Liquid extraction of La^{III}, Gd^{III}, and Yb^{III} ions by phosphorylated calix[4]resorcinarene derivatives

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New phosphorylated calix[4]resorcinarene and cavitands were synthesized. Their extraction ability toward La^{III}, Gd^{III}, and Yb^{III} ions was studied. The cavitands are more efficient extracting agents than octasubstituted calix[4]resorcinarenes. The nature of substituents at the nitrogen atom at the upper rim and hydrophobic substituents at the lower rim exerts a substantial effect on the solubility of the extracted complex in chloroform. Coordination of two lanthanide ions with an extragent molecule results in their efficient but non-selective extraction. The literature and our spectral (^{31}P NMR) data suggested that the ligand in the extracted complex has most probably a "kite" conformation.

Key words: calix[4]resorcinarenes, cavitands, extraction, lanthanide ions.

Increasing interest in selective and efficient methods for extraction of ions of 4(5)f-elements is caused by their use in nuclear fuel or radioactive waste processing.[1] Due to similarity of the electronic properties of 4f- and 5f-atoms, lanthanide ions represent a convenient model of radioactive actinides, whose handling is hazardous and requires special care.

Separation of lanthanide ions is a complicated problem, because their thermodynamic parameters of complex formation are similar due to the ionic character of bonding.[2] Unlike alkaline and alkaline-earth metals, high selectivity of lanthanide extraction is hardly attainable, because the change in the stability constants along the series is determined by the result of opposite effects of different factors: size, solvation, metal ion charge, ligand mobility, *etc.*[3] High coordination numbers of lanthanides are a prerequisite for their coordination by macrocycles.[4] Efficient extraction is achieved in the case of macrocyclic compounds that actually and selectively bind specific metal ions through the polycentered interaction, when the binding sites of the macrocycle and substrate are in geometric correspondence. High lipophilicity of the most part of metal ion complexes with calixarenes in combination with high efficiency serves as a reason for the use of calixarenes in liquid extraction.[4,5] The highest efficiency and selectivity of extraction were observed for functionalization of calixarenes by substituents containing the P=O groups.[6] It is known[4,7—15] that immobilization and pre-organization of phosphineoxide, carbamoyloxide, and carbamoylphosphate groups at the rim of the calixarene or cavitand matrix enhance the efficiency and selectivity of extraction. The degree of lanthanide extraction by the carbamoylphosphineoxide extracting agents decreases in the order $La^{III} \approx Eu^{III} > Yb^{III}$.[10] Calix[4]resorcinarenes are convenient platforms for extracting agents because make it possible to change simultaneously both the complexation properties and hydrophobicity. Since the pre-organization of donor centers affects the selectivity of complex formation with lanthanide ions, it is natural to expect that the complexation properties would change substantially on going from the calix[4]resorcinarene matrix to related cavitand structures. Examples for using phosphorylated cavitands as extracting agents of alkaline metals have earlier[16] been published. They bind large ions (*e.g.*, Cs^+) in a metal to ligand ratio of 1 : 1, whereas small ions (Li^+) exhibit the 2 : 1 ratio. The phosphorylated cavitands were shown[17] to bind bulky organic ions (1-azabicyclo[2.2.2]octane hydrochloride) in a ratio of 1 : 1 to form complexes in which the ligand has the high-symmetry conformation C_{4v}. At the same time, complex formation of these ligands with lanthanide triflates in CD_3OD affords complexes with the ratio metal : ligand = 4 : 2. In these complexes, unlike the 1 : 1 complexes, the ligand has the "kite" conformation with the C_{2v} symmetry.

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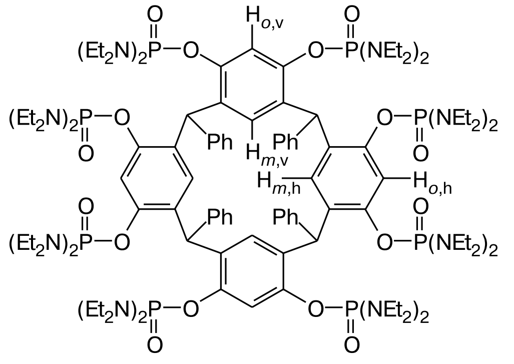
The present work is aimed at the synthesis of new phosphorylated cavitands **1—3** and study of their extraction ability toward the La^{III}, Gd^{III}, and Yb^{III} ions from the aqueous to organic phase (chloroform).



