Sodium picrate effect on extraction of lanthanum and lutetium by aminophosphonate calix[4]resorcinarenes*

S. V. Fedorenko,[a]★ A. R. Mustafina,[a] E. Kh. Kazakova,[a] S. N. Pod´yachev,[a] N. I. Kharitonova,[a] M. A. Pudovik,[a] A. I. Konovalov,[a] I. G. Tananaev,[b] and B. F. Myasoedov[b]

[a]*A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences,*
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843 2) 75 2253. E-mail: svetlana@iopc.kcn.ru
[b]*V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,*
19 ul. Kosygina, 119991 Moscow, Russian Federation.
Fax: +7 (095) 938 2054

Aminophosphonate calix[4]resorcinarene derivatives extract lanthanum and lutetium ions from aqueous solutions to chloroform much more efficiently than *O*,*O*-diethyl[(4-nitrophenyl)aminobenzyl] phosphonate does. In an excess of the metal ion in the aqueous phase with respect to the amounts of the extracting agent and sodium picrate, extraction occurs at the 1 : 1 molar ratio of the metal ion to extracting agent. In a twofold excess of the extracting agent and a considerable excess of sodium picrate over the metal ion, the composition of the extracted complex depends substantially on both the length of the alkyl substituent in the $(AlkO)_2P(O)$ group in the extracting agent and the number of lanthanide.

Key words: calix[4]resorcinarene, extraction, lanthanides, picrate effect.

Complex formation involving macrocycles in phase transfer processes is one of the main problems of supramolecular chemistry, in particular, in extractive separation of lanthanide and actinide ions. Derivatives of calix[*n*]arenes and calix[4]resorcinarenes have recently been found increasing use as extracting agents for metal ions. For example, calix[*n*]arenes containing the alkoxyphosphoryl, phosphine oxide, and carbamoylphosphine oxide groups and calix[4]resorcinarenes with carbamoyl phosphonate and carbamoylphosphine oxide substituents efficiently extract lanthanides from aqueous solutions.[1—4] Since lanthanide ions are extracted with neutral ligands as ion associates, the nature of the counterion substantially affects the degree of extraction. Therefore, picrate anions (Pic) found the most application as counterions of extracted metal ions due to their lipophilicity. It is also known that the tetradialkoxyphosphoryl derivative of calix[4]arene more efficiently extracts lanthanide tripicrates in the "partial cone" conformation than in the "cone" conformation, although the efficiency of inner-sphere coordination of lanthanide is higher in the latter case.[2] This is caused by an additional stabilization of the extracted complex due to staking interaction of the picrate anion with the aromatic fragment of calixarene.

The following aminophosphonate derivatives of calix[4]resorcinarene[5,6] were prepared by the introduction of aminophosphonate groups into the *ortho*-position with respect to the hydroxyl groups of calix[4]resorcinarene: 2,8,14,20-tetramethylpentacyclo[$19.3.1.1^{3,7}.1^{9,13}.1^{15,19}$]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octahydroxy-5,11,17,23-tetra(*N*-methyl-*N*-dimethoxyphosphonylbenzylaminomethyl) (**1**), 2,8,14,20-tetramethylpentacyclo[$19.3.1.1^{3,7}.1^{9,13}.1^{15}$]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octahydroxy-5,11,17,23-tetra(*N*-methyl-*N*-diethoxyphosphonylbenzylaminomethyl) (**2**), and 2,8,14,20-tetramethylpentacyclo[$19.3.1.1^{3,7}.1^{9,13}.1^{15}$]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octahydroxy-5,11,17,23-tetra(*N*-benzyl-*N*-(butoxyphosphonylmethyl)aminomethyl) (**3**). The hydroxyl groups in these compounds allow calix[4]resorcinarene to exist in the "cone" conformation.[7] Fixation of four aminophosphonate groups on the calixresorcinarene matrix facilitates polydentate coordination with the lanthanide ions, while the spatial organization of the aromatic fragments provides additional interactions with picrate the anions.

In this work we studied the extraction abilities of compounds **1—3** toward lanthanum and lutetium ions and the effect of the sodium picrate concentration on the efficiency of extraction. The extraction of lanthanum with *O*,*O*-diethyl((4-nitrophenyl)aminobenzyl) phosphonate (**4**) was studied to reveal the role of the cyclophane structure.

