

Effect of *p*-*tert*-Butylcalix[4]arene Fitted with Phosphinoyl Pendant Arms as Synergistic Agent in the Solvent Extraction and Separation of Some Trivalent Lanthanoids with 4-Benzoyl-3-methyl-1-phenyl-5-pyrazolone

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Abstract

The synergistic solvent extraction of five selected lanthanoid ions (La^{3+} , Nd^{3+} , Eu^{3+} , Ho^{3+} and Lu^{3+}) with a 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (HP) and the 5,11,17,23-*tert*-butyl-25,26,27,28-tetrakis(dimethylphosphinoylmethoxy)calix[4]arene, (S) in CHCl_3 has been studied. It was found that in presence of this phosphorus-containing calix[4]arene the lanthanoids have been extracted as $\text{LnP}_3 \cdot \text{S}$. On the basis of the experimental data, the values of the equilibrium constants have been calculated. The influence of the synergistic agent on the extraction process has been discussed. A synergistic effect of almost three orders of magnitude occurs in the extraction of Ln(III) with mixture of HP and S. The values of the separation factors (S.F.) between the adjacent elements have been evaluated. On the basis of the IR and NMR spectra the stoichiometry and the structure of the solid complexes of Eu(III) with HP and Eu(III) with HP and S were proposed.

Introduction

The interesting properties of the calixarenes have provoked a remarkable interest in almost all fields of chemistry. Data for synthesis, modification and chemistry of various types calix[*n*]arenes are given in the collection of papers [1]. The use of calixarenes in analytical chemistry and separation chemical technology has been discussed in the review of Ludwig [2]. The solvent extraction of trivalent lanthanoids and actinoids has been investigated by Ludwig et al. [3, 4], Arnaud-Neu et al. [5–8] and Roundhill and Shen [9]. The influence of various factors such as cavity size ($n = 4, 6, 8$), hydrophobicity of the ligand, the position of the donor atoms and the diluent has been studied. Bünzli et al. [10, 11] have synthesized and characterized *p*-*tert*-butylcalix[4]arene and *p*-*tert*-butylcalix[6]arene both fitted with phosphinoyl pendant arms. The authors have also obtained complexes of La(III), Eu(III), Gd(III) and Tb(III) with these phosphorus-containing calixarenes (composition metal:ligand 1:1 and 1:2) in ethanol and acetonitrile.

The investigations devoted to the synergistic solvent extraction of lanthanoids with mixtures of extractants including calixarenes are not numerous. Kuznetsova et al. [12–14] have studied the extraction of some lanthanoid ions with calix[4]resorcinarene or its alkylaminomethylated derivatives in the presence of 1,10-phenanthroline. The authors have found that the synergistic effect is due to the formation of outer-sphere complex between the cation $[\text{Ln}(\text{phen})_2]^{3+}$ and deprotonated forms of the calix[4]resorcinarene, $[\text{H}_5\text{L}]^{3-}$ as well as that the derivatives are more effective extractants in comparison with the unsubstituted calix[4]resorcinarene. Kyrš et al. [15, 16] have observed synergistic effect in the solvent extraction of Eu(III) with mixtures of conformers of tetrathio-calixarene and dicarbollide. The influence of the molar ratio of the two extractants, the total extractants concentrations, the aqueous acidity, the phase volume and the metal concentration on the extraction of Eu(III) has been investigated.

Recently, Shimojo and Goto [17] have established that the combination of calix[6] arene carboxylic acid derivative with *tert*-octyl groups at upper rim and bis-(2-ethylhexyl)phosphoric acid in isooctane causes

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synergism in the extraction of nucleobases (adenine and cytosine). Earlier, Natatou et al. [18] have found that mixtures of macrocyclic crown ethers (dicyclohexano-18-crown-6, dibenzo-18-crown-6, 18-crown-6 and benzo-15-crown-5) and *p-tert*-butylcalix[4]arene in dichloroethane exhibit synergistic effect in the extraction of alkali metals.

