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PHYSICAL CHEMISTRY OF SOLUTIONS

Extraction of Lanthanides(III) by Phosphorylated Naphthyridine Ligands from Carbonate Solutions

A. M. Safiulina[a], O. A. Sinegribova[b], A. G. Matveeva[c], E. I. Goryunov[c], M. S. Grigoriev[a], E. E. Nifant'ev[c], and I. G. Tananaev[a]

[a] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia*

[b] *Mendeleev University of Chemical Technology, Miusskaya pl. 9, Moscow, 125047 Russia*

[c] *Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*

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Abstract—The extraction capacities and selectivities of 1,8-naphthyridine-based neutral organophosphorus reagents in extracting trivalent lanthanides (Ln, Nd, Ho, Yb) from carbonate solutions were studied. The length and nature of the linker between the naphthyridine and phosphoryl moieties were found to have considerable influence on the efficiency and selectivity of lanthanide extraction.

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Recycling spent nuclear fuel and analyzing sewage and oils in fuel disposal places still remain topical. The PUREX process and TRUEX process, aqueous methods which are based on the extraction recovery of nuclear fuel components from nitric acid solutions, have been in greatest use for separating and preconcentrating transplutonium and rare-earth elements. Both processes employ neutral mono- and bidentate organophosphorus compounds as extraction agents [1–3]. The rapidly developing in recent years carbonate method (CarbEx process) provides processing spent nuclear fuel by means of extraction from carbonate solutions using quaternary ammonium salts as extractants [4]. To our knowledge, bi- and polydentate neutral organophosphorus compounds have not been tested for use in extraction from carbonate solutions. For monodentate phosphorus compounds, it is well known that they do not extract lanthanides and actinides from carbonate solutions [5, 6]. However, 1,8-naphthyridine-based neutral phosphorylated ligands, which virtually do not extract actinides and lanthanides from nitric acid solutions, can quite successfully recover trivalent lanthanides from carbonate solutions [7].

Our goal was to study the extraction of trivalent lanthanides of the cerium subgroup (lanthanum and neodymium) and the yttrium subgroup (holmium and ytterbium) from carbonate solutions by two naphthyridine ligands that differ from each other in the length and nature of the linker between the naphthyridine core and the diphenylphosphoryl group.

EXPERIMENTAL

Materials and reagents. Solutions were prepared using bidistilled water, chloroform (reagent grade), Arsenazo III (analytical grade); $Na_2CO_3 \cdot 10H_2O$, $La(NO_3)_3 \cdot 6H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$, and NaCl were of reagent grade; and $Ho(NO_3)_3 \cdot 6H_2O$, and $Yb(NO_3)_3 \cdot 6H_2O$ were of pure grade. Dibenzo-18-crown-6 (from Aldrich) was used as received.

^1H and $^{31}P\{^1H\}$ NMR spectra of ligands were recorded on Bruker Avance TM-400 (the working frequency was 400.13 and 161.98 MHz, respectively) in 0.05 M solutions in $CDCl_3$ or DMSO-d_6; the internal reference for ^1H NMR spectra was signals from residual protons of the deuterated solvents; the external reference for the $^{31}P\{^1H\}$ NMR spectra was 85% H_3PO_4.

2-[2-(Diphenylphosphoryl)ethyl]-1,8-naphthyridine (I) was prepared as described earlier [8].

2-(Diphenylphosphorylamido)-5,7-dimethyl-1,8-naphthyridine (II) was synthesized by an improved procedure. A solution of 1.24 g (5.25 mmol) of diphenylchlorophosphinate in 5 mL of absolute chloroform was added droppwise to a mixture of 0.87 g (5 mmol) of finely divided 5,7-dimethyl-2-amino-1,8-naphthyridine,[1] 0.60 g (6 mmol) of absolute triethylamine, 30.5 mg (0.25 mmol) of 4-dimethylaminopyridine, and 10 mL of absolute chloroform under stirring on a