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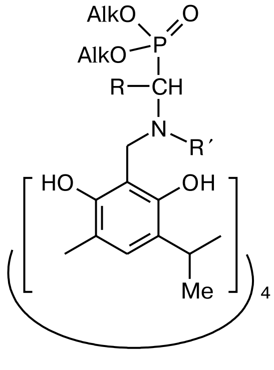
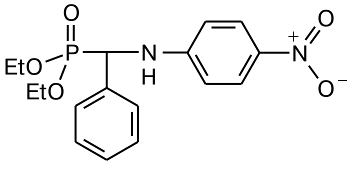


1—3

Compound	R	R′	Alk
1	Ph	Me	Me
2	Ph	Me	Et
3	H	Ph	Bu



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Experimental

^{1}H NMR spectra were recorded on a Bruker WM-250 (250.13 MHz) spectrometer in $CDCl_3$ using HMDS as internal standard. Electronic absorption spectra were obtained on a Specord UV—Vis spectrometer.

Picric acid (reagent grade), $LaCl_3 \cdot 7H_2O$, and $LuCl_3 \cdot 6H_2O$ were used for preparation of solutions. The concentration of Ln^{3+} in the initial solutions were determined trilonometrically using Thymol Blue and Xylenol Orange as indicators.[8] Compounds **1—4** were synthesized using known procedures.[5,6,9]

Extraction procedures. ***A.*** An aqueous solution (5 mL) of $LnCl_3$ ($4 \cdot 10^{-4}$ mol L^{-1}) and NaPic (0.1 mol L^{-1}) (pH 5.5) was added by a solution (5 mL) of compounds **1—3** ($4 \cdot 10^{-4}$—$4 \cdot 10^{-3}$ mol L^{-1}) or **4** ($4 \cdot 10^{-4}$—$2 \cdot 10^{-1}$ mol L^{-1}) in $CHCl_3$. The resulting two-phase system was magnetically stirred for 3 h in a closed flask. After extraction, the concentration of Ln^{3+} in the aqueous phase was determined spectrophotometrically using Xylenol Orange as indicator[10] at pH 6.0 in an acetate buffer.

B. To an aqueous solution (5 mL) of $LnCl_3$ ($1.2 \cdot 10^{-2}$ mol L^{-1}) and NaPic ($1.2 \cdot 10^{-3}$ mol L^{-1}) in an acetate buffer with pH 5.5 and a ionic strength of 0.1 mol L^{-1} was added a solution (5 mL) of compounds **1—3** ($4 \cdot 10^{-4}$—$4 \cdot 10^{-3}$ mol L^{-1}) in $CHCl_3$. The two-phase system was stirred for 3 h in a closed flask using a magnetic stirrer. After extraction, the concentration of Ln^{3+} in the aqueous phase was determined spectrophotometrically by the peak intensity of the absorbance of the picrate ion at 364 nm.[11,12]

The stoichiometry and extraction constants were determined by both the graphical solution of the logarithmic equation of the law of mass action and mathematical processing using the CPESSP program.[13] The model is based on the equations for formation of complexes with different stoichiometry in the two-phase system. In the framework of this model, using the iteration procedure we determined the complexation constants in the two-phase system ($\beta_{i...k}$) corresponding to a minimum of the functional

$$F = \Sigma[(Q_{k,\exp} - Q_{k,\mathrm{calc}})W_k]^2,$$

where $Q_{k,\exp}$ and $Q_{k,\mathrm{calc}}$ are the measured property of the solution in the kth experiment and its theoretical analog, and W_k is the root-mean-square error.

The correspondence of this model of complex formation, including the stoichiometry and complexation constant, to the experimental relation for the absorbance intensity of the picrate ion to the picrate and extracting agent concentrations can be characterized by the $F_{\min}$ value obtained by minimization of the F functional. Adequacy of the model was evaluated using the Fischer criterion

$$F_{\min}/[\delta^2(N - 2m)] \le F_{\mathrm{v}},$$

where δ is the experimental error, m is the number of approximated parameters, F_{v} is the value determined from the table of F-distribution at specified degrees of freedom, and N is the number of experiments.

The model characterized by the least $F_{\min}$ value, the addition to which of equilibria (reasonable from the viewpoint of the process mechanism) does not contribute remarkably to $F_{\min}$, was accepted as the most reliable model.