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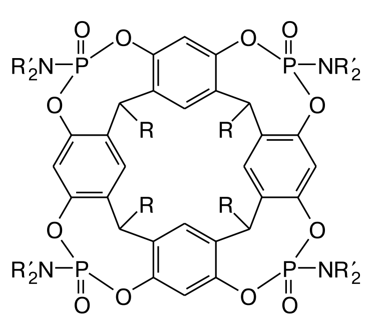


2: R = Me, R$'_2$ = $(CH_2)_5$
3: R = C_5H_{11}, R′ = Et

Experimental

Commercial $La(NO_3)_3 \cdot 6H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$, $YbCl_3 \cdot 7H_2O$, and $C_6H_2(NO_2)_3OH$ (HPic) (all reagent grade) were used. Chloroform (reagent grade) was purified according to a standard procedure.[18] The concentration of Ln^{III} in the initial solutions was determined trilonometrically with thymol blue and xylenol orange as indicators.[19]

Extraction procedure. A chloroformic solution (5 mL) of compounds **1—3** ($C = (4.9—7.7) \cdot 10^{-4}$ mol L^{-1}) was added to an aqueous solution (5 mL) of $Ln(NO_3)_3$ ($C = 1 \cdot 10^{-3}$ mol L^{-1}) and HPic ($C = 6 \cdot 10^{-4}$ mol L^{-1}). The two-phase system was magnetically stirred for 1.5 h in a closed flask and left for 24 h in the dark. After extraction, the Ln^{III} concentration in the aqueous phase was determined spectrophotometrically from the intensity of the absorption peak of the picrate ion at 353.4 nm.[20,21] The procedure was carried out at pH 6.00 in the acetate buffer. The pH value of the buffer solution was measured on an I-130 ionometer. Electronic absorption spectra were recorded on a Specord UV—Vis instrument.

^{31}P NMR spectra were measured on a Cxp-100 spectrometer (36.5 MHz) in $CHCl_3$. H^1 NMR spectra were recorded on a Bruker Avance-600 spectrometer (600 MHz) in $CDCl_3$ (C_3 = 0.005 mol L^{-1}). The MALDI-TOF mass spectrum of compound **2** was obtained on a Finnigan MALDI-TOF Dynamo mass spectrometer.

2,8,14,20-Tetraphenyl-4,6,10,12,16,18,22,24-octakis(tetraethyldiamidophosphate)pentacyclo[19.3.1.1^{3,7}1^{9,13}1^{15,19}]octakis-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (1). A mixture of tetraphenylresorcinarene (0.06 mmol) and hexaethyltriamidophosphite (1 mmol) was stirred for 4 h at 20 °C. Excess triamide was distilled off, the residue was dissolved in 4 mL of methylene chloride (δ_P 123.8, 126.5), and a hydrogen peroxide—urea adduct (0.5 mmol) was added. The reaction mixture was stirred for 4 h at 20 °C. The precipitate was filtered off, the filtrate was washed with water, and the organic layer was separated. The solvent was completely evaporated, and the product was dried at 60 °C *in vacuo* (1 Torr). The yield was 87% (white powder, m.p. 243—244 °C). Found (%): C, 60.23; H, 8.40; N, 9.70; P, 10.73. $C_{116}H_{192}N_{16}O_{16}P_8$. Calculated (%): C, 60.19; H, 8.36; N, 9.68; P, 10.71. ^{31}P NMR ($CDCl_3$), δ: 12.7, 13.8. ^1H NMR ($CDCl_3$), δ: 0.71—1.26 (m, 96 H, $NCH_2C\underline{H}_3$); 2.45—3.09 (m, 64 H, $NC\underline{H}_2CH_3$); 5.84 (s, 4 H, CH); 5.87 (s, 2 H, $H_{m,v}$); 6.61 (br.s, 8 H, H_{Ph}); 7.10 (m, 12 H, H_{Ph}); 7.27 (s, 2 H, $H_{m,h}$); 7.46 (s, 2 H, $H_{o,v}$); 7.57 (s, 2 H, $H_{o,h}$).

Extragents **2** and **3** were synthesized in two steps through the corresponding amidophosphites **4** and **5**.

1,21,23,25-Tetramethyl-5,9,13,17-tetrakis(piperidylamido)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2-λ^3]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:4,5-*d*′]bis[1,3,2-λ^3]-benzodioxaphosphocine (4). A solution of tetramethylresorcinarene (0.39 g, 0.717 mmol) and tripiperidylamidophosphite (0.8 g, 2.827 mmol) in dioxane (7.6 mL) was stored for 7 days at 20 °C. A precipitate formed was filtered off, washed with hexane, and dried at 70—90 °C *in vacuo* (1 Torr). The yield was 52% (colorless crystals, m.p. >350 °C). Found (%): C, 62.64; H, 6.39; N, 5.58; P, 12.4. $C_{52}H_{64}N_4O_8P_4$. Calculated (%): C, 62.65; H, 6.43; N, 5.62; P, 12.45. ^{31}P NMR ($CDCl_3$), δ: 139.6. ^1H NMR ($CDCl_3$), δ: 1.60 (br.s, 24 H, $N(CH_2C\underline{H}_2)_2C\underline{H}_2$); 1.72 (d, 12 H, $CHC\underline{H}_3$, $^3J_{H,H}$ = 7.2 Hz); 3.27 (m, 16 H, $N(C\underline{H}_2CH_2)_2CH_2$, $^3J_{P,H}$ = 7.2 Hz); 4.80 (q, 4 H, $C\underline{H}Me$, $^3J_{H,H}$ = 7.2 Hz); 6.52 (s, 4 H, *o*-H arom.); 7.24 (s, 4 H, *m*-H arom.).