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[1] 2-Amino-5,7-dimethyl-1,8-naphthyridine was synthesized by a known procedure [9] and purified by crystallization from ethanol–dimethylformamide; mp = 221.5–222.5°C. ^1H NMR spectrum (DMSO-d_6, d, ppm, J, Hz): 2.47 (s, 3H, 5-CH_3); 2.48 (s, 3H, 7-CH_3); 6.64 (br.s, 2H, NH_2); 6.75 (d, 1H, $H_{naphth}(3)$, $^3J_{H-H} = 8.8$); 6.89 (s, 1H, $H_{naphth}(6)$); 8.03 (d, 2H, $H_{naphth}(4)$, $^3J_{H-H} = 8.9$).

magnetic stirrer, and the mixture was stirred at room temperature until a homogeneous solution was formed.

The solvent and excess triethylamine were removed in vacuo (~15 Torr); the residue was washed with water (3 × 20 mL) and dried in vacuo over P_2O_5 (110°C, 2 h, ~1 Torr). Yield: 1.77 g (95%). The product was obtained as a light yellow fine-crystalline substance. Mp = 210–211.5°C (chloroform–hexane 1 : 2). Literature data: mp = 191–193°C [7, 10][2].

For $C_{22}H_{20}N_3OP$ (FW = 373.39 g/mol) anal. calcd, %: C, 70.77; H, 5.40; N, 11.25; P, 8.29.

Found, %: C, 70.47; H, 5.47; N, 11.09; P, 8.35.

^{1}H NMR spectrum ($CDCl_3$, δ, ppm, J, Hz): 2.49 (s, 3H, 5-CH_3); 2.58 (s, 3H, 7-CH_3); 6.93 (s, 1H, H_{naphth}(6)); 7.16 (d, 1H, H_{naphth}(3), $^3J_{H-H}$ = 9.1); 7.43 (td, 4H, m-C_6H_5, $^3J_{H-H}$ = 7.3 Hz, $^4J_{H-P}$ = 2.1); 7.49 (t, 2H, p-C_6H_5, $^3J_{H-H}$ = 7.3); 7.85–7.97 (m, 5H, o-C_6H_5 + H_{naphth}(4)).

$^{31}P\{^1H\}$ spectrum ($CDCl_3$, δ, ppm): 21.2 br.s.

^{1}H NMR spectrum (DMSO-d_6, δ, ppm, J, Hz): 2.48 (s, 3H, 5-CH_3); 2.50 (s, 3H, 7-CH_3); 7.06 (s, 1H, H_{naphth}(6)); 7.26 (d, 1H, H_{naphth}(3), $^3J_{H-H}$ = 9.2); 7.49 (td, 4H, m-C_6H_5, $^3J_{H-H}$ = 7.0 Hz, $^4J_{H-P}$ = 2.3 Hz); 7.53 (t 2H, p-C_6H_5, $^3J_{H-H}$ = 6.9 Hz); 7.84 (dd, 4H, o-C_6H_5 $^3J_{H-H}$ = 7.1, $^3J_{H-P}$ = 12.1 Hz; 8.20 (br.d, 1H, H_{naphth}(4)).

$^{31}P\{^1H\}$ NMR spectrum (DMSO-d_6, δ, ppm): 16.8 br.s.

The solutions were prepared by a volumetric–gravimetric method. The concentrations of sodium carbonate solutions were refined by potentiometric titration with 0.1 M HCl (standard solution). Lanthanide nitrate solutions were prepared by dissolving weighed portions of nitrates in 0.01 M nitric acid. The concentrations of lanthanide nitrate solutions (0.001 mol/L) were refined spectrophotometrically as described in [11] on a Cary50 Scan (Varian) spectrometer.

pH of solutions for extraction was measured on pH/ion Analyzer Radelkis-125, model OR-300, with an accuracy of ±0.01 pH units. The electrode pair was calibrated against standard buffer solutions with pH of 1.68, 4.01, and 9.22 (at 20°C).