Results and Discussion

The degree of extraction of lanthanum is independent of the pH for compounds **1—3** in an interval of 4.4—6 pH units. Therefore, aminophosphate calix[4]resorcinarenes and aminophosphate **4** are neutral extracting agents, under these conditions, and extract lanthanum in the form of the $(La^{3+})(A^-)_3$ ionic associate according to the scheme

$$La^{3+} + 3\,A^- + m\,L \rightleftharpoons LaA_3L_m, \qquad (1)$$

where L = **1—4**, and A^- is counterion.

Extraction is absent at the ratio Ln^{3+} : Pic^- : L (**1—4**) = 1 : 3 : 1 ($I = 3.6 \cdot 10^{-3}$ mol L^{-1}, where I is the ionic strength in the aqueous phase). Equilibrium (1) can be shifted toward ionic associate formation by increasing the concentration of any initial component. For example, a 250-fold increase in the concentration of NaPic (C = 0.1 mol L^{-1}) can result in an efficient extraction of Ln^{3+} already at low (10^{-4}—10^{-3} mol L^{-1}) concentrations of extracting agents **1—3** in the organic phase (procedure A). The stoichiometry (m) of the extracted complexes (Fig. 1) and $\log K_{\mathrm{extr}}$ were determined from the graphical analysis of the extraction data under the assumption that the extracted lanthanum complex contained three picrate ions (n = 3) using the correlation

$$\log K_{\mathrm{extr}} = \log q - m\log[\mathrm{L}]_{\mathrm{org}} - 3\log[\mathrm{Pic}^-]_{\mathrm{aq}},$$

where $q = [La(Pic)_3L_m]_{org}/[La^{3+}]_{aq}$; $[La(Pic)_3L_m]_{org}$ and $[L]_{org}$ are the equilibrium concentrations of the complex and extracting agent **1—4** in $CHCl_3$, and $[La^{3+}]_{aq}$ and $[Pic^-]_{aq}$ are the equilibrium concentrations of $LaCl_3$ and NaPic, respectively, in the aqueous phase.

The composition of the extracted complex depends on the size of the hydrocarbon group at the P atom (Fig. 1, Table 1). Lanthanum tripicrate is extracted with compound **1** at the 1 : 1 molar ratio, and in the case of compounds **2** and **3** it is extracted at the 1 : 2 ratio (two host molecules per lanthanum ion).

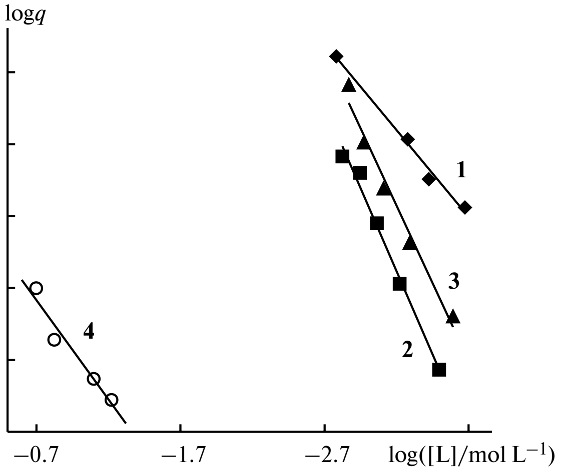

Fig. 1. Plot of log$q$ *vs.* log[L] in the extraction of La^{3+} with compounds **1**—**4** in an excess of NaPic in the aqueous phase; m = 1 (**1**, **4**) and 2 (**2**, **3**).

According to the law of mass action, an increase in the concentration of lanthanum chloride in the aqueous phase to $1.2 \cdot 10^{-2}$ mol L^{-1} (procedure *B*) can also result in a noticeable (≥8%) extraction of lanthanum. The ionic strength was maintained constant (I = 0.1 mol L^{-1}) by the addition of an acetate buffer with pH 5.5 to the aqueous phase.

To reveal the stoichiometry of the complex formed upon extraction in an excess of lanthanum chloride, the concentration of sodium picrate in the aqueous phase was varied from $8 \cdot 10^{-4}$ to $4.8 \cdot 10^{-3}$ mol L^{-1}. The number of picrate ions in the composition of the extracted complex can be determined by the equation