1,21,23,25-Tetramethyl-5,9,13,17-tetrakis(piperidylamido)-5,9,13,17-tetraoxo-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2-λ^5]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo-[1,2-*d*:4,5-*d*′]bis[1,3,2-λ^5]benzodioxaphosphocine (2). A solution of amidophosphitocavitand **4** (0.31 g, 0.3112 mmol) and the adduct $H_2O_2 \cdot (NH_2)_2CO$ (0.13 g, 1.38 mmol) in methylene chloride (7 mL) was stirred for 1 h at 20 °C. A precipitate of $H_2O \cdot (NH_2)_2CO$ was filtered off, and the filtrate was washed with water for complete removal of urea. Methylene chloride was distilled off, and the residue was dried *in vacuo*. The yield was 67% (white powder, m.p. >360 °C). Found (%): C, 58.82; H, 6.08; N, 5.23; P, 11.68. $C_{52}H_{64}N_4O_{12}P_4$. Calculated (%): C, 58.87; H, 6.03; N, 5.28; P, 11.70. ^{31}P NMR ($CDCl_3$), δ: −1.9. ^1H NMR ($CDCl_3$), δ: 1.60 (br.s, 24 H, $N(CH_2C\underline{H}_2)_2C\underline{H}_2$); 1.80 (d, 12 H, $CHC\underline{H}_3$, $^3J_{H,H}$ = 7.3 Hz); 3.29 (m, 16 H, $N(C\underline{H}_2CH_2)_2CH_2$, $^3J_{P,H}$ = 9.4 Hz); 4.77 (q, 4 H, $C\underline{H}Me$, $^3J_{H,H}$ = 7.3 Hz, $^5J_{P,H}$ = 2.8 Hz); 6.85 (t, 4 H, *o*-H arom., $^4J_{P,H}$ = 1.9 Hz); 7.21 (s, 4 H, *m*-H arom.). MALDI-TOF mass spectrum, *m/z*: 997.8 $[M + H]^+$.

1,21,23,25-Tetrapentyl-5,9,13,17-tetrakis(diethylamido)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2-λ^3]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*,2-*d*:5,4-*d*′]bis-

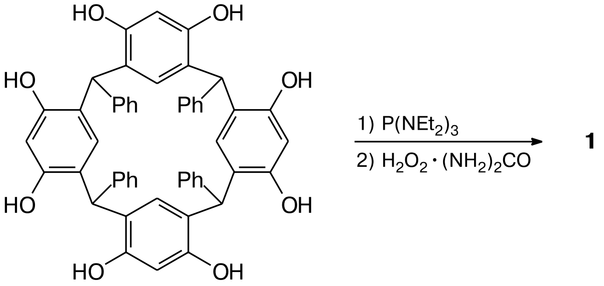
[1,3,2-λ^3]benzodioxaphosphocine (5). Phosphocavitand **5** was synthesized similarly to compound **4** by the reaction of tetrapentylresorcinarene (2.8 mmol) with hexaethyltriamidophosphite (11.2 mmol) for 10 days. The yield was 77% (colorless crystals, m.p. 211—215 °C). Found (%): C, 65.55; H, 8.27; N, 4.78; P, 10.58. $C_{64}H_{96}N_4O_8P_4$. Calculated (%): C, 65.55; H, 8.25; N, 4.77; P, 10.56. ^{31}P NMR, δ: 142.2. ^{1}H NMR ($CDCl_3$), δ: 0.90 (t, 12 H, $CHCH_2(CH_2)_3C\underline{H}_3$, $^3J_{H,H}$ = 6.98 Hz); 1.18 (t, 24 H, $NCH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.05 Hz); 1.37 (m, 24 H, $CHCH_2(C\underline{H}_2)_3Me$); 2.20 (t, 8 H, $CHC\underline{H}_2(CH_2)_3Me$, $^3J_{H,H}$ = 6.29 Hz); 3.29 (m, 16 H, $NC\underline{H}_2Me$, $^3J_{P,H}$ = 10.35 Hz); 4.59 (t, 4 H, CH, $^3J_{H,H}$ = 6.97 Hz); 6.51 (s, 4 H, *o*-H arom.); 7.12 (s, 4 H, *m*-H arom.).