Extraction experiments. To a ground-stoppered test tube was added 1.5 mL of water or a sodium carbonate solution (0.104 or 0.473 mol/L), 0.5 mL of a 0.001 M solution of a metal nitrate, and 2 mL of 0.01 M solution of a ligand in chloroform. pH of solutions for extraction was 2.71, 10.67, and 10.89, respectively. Phases were stirred for 20 min. The extraction equilibration time was verified by increasing the phase contact time to 120 min, distribution ratios did not change. Phase separation was accomplished by centrifugation. After phase separation, concentration of lanthanides in the aqueous phase were determined spectrophotometrically [11]. For each concentration, five independent experiments were carried out. All experiments were carried out at 20 ± 1°C.

Na^+ determination in the organic phase after extraction of neodymium(III) from a carbonate solution (0.078 mol/L) was carried out by flame atomic-emission spectrometry (the detection limit was 10^{-10} g/mL) [12]. Calibration solutions of NaCl in water and in chloroform (in the presence of dibenzo-18-crown-6) were prepared by a volumetric–gravimetric method. Preliminarily, the ligand solutions in chloroform and the organic phase of a model experiment (extraction in the absence of a lanthanide salt in the aqueous phase) were verified for the absence of trace Na^+.

X-ray crystallography. Transparent crystals of naphthyridine monohydrate **II** suitable for X-ray crystallography were obtained by the isothermal evaporation at room temperature of a solution of the compound in chloroform. Colorless crystals of $C_{22}H_{22}N_3O_2P$ (II) (FW = 391.450) are monoclinic; at 100(2) K, a = 15.239(3) Å, b = 17.953(3) Å, c = 8.1009(18) Å, β = 115.954(5)°, V = 1992.7(7) Å^3, space group Cc, Z = 4, ρ_{calc} = 1.305 g/cm^3. An experimental array of 18 611 reflections was collected on a Bruker Kappa Apex II automated four-circle diffractometer equipped with an area detector (MoK_α radiation, a graphite monochromator, φ- and ω-scans) at 100 K from a single-crystal chip 0.40 × 0.20 × 0.06 mm in size. After averaging equivalent reflections, a total of 4193 unique reflections were obtained (R_{int} = 0.0498) to be further used in solving and refining the structure. The structure was solved by a direct method; all non-hydrogen atoms were refined for F^2_{hkl} in the anisotropic approximation. The water hydrogen atoms were located from difference electron density syntheses and refined isotropically without any constraint. The hydrogen atoms of the NH, CH, and CH_3 groups were positioned in geometrically calculated positions and refined with isotropic temperature parameters, which were 1.2 U_{eq} of an N or C atom for NH and CH, respectively, and 1.5 U_{eq} of a C atom for CH_3. The SHELXTL program package [13] was used in all calculations. The final refinement values were as follows: R_1 = 0.0483 (over F_{hkl} for 2173 reflections with $I > 2\sigma(I)$), wR_2 = 0.1041 (over F^2_{hkl} for all reflections); GOOF = 1.018. The data collection completeness was 96.8%; the number of refined parameters was 261; and the maximal and minimal residual peaks were 0.264 and –0.315 e Å^{-3}, respectively. The Flack parameter x,

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[2] Lemport et al. [10] were also mistaken in indicating $CDCl_3$ instead of DMSO-d_6 as the solvent used for recording NMR spectra for ligand **I**.