The present work was undertaken in order to study the effect of lower rim substituted calix[4]arene such as 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-(dimethylphosphinoyl-methoxy)calix[4]arene, S, on the solvent extraction of five selected lanthanoid ions (La^{3+} , Nd^{3+} , Eu^{3+} , Ho^{3+} and Lu^{3+}) with 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone, HP, as chelating agent in CHCl_3 and to determine the stoichiometry of the complexes extracted in the organic phase as well as the selectivity among these metal ions. Solid complexes of Eu^{3+} with HP and of Eu^{3+} with HP and S were also prepared.

Experimental

Reagents

The commercial product 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone, HP (purity >99%, Fluka) was used as received. The lower rim substituted calix[4]arene, S, was synthesized according to the method described in reference [10]. Its quality has been checked by ^1H NMR in CDCl_3 (Bruker DRX 250 MHz): 6.800(8H, s, Ar-H), 4.836(4H, d, $^2J_{\text{HH}} = 13.0$, Ar- CH_2 -Ar), 4.688(8H, d, $^2J_{\text{HP}} = 1.3$, $\text{CH}_2\text{P}=\text{O}$), 3.268(4H, d, $^2J_{\text{HH}} = 13.0$, Ar- CH_2 -Ar), 1.532(24H, d, $^2J_{\text{HP}} = 12.9$, $(\text{CH}_3)_2\text{P}=\text{O}$), 1.074(36H, s, $(\text{CH}_3)_3\text{C}$).

Stock solutions of La(III), Nd(III), Eu(III), Ho(III) and Lu(III) were prepared by dissolving appropriate amounts of their oxides (Fluka, puriss.) in hydrochloric acid. The diluent was CHCl_3 (Merck, p.a.). Arsenazo III (Fluka) was of analytical grade purity as were the other reagents used.

Apparatus

A S-20 Spectrophotometer Boeco (Germany) was used for measuring absorbances. A pH 211 HANNA digital pH meter was used for the pH measurements. The melting points (uncorrected) were measured on a Boetzius microheating plate PHMK05 (Germany). Infrared spectra ($400\text{--}4000\text{ cm}^{-1}$) were recorded on a FTIR Bruker IFS113v IR spectrometer in KBr pellets. The ^1H NMR spectra were recorded on a Bruker Avance DRX250 250 MHz high performance digital FT-NMR spectrometer in CDCl_3 or CD_3OD . The chemical shifts are given relative to TMS.

Extraction procedure

The experiments were carried out using 10 cm^3 volumes of aqueous and organic phases. The samples were shaken

mechanically for 45 min at room temperature which was sufficient to reach equilibrium. After the separation of the phases, the metal concentration in the aqueous phase was determined photometrically using Arsenazo III [19]. The concentration of the metal ion in the organic phase was obtained by material balance. These concentrations were used to calculate the distribution coefficient. The acidity of the aqueous phase was measured by a pH-meter with an accuracy of 0.01 pH unit. The ionic strength was maintained at 0.1 mol/dm^3 with $(\text{Na}, \text{H})\text{Cl}$. The initial concentration of the metal ions was $2.5 \times 10^{-4}\text{ mol/dm}^3$ in all experiments.

The distribution coefficients of the lanthanoid ions were determined in three series of experiments, viz.:

- with fixed HP and S concentration and varied pH
- with fixed pH and S concentration and varied HP concentration
- with fixed pH and HP and varied S concentration

Preparation of metal complexes

Complex of Eu(III) with HP

The transparent colourless solution of 59 mg (0.2 mmol) $\text{EuCl}_3 \cdot 2\text{H}_2\text{O}$ in 2 cm^3 absolute ethanol was added at room temperature to a stirred yellow solution of 167 mg, (0.6 mmol) 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone in 2 cm^3 absolute ethanol. The reaction mixture was stirred additionally at room temperature for 5 h and the solvent was evaporated under reduced pressure. The residue, a yellow crystal product, formed was washed twice with small amount of diethyl ether and dried in high vacuum over P_2O_5 . It melts at $184\text{--}185\text{ }^\circ\text{C}$. Yield 210 mg (82%). IR spectrum (KBr, cm^{-1}): 1296 (O(C=C)), 1636 (C=O), 1610–1577 and 1500–1471 (Ar), 764–731 and 703–692 (monosubstituted Ar).