1,21,23,25-Tetrapentyl-5,9,13,17-tetrakis(diethylamido)-5,9,13,17-tetraoxo-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2-λ^5]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo-[1,2-*d*,2-*d*:5,4-*d*′]bis[1,3,2-λ^5]benzodioxaphosphocine (3). Phosphocavitand **3** was synthesized similarly to compound **2** by the reaction of amidophosphitocavitand **5** (0.2 mmol) and the hydrogen peroxide—urea adduct (0.8 mmol) for 4 h. The yield was 84% (white powder, m.p. 224—226 °C). Found (%): C, 62.10; H, 7.81; N, 4.52; P, 10.00. $C_{64}H_{96}N_4O_{12}P_4$. Calculated (%): C, 62.12; H, 7.82; N, 4.53; P, 10.01. ^{31}P NMR, δ: 0.97. ^{1}H NMR ($CDCl_3$), δ: 0.90 (t, 12 H, $CHCH_2(CH_2)_3C\underline{H}_3$, $^3J_{H,H}$ = 6.98 Hz); 1.18 (t, 24 H, $NCH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.05 Hz); 1.37 (m, 24 H, $CHCH_2(C\underline{H}_2)_3Me$); 2.20 (t, 8 H, $CHC\underline{H}_2(CH_2)_3Me$, $^3J_{H,H}$ = 6.29 Hz); 3.29 (m, 16 H, $NC\underline{H}_2Me$, $^3J_{P,H}$ = 10.35 Hz); 4.59 (t, 4 H, CH, $^3J_{H,H}$ = 6.97 Hz); 6.78 (s, 4 H, *o*-H arom.); 7.28 (s, 4 H, *m*-H arom.).

Results and Discussion

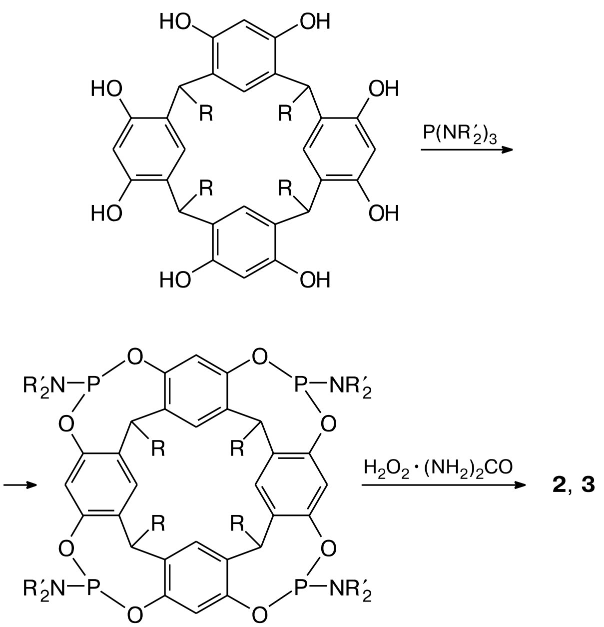
Octaphosphorylated calix[4]resorcinarene **1** was synthesized in one step (Scheme 1).

Scheme 1



Phosphocavitands **2** and **3** were synthesized in two steps isolating intermediate cavitands with the three-coordinate phosphorus atom (Scheme 2).

Scheme 2



4: R = Me, $R'_2 = (CH_2)_5$
5: R = C_5H_{11}, R′ = Et

The extraction ability of the synthesized compounds was studied in liquid extraction of the La^{III}, Gd^{III}, and Yb^{III} ions from the aqueous to organic phase (chloroform). When calix[4]resorcinarene of the type of compound **1** (R = Me) is used, a precipitate is formed at the water—chloroform interface, resulting in the irreversible extraction of the lanthanide ions. Nevertheless, cavitand **2** (R = Me) provides conditions for the reversible extraction of the lanthanide ions. Calix[4]resorcinarene **1** with the hydrophobic phenyl substituents and cavitand **3** give no precipitate at the interface, unlike their less hydrophobic analog. Additional hydrophobicity of extragent **3** is probably provided by the pentyl substituents at the lower rim of the cavitand.

In the case of extraction with cavitand **3**, after extraction the solution contained free cavitand **3** (0.000156 mol L^{-1}) along with the [Ln_2L] complex (0.000414 mol L^{-1}).

The degree of extraction (E_{Pic}) was calculated by the formula

$$E_{Pic} = (1 - A/A^0) \cdot 100\%, \qquad (1)$$

where A^0 and A are the absorbances before and after extraction, respectively.

According to the equilibrium

$$m\,Ln^{3+}{}_{aq} + 3m\,Pic^{-}{}_{aq} + n\,L_{org} \rightleftharpoons$$
$$\rightleftharpoons Ln_m(Pic)_{3m}L_{n,org} \qquad (2)$$

the extraction constant and its logarithm (K_{ex} and $\log K_{ex}$) were calculated by the equations

$$K_{ex} = [Ln_m(Pic)_{3m}L_n]_{org}/([L]^n[Ln^{3+}]^m[Pic^-]^{3m}), \qquad (3)$$

$$\log K_{ex} = \log[Ln_m(Pic)_{3m}L_n]_{org} - n\log[L] -$$
$$- m\log[Ln^{3+}] - 3m\log[Pic^-], \qquad (4)$$

where $[Ln_m(Pic)_{3m}L_n]_{org}$ is the concentration of the complex in the organic phase; [L] is the equilibrium concentration of the extracting agent in the organic phase; $[Ln^{3+}] = C_{Ln}$ is the equilibrium concentration of lanthanides in the aqueous phase, which can be considered equal to the initial concentration, because the lanthanide ions are in excess over the extragent; $[Pic^-]$ is the equilibrium concentration of the picrate ion. The concentration of the complex in the organic phase was calculated using the equation

$$[Ln_m(Pic)_{3m}L_n]_{org} = [(E_{Pic}/100\%) \cdot C_{Pic}]/3, \quad (5)$$

where C_{Pic} is the concentration of picric acid.