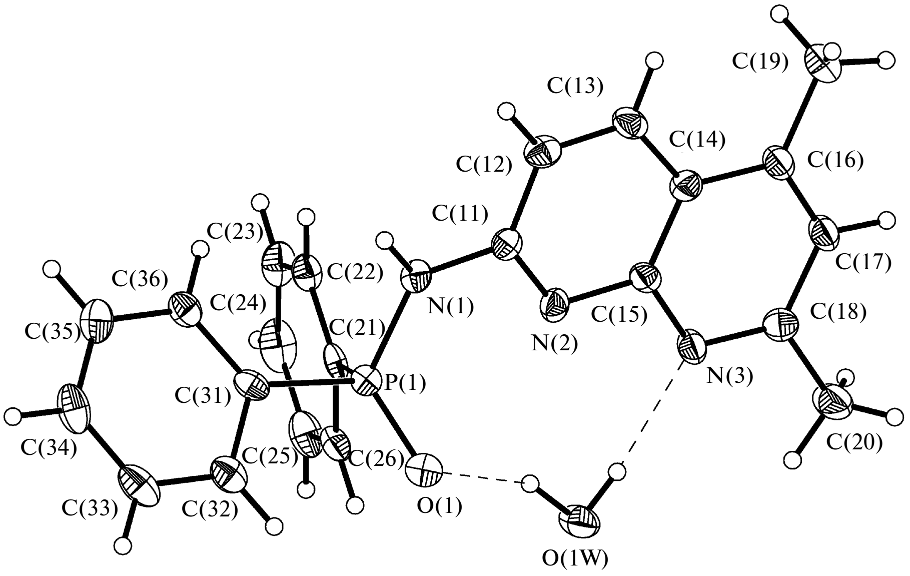


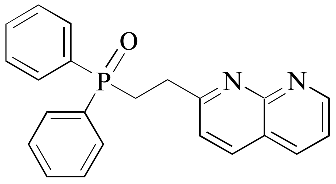
Fig. 1. Molecular structure of naphthyridine **II** monohydrate. Thermal displacement ellipsoids are given with 50% probability. Hydrogen atoms are imaged by spheres of arbitrary radius. Hydrogen bonds are shown by dashed lines.

which equals 0.03(14), validates the adequacy of absolute structure determination [14].

The complete tables of atomic coordinates, bond lengths, and bond angles are available from the Cambridge Structural Database (CCDC code: 785052).

RESULTS AND DISCUSSION

The ligands under study, namely, 2-[2-(diphenylphosphoryl)ethyl]-1,8-naphthyridine (**I**) and 2-(diphenylphosphorylamido)-5,7-dimethyl-1,8-naphthyridine (**II**), which differ from each other in the length and nature of the linker between the naphthyridine moiety and diphenylphosphoryl group, are potentially tridentate ligands, which are capable of being coordinated to lanthanide cations with formation of stable complexes [15–17].



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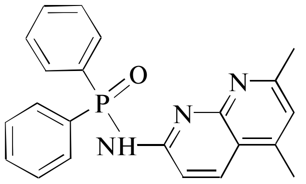
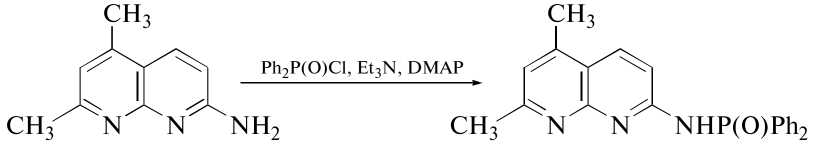


II

Naphthyridine **I** was prepared as described in [8]; for naphthyridine **II**, the synthesis procedure was improved. The reaction of 2-amino-5,7-dimethyl-2-amino-1,8-naphthyridine and diphenylchlorophosphinate in the presence of triethylamine as a hydrogen chloride scavenger was carried out in the presence of catalytic amounts of 4-(dimethylamino)pyridine (DMAP) (Scheme 1). The use of this catalyst allowed the process to be carried out at room temperature and the target product yield to be increased appreciably (up to 95%).



II

Scheme 1.

Inasmuch as the melting temperature of the naphthyridine **II** synthesized by this procedure was nearly 20°C higher than reported earlier [7, 10], we determined the structure of our synthesized compound using X-ray crystallography (Fig. 1). The bond lengths and bond angles fall within the ranges typical of the relevant class of compounds [18] (Table 1). The naphthyridine ring N(2)N(3)C(11)–C(18) is planar; the atoms depart from the plane of the ring by 0.03(1) Å on the average. Noteworthy, the P(1)N(1)C(11) moiety lies virtually in the plane of the naphthyridine ring: torsion angles P(1)N(1)C(11)N(2) and P(1)N(1)C(11)C(12) are –6.2(4)° and 175.1(3)°, respectively. On the whole, the geometric parameters of the compounds are close to those found earlier for related phosphorylated 1,8-naphthyridines, namely, 2-[2-(diphenylphosphoryl)-2-methylpropyl]-1,8-naphthyridine [8] and 5,7-dimethyl-2-(diethoxyphosphorylamido)-1,8-naphthyridine [10].

