQ_4]^-$ upon the preparation of complexes of 4-acylpyrazol-5-ones (HQ) with lanthanide nitrates [44,50]. So, ionic complexes $[H_3O]^+[LnQ_4]^-$ formed as additional product (5%) along with expected neutral complexes [Ln(Q)$_3$(solv)$_2$] at Ln:HQ = 1:3 in ethanol [48], while ionic complexes become the main products (74%) upon extraction into chloroform [49]. We observed no formation of the noted complexes in the experiments performed in the present work.

Table 7
Solvent properties (ε, μ), values of $K_{Py,L}$ for Eu(III) extraction with **HPy**–**L1** mixture and content (%) of NH-keto form of **HPy** and ionic form of [La**Py**$_3$**L1**] complexes (c = 0.02 M) in different solvents.

Solvent/Diluent[a]	ε [38]	μ [38]	log$K_{Py,L}$(**L1**)	Content (%)[b]	
				NH-keto form of **HPy**	Ionic form of [La**Py**$_3$**L1**]
Carbon tetrachloride	2.23	0	3.74	0 [46]	–
Toluene	2.58	0.36	2.99	0	0
Chloroform	4.79	1.87	0.77	10	17

[a] All data are given for pure solvents except for log$K_{Py,L}$(**L1**), which are given for diluent.
[b] According to NMR data.

Thus, nonpolar chloroform capable of solvating due to H-bonding shoud not be used as diluent for synergistic extraction of Ln(III) with **HPy**–**L** mixtures.

4. Conclusions

Solvent extraction of lanthanide (III) ions with mixtures of 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (**HPy**) and neutral tripodal ligands on the triphenylphosphine oxide platform with anchored carbamoyl side arms $(2\text{-}R_2NC(O)CH_2OC_6H_4)_3P(O)$, where R = Bu (**L1**) and *cyclo*-Hex (**L2**) has been studied. A remarkably large synergistic effect (up to 10^7) was observed for the Ln(III) ions extraction from chloride medium in toluene. This effect is associated with the replacement of **HPy** in self-adducts Ln**Py**$_3$**HPy** by organophosphorus ligands **L1** or **L2**. The stoichiometry of the Ln(III) extracted complexes in **HPy**–**L1** and **HPy**–**L2** systems was determined by slope analysis and the equilibrium constants were calculated. The lanthanum complexes with the same stoichiometry (1:3:1) as those of the extracted mixed complexes in solution were also obtained. Solution structure of the above complexes [La**Py**$_3$**L1**] and [La**Py**$_3$**L2**] was examined by IR and multinuclear (^{1}H, ^{13}C, and ^{31}P) NMR spectroscopy in toluene-d_8 and $CDCl_3$.

In toluene solution, the mixed complexes [La**Py**$_3$**L**] of both ligands are neutral mononuclear complexes, whose structural difference consists mainly in coordination mode of the tripodal ligand **L**. Ligand **L1** in complex [La**Py**$_3$**L1**] exhibits P(O),C(O)-coordination to form species of the same structure in solution; equilibrium of neutral complexes of different composition where ligand **L2** is coordinated mainly in P(O),C(O),O_{eth}-tridentate mode is observed in solution of complex [La**Py**$_3$**L2**]. The synergistic effect upon lanthanide extraction into toluene with **HPy**–**L2** mixtures is higher than that with **HPy**–**L1** mixtures, which seems to be due to different ligand coordination mode in extracted mixed complexes, because the lipophilicity of ligands **L1** and **L2** is almost the same.

In chloroform solution, the mixed [La**Py**$_3$**L**] complexes of both ligands exhibits equilibrium with participation of ionic and two kinds of neutral complexes with coordinated and noncoordinated phosphoryl group. Coordination mode of the tripodal ligands **L1** and **L2** in neutral complexes in toluene and chloroform is the same. The content of ionic complexes in chloroform is ~20%.

Diluent effect on synergistic extraction was studied by the example of Eu(III) with mixtures of **HPy** and compound **L1**. The extraction efficiency increased in the order: chloroform $\ll$ 1,2-dichloroethane < toluene < carbon tetrachloride < cyclohexane. The absence of ionic-type complexes in toluene and their high content in chloroform is the main reason of low efficiency of Ln(III) extraction into chloroform.

Tripodal ligands **L1** and **L2** demonstrate a higher synergistic effect on extraction of Ln(III) than known organophosphorus extractant $Ph_2P(O)CH_2C(O)NBu_2$ (**L3**).

Thus, the use of mixtures of available chelating agent **HPy** with tripodal ligand **L1** or **L2** for the high performance recovery of Ln(III) requires no considerable excess of Cl^- ions in aqueous phase and high extractant concentration, which is a common condition in traditional extraction procedure.

Further application of tripodal ligands on the triphenylphosphine oxide platform in coordination and extraction chemistry is expected.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2019.01.036.

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