The degrees of extraction of the La^{III}, Gd^{III}, and Yb^{III} ions from the aqueous phase to chloroform at different concentrations of calix[4]resorcinarene **1** and cavitands **2** and **3** ($C = (2.9—7.7) \cdot 10^{-4}$ mol L^{-1}) are presented in Fig. 1.

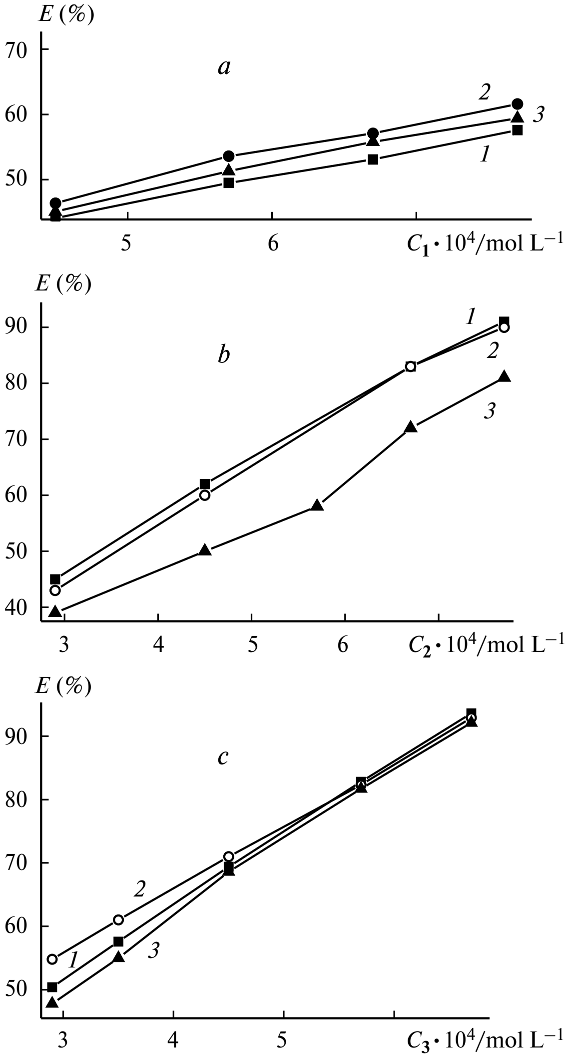


Fig. 1. Dependences of the degree of extraction (*E*) of $Ln(Pic)_3$ from the aqueous to organic phase on the concentration of compound **1** (*a*), **2** (*b*), and **3** (*c*) in chloroform: Ln = La (*1*), Gd (*2*), and Yb (*3*).

Analysis of the plots of the logarithm of the equilibrium concentration of the complexes *vs.* the logarithm of the equilibrium concentration of the extragent (see Eq. (4)) made it possible to estimate stoichiometry of the extraction (Fig. 2). The data presented show that