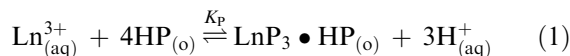
Complex of Eu(III) with HP and S

A colourless solution of 29 mg (0.1 mmol) $\text{EuCl}_3 \cdot 2\text{H}_2\text{O}$ in 2 cm^3 absolute ethanol was added at stirring to a transparent solution of 101 mg (0.1 mmol) S and 83.5 mg (0.3 mmol) HP in 4 cm^3 absolute ethanol. The volume of the prepared transparent solution was reduced to 3 cm^3 by evaporation of a part of the solvent via slight heating (below $50\text{ }^\circ\text{C}$) and stirred at room temperature for 5 h. The solvent was evaporated under reduced pressure. The residue, a slightly yellow solid product, was washed twice with diethyl ether and dried in high vacuum over P_2O_5 . Yield: 183 mg of yellow crystal product with m.p. $308\text{--}309\text{ }^\circ\text{C}$. IR spectrum (KBr, cm^{-1}): 1142 (P=O), 1300 (P(CH₃)), 1622–1578 and 1500–1479 (Ar), 947 (1,2,3,5 tetra substituted Ar), 2900–2790 (*tert*-butyl in substituted Ar), 1653 (C=O).

The ^1H NMR spectra of the free ligands and complex in CD_3OD at 338 K are given in Table 2. The chemical shifts temperature dependence of complex in CD_3OD is presented in Figure 5.

Results and discussion

The solvent extraction of the lanthanoid(III) ions with HP in CHCl_3 has been studied previously [20]. It has been found that the metal extraction can be represented by the following equation:



The synergistic solvent extraction of the lanthanoids was studied using a traditional and effective means of obtaining both stoichiometric and equilibrium constant information about extraction processes, called “slope analysis”. It is based on an examination of the variation of $D_{P,S}$ (the distribution coefficient due to the synergistic effect) as a function of the relevant experimental variables. As the lanthanoid extraction with the calix[4]arene, S, alone is negligible under the experimental conditions of the present study, the values of the distribution coefficient D obtained experimentally are the sum of $D_{P,S}$ and D_P (D_P is the distribution coefficients due to the lanthanoid extraction with HP alone under the same experimental conditions). So, the values of $D_{P,S}$ were calculated as $D - D_P$. A log-log plot of $D_{P,S}$ versus one of the variables $[\text{H}^+]$, $[\text{HP}]$ and $[\text{S}]$ keeping the other two constant, indicates the stoichiometry of the extractable complex. This leads to the derivation of a suitable equilibrium expression and then to the calculation of the equilibrium constant. If the concentration of the extractants is constant and the hydrolysis in the aqueous phase as well as the polymerization in the organic phase occur to a negligible extent only, then the plots will be straight lines and their slopes will give the number of the ligands of the adducts.

The experimental data for the extraction of the Ln(III) with mixture of HP and S are given in Figures 1–3. The plots of $\log D_{P,S}$ versus pH and $\log[\text{HP}]$ are linear with slope close to three and the plots of $\log D_{P,S}$ versus $\log[\text{S}]$ with slope close to one. Therefore, in the presence of HP-S the lanthanoids extraction can be expressed by the following equations:

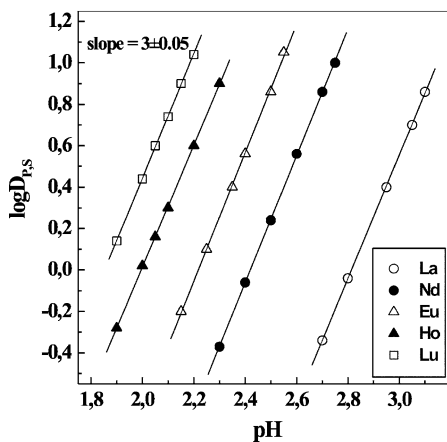


Figure 1. $\log D_{P,S}$ versus pH for the extraction of lanthanoid elements with mixtures of: $[\text{HP}] = 3 \times 10^{-2} \text{ mol/dm}^3$ and $[\text{S}] = 1 \times 10^{-3} \text{ mol/dm}^3$.