$$\log K_{\text{extr}} = \log d - \log C' - \log[\text{La}^{3+}]_{\text{aq}},$$

where $d = C^0{}_{\text{Pic}-}[\text{LaA}_3\text{L}_m]_{\text{org}}/[\text{Pic}^-]_{\text{aq}}$, $C' = C^0{}_{\text{Pic}-}n[\text{L}]_{\text{org}}$ ($C^0{}_{\text{Pic}-}$ is the initial concentration of sodium picrate in the aqueous phase). However, the linear plot of the d value *vs.* $C^0{}_{\text{Pic}-}$ does not allow n to be correctly determined as the slope ratio of the plot of log$d$ *vs.* logC'. Therefore, to determine n in the extracting agent **2**—$LaCl_3$—NaPic system, we processed the extraction data by the CPESSP program. The least correspondence criterion (F_{min} = 1.9) was found for the 1 : 1 : 1 complex, which contains one lanthanum ion and one picrate ion for the host molecule. Taking into account that the extracted complex is electroneutral, the deprotonation of two hydroxyl groups of the extracting agent can be assumed. However, the previously mentioned absence of a relation of the extraction of lanthanum to the pH for extraction in the pH 4.4—6 interval indicates that the extracting agent is not deprotonated at pH 5.5. It can be assumed that the acetate ions, which are less lipophilic than the picrate ions but exist in a much greater excess than the picrate ions (~90 : 1), are involved in complex formation. We have previously shown[6] than lanthanum is not extracted with extracting agent **3** in the form of $La(Ac)_3$ at the concentrations used. Therefore, lanthanum extraction as a mixture of $La(Ac)_3$ and $La(Pic)_3$ is improbable. Under the assumption that the extracted complex contains two acetate ions, we determined the stoichiometry and logK_{extr} values for the La^{3+} complexes and aminophosphate calix[4]resorcinarenes **1**—**3** (Fig. 2, see Table 1) according to the equation

$$\log K_{\text{extr}} = \log q - m\log[\text{L}]_{\text{org}} - \log[\text{Ln}^{3+}]_{\text{aq}} - 2\log[\text{Ac}^-]_{\text{aq}},$$

where $q = [\text{LaPic(Ac)}_2\text{L}_m]_{\text{org}}/[\text{Pic}^-]_{\text{aq}}$, and $[\text{Ac}^-]_{\text{aq}}$ is the equilibrium concentration of sodium acetate in the aqueous phase. Unlike the extraction of $La(Pic)_3$ in an excess of sodium picrate, at equimolar amounts of sodium picrate and the extracting agent, the stoichiometry of the extracted complex is 1 : 1 and the corresponding extraction constants for compounds **1**—**3** are almost the same (see Table 1). A change in stoichiometry of the extracted complex for compounds **2** and **3**, compared to extraction in an excess of sodium picrate, is caused, first, by an excess of lanthanum over the extracting agent, resulting in the predomination of the 1 : 1 complex.

Table 1. Stoichiometry (m) of the extracted complex $LnA_3 \cdot mL$ and logK_{extr} as a function of the nature of extracting agent **1**—**4** at a $LnCl_3$: NaPic ratio of 1 : 250 (*A*) and 10 : 1 (*B*)

Extracting agent	Ln	*A*		*B*	
		m	logK_{extr}	m	logK_{extr}
1	La	1	6.55±0.07	1	6.78±0.07
	Lu	2	8.58±0.04	1	6.48±0.06
2	La	2	9.01±0.04	1	6.67±0.04
	Lu	2	8.23±0.03	1	6.24±0.03
3	La	2	9.31±0.06	1	6.97±0.14
	Lu	2	6.36±0.06	—[a]	—
4[b]	La	1	3.09±0.10	—[a]	—

[a] No data.

[b] No data for $LuCl_3$.

A comparison of the extraction constants for compounds **1** and **4** indicates an additional stabilization of the aminophosphonate calix[4]resorcinarene complexes with lanthanum tripicrate compared to aminophosphonate **4** (see Table 1). It is most likely that the macrocyclic and/or chelate effects are the most probable reason for the stabilization of the complexes under question.