X-ray crystallography shows that naphthyridine **II** single crystals contain solvation water molecules, each being involved in three strong intermolecular hydrogen bonds (Fig. 2, Table 2). The proton acceptors in these bonds are a phosphoryl oxygen atom and one of the nitrogen atoms (N^8) of the naphthyridine core; the NH-group is the proton donor in the H-bond with the oxygen atom of a water molecule (Table 2). As a result, hydrogen bonds link naphthyridine II and water molecules into chains that run in the direction [101] of the crystal (Fig. 2).

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the structure of the naphthyridine **II** monohydrate

Bond	*d*, Å	Angle	ω, deg
P(1)–O(1)	1.481(3)	O(1)P(1)N(1)	116.92(16)
P(1)–N(1)	1.674(3)	O(1)P(1)C(21)	111.58(18)
P(1)–C(21)	1.807(4)	N(1)P(1)C(21)	106.21(17)
P(1)–C(31)	1.808(4)	O(1)P(1)C(31)	111.79(17)
N(1)–C(11)	1.402(5)	N(1)P(1)C(31)	103.55(17)
N(1)–H(1)	0.88	C(21)P(1)C(31)	105.92(17)
		C(11)N(1)P(1)	121.8(3)
		C(11)N(1)H(1)	119.1
		P(1)N(1)H(1)	119.1

The extraction capacity of naphthyridine ligands **I** and **II** was studied in the extraction of lanthanum(III), neodymium(III), holmium(III), and ytterbium(III) into the organic phase from dilute nitric acid solutions (pH 2.71) and carbonate solutions.

Distribution ratios (D = $[\mathrm{Ln(III)}]_{\mathrm{org}}/[\mathrm{Ln(III)}]_{\mathrm{aq}}$, where [Ln(III)] is the overall concentration of all spe-