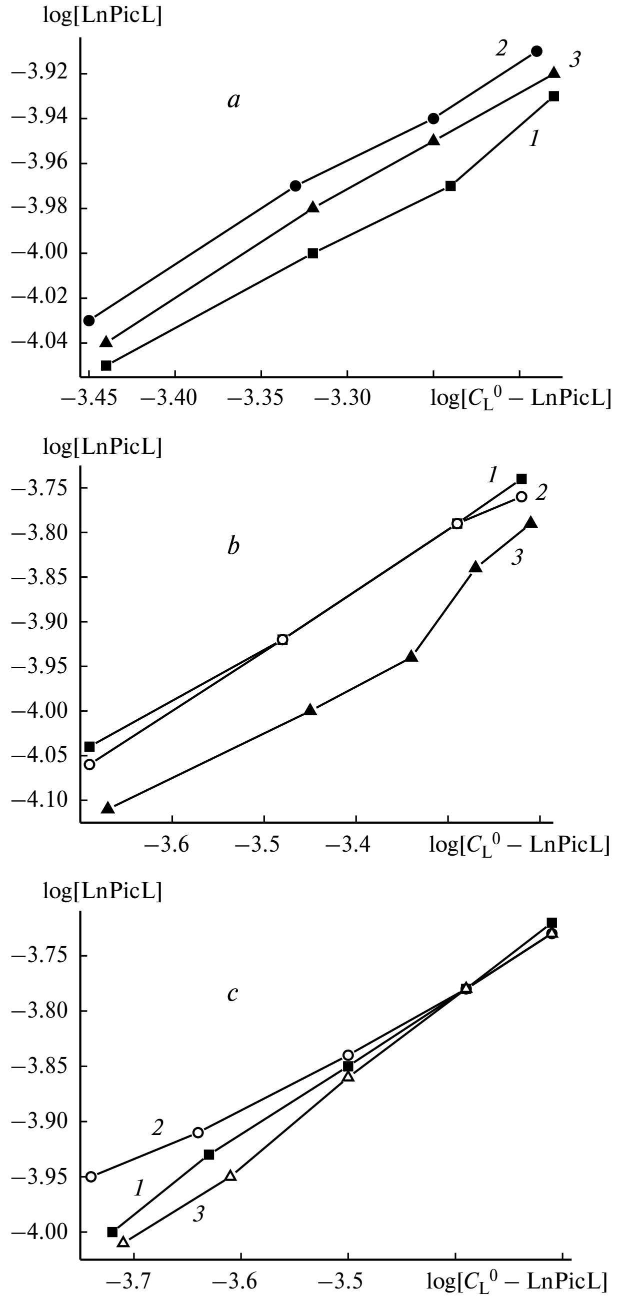


Fig. 2. Dependence of the degree of extraction of the La^{III} (*1*), Gd^{III} (*2*), and Yb^{III} ions (*3*) from the aqueous phase to chloroform on the concentration of compound **1** (*a*), **2** (*b*), and **3** (*c*) in the coordinates log[LnPicL]—log[C_L^0 − LnPicL].

Table 1. Logarithms of the extraction constants for the complexes with the composition Ln : **1—3** = 2 : 1 extracted from the aqueous phase to chloroform ($C_{\mathrm{Ln^{III}}} = 1 \cdot 10^{-3}$ mol L^{-1}, $C_{\mathbf{1-3}}$ = (2.9—7.7) • 10^{-4} mol L^{-1})

Compound	Ln^{III}		
	La^{III}	Gd^{III}	Yb^{III}
1	5.3	5.34	5.32
2	5.54	5.53	5.47, 2.42*
3	5.65	5.67	5.63

* For the 1 : 1 complex.

cavitands **2** and **3** under the given concentration conditions are more efficient extracting agents for the lanthanide ions only if compared to calix[4]resorcinarene **1**.

However, only extragent **2** manifests a perceptible selectivity toward the ions under study (see Fig. 2, *b*). For compounds **1—3**, lanthanide extraction results in the formation of complexes with the stoichiometric ratio metal : ligand = 2 : 1 in the studied concentration region, and only for the extraction of Yb^{III} with extragent **2** at its concentration >6.7 • 10^{-4} mol L^{-1} the stoichiometry of the complex is 1 : 1. The corresponding constants are given in Table 1.

According to the spectral data, the extracting agents under study are *rccc*-isomers. According to the data for the ^{1}H and ^{31}P NMR spectra presented in Experimental, cavitands **2** and **3** exist in the "cone" conformation with the C_{4v} symmetry. By analogy to the octasubstituted phosphorylated calix[4]resorcinarene earlier[22] characterized by X-ray diffraction analysis, it is natural to assume that compound **1** has the "kite" conformation with the C_{2v} symmetry. According to literature data, coordination of two metal ions with both octasubstituted calix[4]resorcinarenes[23] and related[17] cavitands stabilizes the conformation with the C_{2v} symmetry. Since results of NMR spectroscopy are sensitive to the conformational state of calix[4]resorcinarenes and their derivatives, the corresponding spectral changes can be expected to appear upon extraction. The change in the ^{31}P NMR spectrum of extragent **3** upon the formation of the complex with the lanthanides is shown in Fig. 3.

The presence of three signals, of which signal *1* refers to the unbound extragent and signals *2* and *3* concern the extracted complex, indicates that the phosphorus atoms in the latter are non-equivalent.

The most pronounced changes in the ^{1}H NMR spectrum due to complex formation are observed in the region of aromatic protons (Fig. 4).