It was also of interest to estimate the selectivity of the extracting agents toward La^{3+} and Lu^{3+}. The data on the extraction of Lu^{3+} with compounds **1**—**3** with excess sodium picrate (procedure *A*) at the equimolar sodium picrate to the extracting agent ratio (procedure *B*) are presented in Table 1. To compare the efficiency of extraction at different concentrations of compounds **1**—**3** forming the 1 : 1 and 1 : 2 complexes, let us introduce the α value, which is the ratio of the equilibrium concentration of

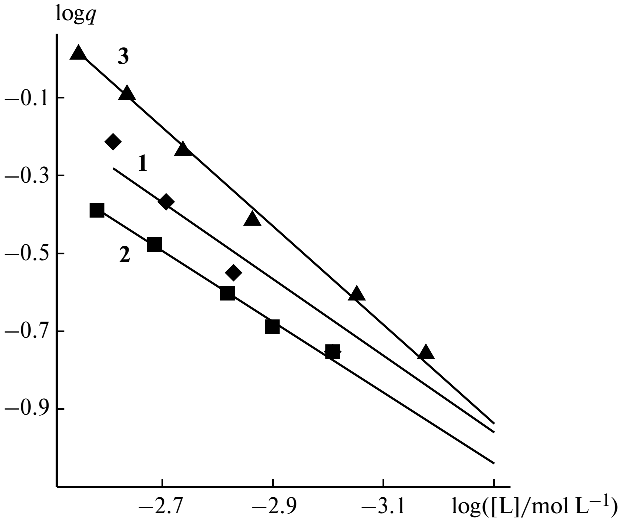

Fig. 2. Plot of log$q$ *vs.* log[L] in the extraction of La^{3+} with compounds **1**—**3** in an excess of La^{3+} in the aqueous phase; $m = 1$.

Ln^{3+} or Pic^- in the organic phase in extraction in an excess of sodium picrate and lanthanum or lutetium chloride, respectively, with respect to the extracting agent. This value characterizes the extraction efficiency of one mole of the extracting agent and makes it possible to compare the extraction efficiencies under different experimental conditions. In an excess of NaPic, the extraction efficiency of lanthanum decreases in the series **1** > **2** ≈ **3** (Fig. 3), which is due to a change in the stoichiometry of extraction from 1 : 1 to 1 : 2 on going from **1** to **2** and **3** (see Table 1). Unlike La^{3+}, in an excess of NaPic the efficiency of Lu^{3+} extraction changes in the series **3** > **1** ≈ **2**, and calixarenes **1** and **2** extract Lu^{3+} more efficiently in an excess of $LuCl_3$ and at the equimolar ratio of NaPic to L. It follows from analysis of the α values for La^{3+} and Lu^{3+} at different concentrations of the extracting agent under identical conditions that calixarene **1** possesses the highest selectivity of extraction in an excess of NaPic (see Fig. 3).