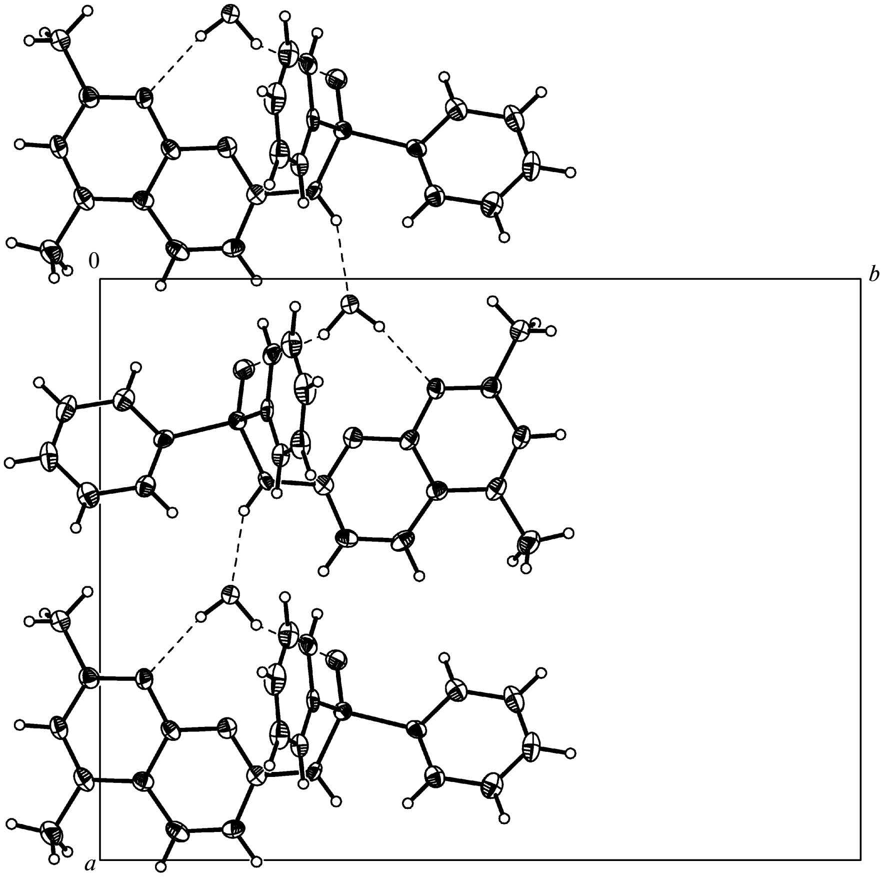


Fig. 2. Fragment of the naphthyridine **II** monohydrate crystal structure: a chain viewed along the axis *c*. Hydrogen bonds are shown by dashed lines.

Table 2. Hydrogen bond geometry (*d*, Å and ω, deg) in the naphthyridine monohydrate **II** structure

D–H···A	D–H	H···A	D···A	∠(DHA)
O(1W)*–H(1A)···O(1)	0.95(5)	2.08(5)	2.936(4)	150(4)
O(1W)*–H(1B)···N(3)	0.87(5)	2.01(5)	2.867(5)	169(4)
N(1)–H(1)···O(1W)*	0.88	2.10	2.857(5)	144

* Symmetry transformation for O(1W): $x + 1/2, -y + 1/2, z + 1/2$.

cies containing Ln(III) in the corresponding phase) were measured at fixed concentrations of the extractant (0.01 mol/L in chloroform) and the lanthanide (0.001 mol/L in the aqueous phase). The results of these experiments are displayed in Figs. 3 and 4 as plots of the distribution ratios versus sodium carbonate concentration.

One can see from Fig. 3 that the naphthyridine ligand **I** with the ethylene linker extracts lanthanide cations rather poorly, although lanthanum(III) and neodymium(III) are extracted a little better than holmium(III) and ytterbium(III). For all lanthanides, distribution ratios are virtually independent of the aqueous phase composition.

Ligand **II**, which has the NH-linker, extracts lanthanides far better. Distribution ratios for all lanthanides studied are one to two orders of magnitude higher than for ligand **I** (Fig. 4). As for ligand **I**, here the cerium subgroup lanthanides (lanthanum(III) and neodymium(III)) are extracted better than the yttrium subgroup lanthanides (holmium(III) and yttrium(III)). However, unlike for ligand **I**, here we observe the different pattern of the effect of the sodium carbonate concentration on the extraction of lanthanides. While distribution ratios for lanthanum, holmium, and ytterbium are almost independent of the sodium carbonate concentration in the range from 0.078 to 0.355 mol/L, for neodymium the extraction coefficient decreases strongly (by a factor of 3.5) as the concentration increases.

Unlike ligand **I**, ligand **II** also has a noticeable selectivity to the lanthanides studied. The separation factor for the (La + Nd)/(Ho + Yb) groups in 0.078 mol/L sodium carbonate solution is $r_f = 5–6$ ($r_f = D_{Ln}/D_{Ho}$ for the La/Ho pair and so on). In 0.355 mol/L sodium carbonate solution, lanthanum can be separated from neodymium, holmium, and ytterbium: the separation factor for the La/Nd pair is ~3, and for the La/(Ho + Yb) group, about 10–15 (see Fig. 4).

It is known that trivalent lanthanides and actinides exist in carbonate solutions in the form of various carbonate complexes [19, 20]. For americium(III), complexes of composition $[Am(CO_3)]^+$ are dominant species even at near neutral pHs while an excess of carbonate ions exists in solution; at pH of about 8.5 (ionic strength of 0.1 mol/L), the dominant species are $[Am(CO_3)]^+$ and $[Am(CO_3)_2]^-$ in almost equal concentrations. At higher pHs, the dominant species are