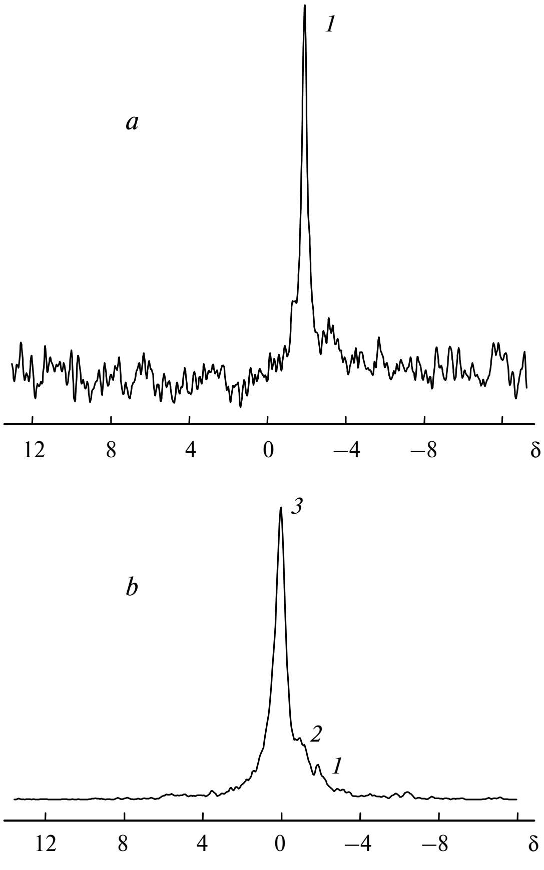


Fig. 3. ^{31}P NMR spectra of phosphorylated cavitand **3** in CHCl$_3$ before (*a*) and after (*b*) extraction (C_3 = 0.005 (*a*) and 0.009 mol L^{-1} (*b*)). For signals *1—3*, see text.

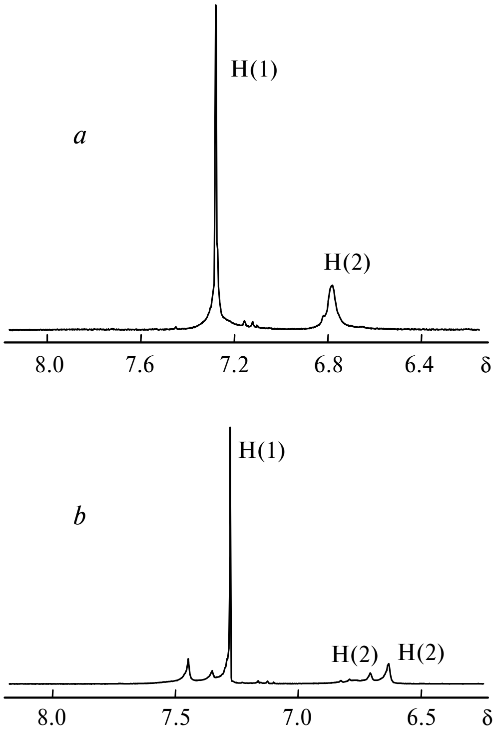
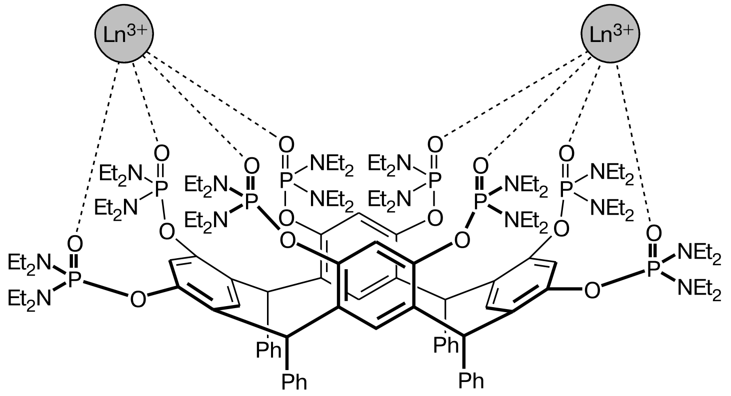


Fig. 4. ^{1}H NMR spectra of phosphorylated cavitand **3** in CDCl$_3$ before (*a*) and after (*b*) extraction (C_3 = 0.005 (*a*) and 0.009 mol L^{-1} (*b*)).



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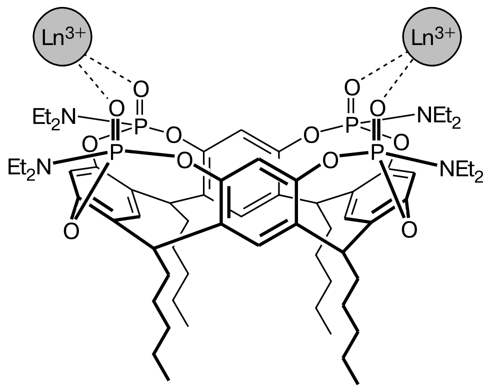

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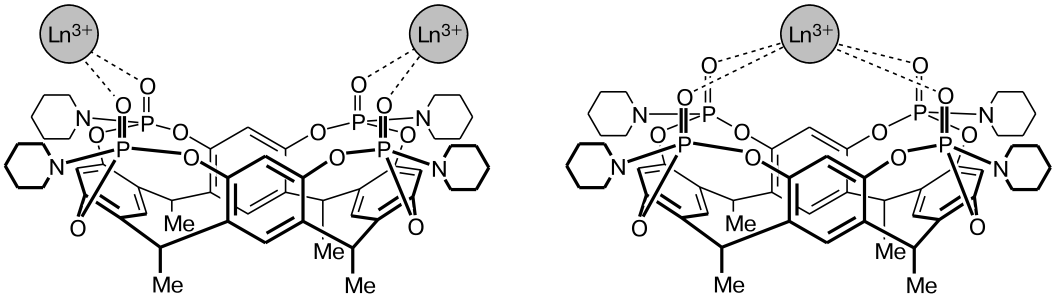

2

The signal of the H(1) proton undergoes a downfield shift from δ 7.28 to δ 7.45, and the signal of the H(2) proton (δ 6.78) during extraction experiences very small upfield shift with splitting into two signals (δ 6.71 and 6.64).