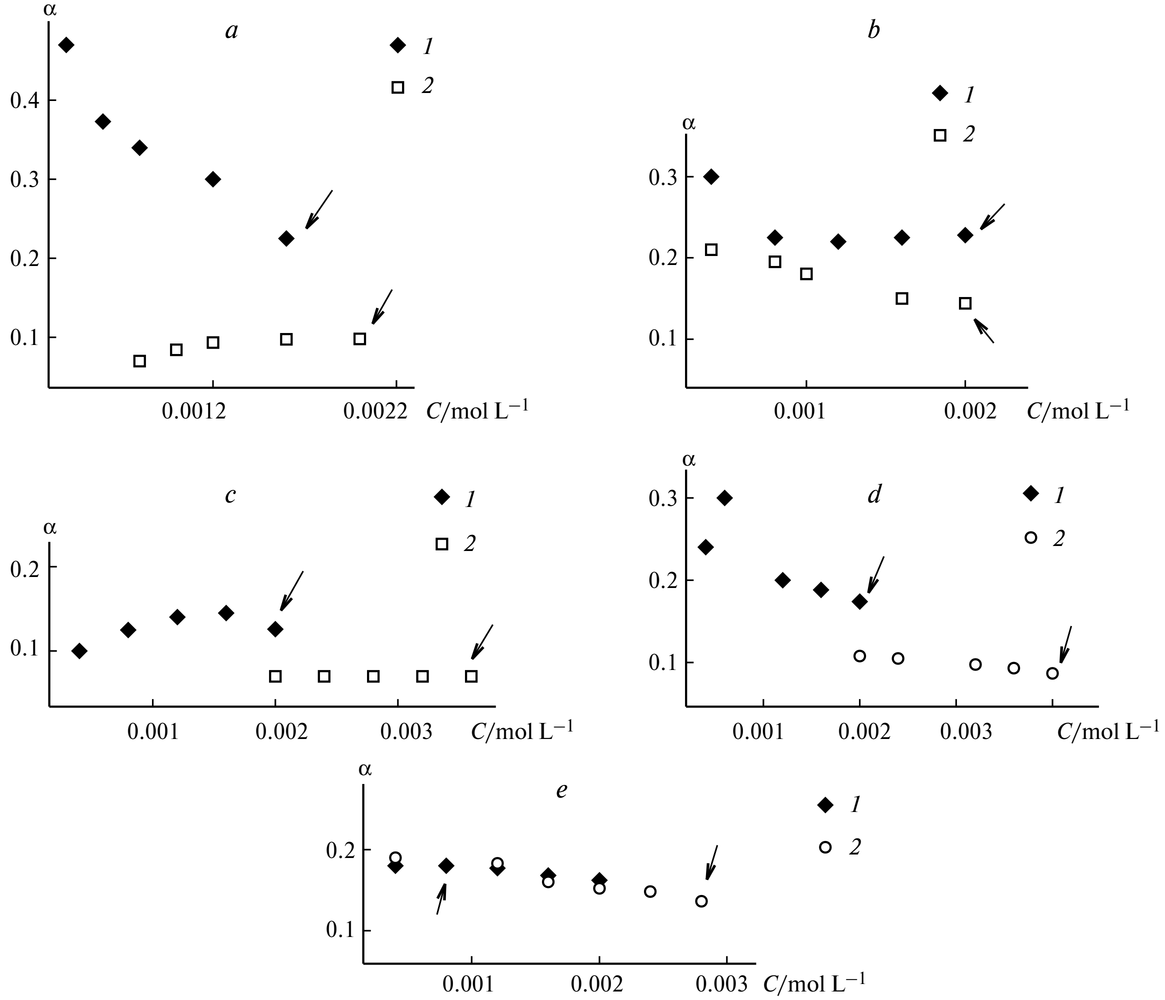

Fig. 3. Formation extent (α) of the extracted complex as a function of the concentration of extracting agent **1** (*a*, *b*), **2** (*c*, *d*), and **3** (*e*); $\alpha = [Ln^{3+}]_{org}/C$ for extraction in an excess of NaPic and $\alpha = [Pic^-]_{org}/C$ for extraction in an excess of $LnCl_3$, where C is the concentration of extracting agent **1**—**3**; *a*, *c*, *e*: $La(Pic)_3$ (*1*) and $Lu(Pic)_3$ (*2*); *b*, *d*: $LaPic(Ac)_2$ (*1*) and $LuPic(Ac)_2$ (*2*).

In the crystal structures of both $[La(Pic)_2(H_2O)_6]Pic$ and $[Lu(Pic)(H_2O)_7](Pic)_2$, picrate ion is a monodentate ligand in the inner coordination sphere of the lanthanum and lutetium complexes.[14,15] Thus, on going from lanthanum to lutetium, the structure of the inner coordination sphere of lanthanide changes due to a decrease in the radius of the metal ion. Taking into account the low electron-donating ability of picrate,[16] we can assume that, when the metal is in a great excess over picrate in the aqueous phase, its entering the first coordination sphere of lanthanides is improbable. Since La^{3+} and Lu^{3+} are characterized by high coordination numbers, the picrates can retain in the inner coordination sphere of both lanthanides at the inner-sphere coordination of compounds **1—3** by the P=O fragments. In this case, the presence of picrates in the inner coordination sphere of lanthanum resulting in additional ligand-ligand interactions induces changes in the stoichiometry of extraction of $La(Pic)_3$ from 1 : 1 for **1** to 1 : 2 for **2** due to some increase in the size of R radical on going from methyl to ethyl. These changes are not characteristic of aliphatic phosphonates.[17] The $Lu(Pic)_3$ complex containing only one picrate ligand in the inner coordination sphere, according to the X-ray diffraction data,[15] exhibits a different than $La(Pic)_3$ dependence of the composition of the extracted complex on the size of the radical at the P=O fragment, due to which calixarene **1** in an excess of NaPic manifests the highest La/Lu-selectivity in extraction. The ^{1}H NMR spectra of a mixture of **2** (**3**) and picric acid in $CDCl_3$ exhibit an upfield shift of the HPic aromatic protons from δ 9.22 to δ 8.88, which is much higher than that for a mixture of aminophosphonate **4** and HPic under the same conditions (from δ 9.22 to δ 9.17). This fact indicates the CH—π-interaction between the picrate ions and extracting agent molecules in addition to hydrogen bonds. However, the interaction of the picrate ion with molecules **2** (**3**) cannot be caused by encapsulation of picrate into the extracting agent cavity because it is known that the introduction of the acceptor group, for example, nitro group, into the aromatic ring prevents the inclusion of the aromatic fragment of the *p*-nitrobenzyltrimethylammonium cation into the calixarene cavity.[18] Therefore, the most probable reason for the upfield shift of the CH-protons of HPic is the formation of a hydrogen bond between the OH group of picric acid and N atom of the aminophosphate fragment and interaction with the aromatic fragments of substituents of molecules **2** (**3**).