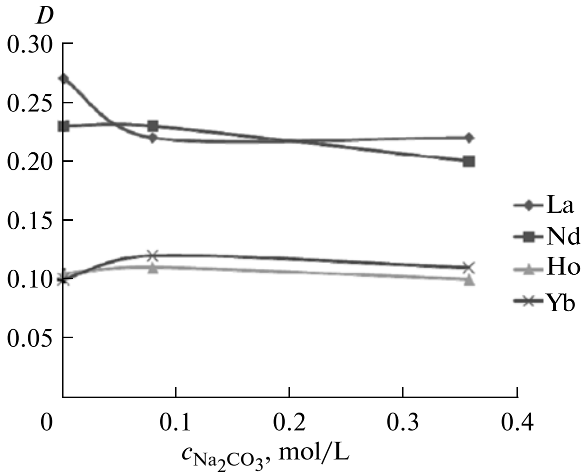


Fig. 3. Lanthanide(III) distribution ratios versus sodium carbonate concentration in extraction with a 0.01 mol/L solution of ligand **I** in chloroform.

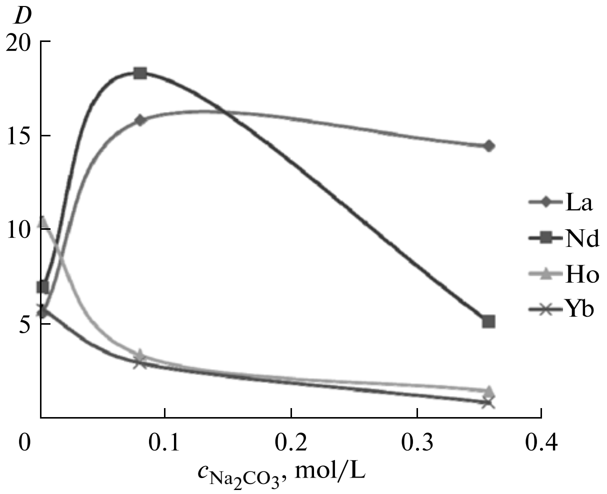


Fig. 4. Lanthanide(III) distribution ratios versus sodium carbonate concentration in extraction with a 0.01 mol/L solution of ligand **II** in chloroform.

$[Am(OH)_2]^+$ and $[Am(CO_3)_2]^-$ [19, 20]. Lanthanide complexes of similar compositions are described in the literature [21], but they are studied in a less detailed manner than actinide complexes [22, 23]. Data obtained for americium(III) were used for further analyzing carbonate solutions of lanthanides.[3]

Because of considerable Na^+ concentrations, lanthanide-containing complex cations and anions and Na^+ containing compounds can both be transferred with neutral compounds to the organic phase in extraction from carbonate solutions. However, no traces of Na^+ were found in the organic phase after extraction of neodymium(III) from a carbonate solution (0.078 mol/L) (flame atomic-emission spectrometer; the detection limit is 10^{-10} g/mL [12]). Thus, the suggested compositions of extracted lanthanide complexes[4] is $[LnL_k(CO_3)]^+ \cdot [LnL_l(CO_3)_2]^-$, and in the range of higher pHs and higher sodium carbonate concentrations, $[LnL_m(OH)_2]^+ \cdot [LnL_n(CO_3)_2]^-$, where k, l, m, and n are likely to be 1 or 2.

Presumably, the scheme of lanthanide extraction from carbonate solutions is as follows (coordinated water molecules are omitted):

$$[Ln(CO_3)]^+_{aq} + [Ln(CO_3)_2]^-_{aq} + (k+l)L_{org}$$
$$= \{[LnL_k(CO_3)]^+[LnL_l(CO_3)_2]^-\}_{org}$$
$$[Ln(OH)_2]^+_{aq} + [Ln(CO_3)_2]^-_{aq} + (n+m)L_{org}$$
$$= \{[LnL_n(OH)_2]^+[LnL_m(CO_3)_2]^-\}_{org}$$
$$k, l, n, m = 0\text{–}2$$

Scheme 2.

Evidently, for different lanthanides the compositions and contents of complex species in the aqueous phase will be dictated by their own equilibrium constants [23, 24], and the lipophilicity of neutral species with hydroxo and carbonato cations can be different. Accordingly, these features should be reflected in the variation of distribution ratios as a function of carbonate ion concentration and pH, and these dependences will be individual for each lanthanide.