The spectral changes observed on going from the free ligand to the extracted complex indicate that P=O and the aromatic fragments of cavitand **3** in a complex with lanthanum are non-equivalent, which agrees well with the C_{2v} symmetry and suggests the most probable structure for the extracted complexes.

Thus, new phosphorylated calix[4]resorcinarene and cavitands were synthesized, and their extraction ability toward the La^{III}, Gd^{III}, and Yb^{III} ions in a water—chloroform system was studied using the picrate method.

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References

1. Y. Marcus and A. S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes*, J. Wiley, London, 1969, **1/1050**, 432.
2. N. A. Kostromina, *Kompleksonaty redkozemel´nykh elementov* [*Rare-Earth Element Complexonates*], Nauka, Moscow, 1980, 219 pp. (in Russian).
3. V. Alexander, *Chem. Rev.*, 1995, **95**, 273.
4. F. Arnaud-Neu, *Chem. Soc. Rev.*, 1994, **23**, 235.
5. I. M. Harrowfield, M. Mocerino, B. J. Peachey, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1996, 1687.
6. L. Atamas, O. Klimchuk, V. Rudzevich, V. Pirozhenko, V. Kalchenko, I. Smirnov, V. Babain, T. Efremova, A. Varnek, G. Wipff, F. Arnaud-Neu, M. Roch, M. Saadioui, and V. Böhmer, *J. Supramol. Chem.*, 2002, **2**, 421.
7. J. F. Malone, D. J. Marrs, M. A. McKervey, P. O´Hagan, N. Thompson, A. Walker, F. Arnaud-Neu, O. Naupriver, M. R. Schwing-Weill, J. F. Dozol, H. Rouquette, and N. Simon, *J. Chem. Soc., Chem. Commun.*, 1995, 2151.
8. M. R. Schwing-Weill and F. Arnaud-Neu, *Gazz. Chim. Ital.*, 1997, **127**, 687.
9. F. Arnaud-Neu, V. Böhmer, J. F. Dozol, C. Grüttner, R. A. Jacobi, D. Kraft, O. Mauprivez, H. Rouquette, M. R. Schwing-Weill, N. Simon, and W. Vogt, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1175.
10. S. Barboso, A. C. Carrera, S. E. Matthews, F. Arnaud-Neu, V. Böhmer, J. F. Dozol, H. Rouquette, and M. R. Schwing-Weill, *J. Chem. Soc., Perkin Trans. 2*, 1999, 719.
11. T. Lambert, G. D. Jarvinen, and A. S. Gopalan, *Tetrahedron Lett.*, 1999, **40**, 1613.
12. H. Boerrigter, W. Verboom, and D. N. Reinhoudt, *J. Org. Chem.*, 1997, **62**, 7148.
13. M. R. Yaftian, M. Burgard, C. Wieser, C. B. Dieleman, and D. Matt, *Solv. Extr. Ion. Exch.*, 1998, **16**, 1131.
14. P. D. Beer, M. G. B. Drew, and M. I. Ogden, *J. Chem. Soc., Dalton Trans.*, 1997, 1489.

15. P. D. Beer, M. G. B. Drew, M. Kan, and P. B. Leeson, *Inorg. Chem.*, 1996, **35**, 2202.
16. P. Delange and J.-P. Dutasta, *Tetrahedron Lett.*, 1995, **36**, 9325.
17. P. Amrhein, P. L. Wash, A. Shivanyuk, and J. Rebek, Jr, *Org. Lett.*, 2002, **4**, 319.
18. A. J. Gordon and R. A. Ford, *The Chemist´s Companion*, Wiley, New York, 1972.
19. S. J. Lyle and M. M. Rahman, *Talanta*, 1963, **10**, 1177.
20. K. E. Koenig, G. M. Lein, P. Stuckler, T. Kaneda, and D. J. Cram, *J. Am. Chem. Soc.*, 1979, **101**, 3553.
21. 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.
22. V. I. Maslennikova, O. S. Serkova, M. Gruner, S. Goutal, I. Bauer, W. D. Habicher, K. A. Lyssenko, M. Yu. Antipin, and E. E. Nifantyev, *Eur. J. Org. Chem.*, 2004, 4884.
23. J. R. Fransen and Ph. J. Dutton, *Can. J. Chem.*, 1995, **73**, 221.

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