Thus, compounds **1—3** are capable of extracting lanthanide ions from an aqueous to chloroform solution more efficiently than aminophosphonate **4**. In an excess of metal ions in the aqueous phase, extraction occurs at the 1 : 1 molar ratio of the metal ion to extracting agent, while in a twofold excess of sodium picrate with respect to the metal ion the composition of the extracted complex depends substantially on both the size of the substituent at the P=O group and the metal ion. This results in a more selective extraction in an excess of sodium picrate.

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References

1. I. M. Harrowfield, M. Mocerino, B. J. Peachey, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1996, 1687.
2. F. Arnaud-Neu, V. Böhmer, J.-F. Dozol, C. Grüttner, R. A. Jacobi, D. Kraft, O. Mauprivez, H. Rouquette, M.-J. Schwing-Weill, N. Simon, and W. Vogt, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1175.
3. P. D. Beer, M. G. B. Drew, and M. I. Ogden, *J. Chem. Soc., Dalton Trans.*, 1997, **9**, 1489.
4. H. Boerrigter, W. Verboom, and D. N. Reinhoudt, *J. Org. Chem.,* 1997, **62**, 7148.
5. A. R. Burilov, N. I. Bashmakova, D. I. Kharitonov, I. L. Nikolaeva, M. A. Pudovik, V. S. Reznik, and A. I. Konovalov, *Zh. Obshch. Khim.*, 1999, **69**, 334 [*Russ. J. Gen. Chem.*, 1999, **69**, 323 (Engl. Transl.)].
6. A. Yu. Ziganshina, E. Kh. Kazakova, S. V. Fedorenko, A. R. Mustafina, and A. I. Konovalov, *Zh. Obshch. Khim.*, 2001, **71**, 1503 [*Russ. J. Gen. Chem.*, 2001, **71**, 1422 (Engl. Transl.)].
7. A. R. Mustafina, V. V. Skripacheva, E. Kh. Kazakova, N. A. Makarova, V. V. Kataev, L. V. Ermolaeva, and W. D. Habicher, *J. Inclus. Phen. Macr. Chem.*, 2002, **42**, 77.
8. S. J. Lyle and M. M. Rahman, *Talanta,* 1963, **10**, 1177.
9. A. N. Pudovik, *Dokl. Akad. Nauk SSSR*, 1952, **83**, 865 [*Dokl. Chem.*, 1952 (Engl. Transl.)].
10. L. S. Serdyuk and V. S. Smirnaya, *Zh. Anal. Khim.*, 1964, **19**, 451 [*J. Anal. Chem. USSR*, 1964, **19** (Engl. Transl.)].
11. R. C. Helgeson, G. R. Weisman, J. L. Toner, T. L. Tarnowski, Y. Chao, J. M. Mayer, and D. J. Cram, *J. Am. Chem. Soc.*, 1979, **101**, 4928.
12. K. E. Koenig, G. M. Lein, P. Stuckler, T. Kaneda, and D. J. Cram, *J. Am. Chem. Soc.*, 1979, **101**, 3553.
13. Yu. I. Sal´nikov, A. N. Glebov, and F. V. Devyatov, *Poliyadernye kompleksy v rastvorakh* [*Polynuclear Complexes in Solutions*], Izd-vo KGU, Kazan, 1989, 287 pp. (in Russian).
14. J. M. Harrowfield, Lu Weimin, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, 1994, **47**, 321.
15. J. M. Harrowfield, Lu Weimin, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, 1994, **47**, 339.
16. U. Olsher, H. Feinberg, H. Frolow, and G. Shoham, *Pure Appl. Chem.*, 1996, **68**, 1195.
17. E. O. Out and A. D. Westland, *Solv. Extr. Ion Exch.*, 1996, **14**, 567.
18. G. Arena, A. Casnati, A. Contino, G. G. Lombardo, D. Sciotto, and R. Ungaro, *Chem. Eur. J.*, 1999, **5**, 738.

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