In dilute nitric acid, lanthanides mainly exist in the form of $[Ln(NO_3)_2]^+$ and $[Ln(NO_3)]^{2+}$, and their extraction may be described by the following scheme (coordinated water molecules are omitted):

$$[Ln(NO_3)_n]^{(3-n)+}_{aq} + (3-n)NO^-_{3\,aq} + mL_{org}$$
$$= [LnL_m(NO_3)_3]_{org}$$
$$[Ln(NO_3)_n]^{(3-n)+}_{aq} + (3-n)NO^-_{3(w)} + mL_{org}$$
$$= \{[LnL_m(NO_3)_2]^+NO_3^-\}_{org}$$
$$n = 0\text{–}2, m = 1\text{–}2$$

Scheme 3.

Comparing these equations we see that, given equal (or close) extractabilities of the complex to the organic phase, extraction from carbonate solutions should be more efficient than from nitric solutions, for the reason that extractable carbonate complexes contain twice lanthanide atoms per neutral species than in nitrate complexes.

Noteworthy, the numbers of ligand molecules in extracted complexes can be different for reagents **I** and **II** as judged from the data available for nitrate complexes. For ligand **I**, for example, complexes of compositions Ln : L 1 : 1 and 1 : 2 have been isolated and characterized [25], while for ligand **II** only complexes of composition 1 : 2 have been prepared under similar conditions [15].

As regards denticities of ligands **I** and **II** in extracted complexes, we might expect them to be the same as in similar complexes of lanthanide nitrates. According to X-ray crystallography and vibration spectroscopy, in cationic and neutral complexes of lanthanides nitrates with 2-phosphoryl-substituted 1,8-naphthyridines, the ligands have tridentate ONN coordination involving the phosphoryl oxygen atom and both nitrogen atoms of the naphthyridine core, and this coordination mode is retained in polar solvents as shown by NMR and IR spectroscopy [15–17, 25, 26]. Accordingly, ligands **I** and **II** are likely to be tridentate when being complexed in dilute nitric acid and carbonate solutions, too.

The linker length between the coordination sites of a bidentate ligand is known to appreciably affect the complexation and extraction properties of the ligand [27, 28]. The review [27] analyzes the extraction capacities of bidentate ligands as a function of linker length. Ligands having the methylene linker between the two functional groups have higher extraction capacities than those having the ethylene linker, and as the linker length increases further, the extraction capacity decreases. And despite the fact that in ligands **I** and **II**, linkers between the naphthyridine moiety and the P(O) group have different natures (–NH– and $-CH_2CH_2-$, respectively), the decrease in extraction capacity with increasing linker length is well pronounced here. The nitrogen of the imide linker is not involved in coordination to the metal [15].

Further, conditions have been found for providing lanthanide re-extraction from a saturated organic phase. By the example of neodymium(III), re-extraction was accomplished by 0.05 M HNO_3 from a saturated organic phase obtained upon neodymium(III) extraction by a solution of ligand **II** in chloroform. Under these conditions, the degree of neodymium(III) recovery reaches ~90%, which proves that re-extraction is virtually complete.

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[3] Neodymium(III) frequently serves as a model for studying the behavior of trivalent actinides [20].

[4] One of the counterions of the extracted species can be free of extractant L molecules.

In summary, our study of the extraction of trivalent lanthanides from dilute nitric acid and carbonate solutions by phosphorylated naphthyridine ligands **I** and **II** to chloroform has demonstrated a high extraction ability of ligand **II** with an NH-linker in carbonate solutions. The maximum extraction efficiency for this ligand to lanthanum and neodymium is observed in decimolar sodium carbonate solutions; the distribution ratio reaches 16–19 (the degree of recovery is 94–95% in one stage). Ligand **II** also has a certain selectivity to the cerium and yttrium subgroups elements. Ligand **I** with an ethylene linker between the naphthyridine and phosphoryl moiety virtually does not extract lanthanides from the tested solutions; the distribution ratio does not exceed 0.25. The change in the nature of linker appreciably changes the extraction efficiency and selectivity of phosphorylated naphthyridine ligands in carbonate and low-acidity solutions.

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