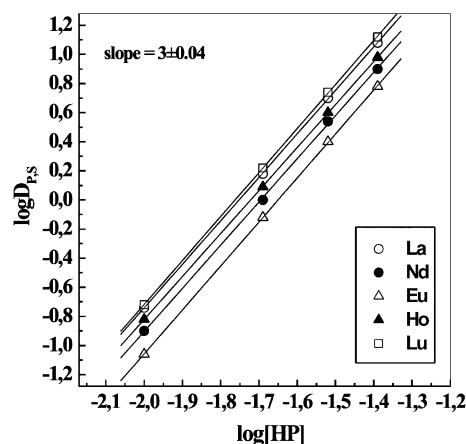
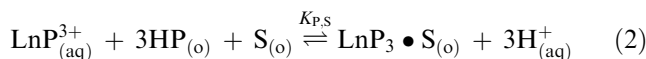


Figure 2. $\log D_{P,S}$ versus $[\text{HP}]$ for the extraction of lanthanoid elements with mixtures of HP(S at: $[\text{S}] = 1 \times 10^{-3} \text{ mol/dm}^3$, La, pH = 3.05; Nd, pH = 2.60; Eu, pH = 2.35; Ho, pH = 2.20; Lu, pH = 2.10.

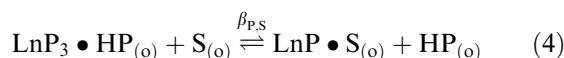


where Ln^{3+} denotes a lanthanoid ion and the subscripts “aq” and “o” where denote aqueous and organic phases, respectively.

Taking into account that the partition of HP [21] and S [10] toward the aqueous phase is very low the overall equilibrium constant values $K_{P,S}$ can be determined by the equations:

$$\log K_{P,S} = \log D_{P,S} - 3\log[\text{HP}] - \log[\text{S}] - 3\text{pH} \quad (3)$$

The formation of mixed complexes in the organic phase can be described by the equations:



The equilibrium constant $\beta_{P,S}$ for the organic phase synergistic reaction can be determined as:

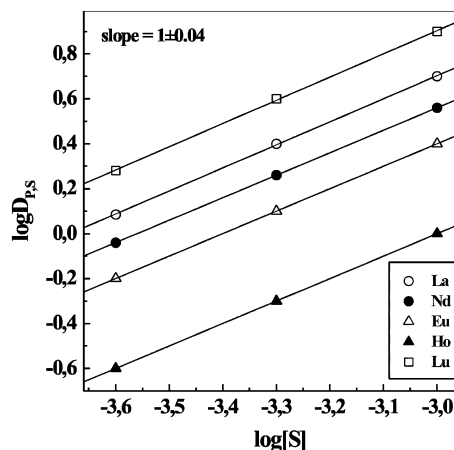


Figure 3. $\log D_{P,S}$ versus $[\text{S}]$ for the extraction of lanthanoid elements with mixtures of HP(S at: $[\text{HP}] = 3 \times 10^{-2} \text{ mol/dm}^3$, La, pH = 3.05; Nd, pH = 2.60; Eu, pH = 2.35; Ho, pH = 2.00; Lu, pH = 2.15.

Table 1. Values of the equilibrium constants K_P , $K_{P,S}$, $\beta_{P,S}$ and synergistic coefficients ($[HP] = 3 \times 10^{-2}$ mol/dm³, $[S] = 1 \times 10^{-3}$ mol/dm³, pH = 2.50) and separation factors for the Ln³⁺ extraction with HP-S mixtures in CHCl₃

Ln ³⁺	log K_P [20]	log $K_{P,S}$	log $\beta_{P,S}$	S.C.	S.F.		
						HP	HP-S
La ³⁺	-5.84	-0.88	4.96	3.48	Nd/La	30.9	15.1
Nd ³⁺	-4.35	0.30	4.65	3.17	Eu/Nd	8.5	3.98
Eu ³⁺	-3.42	0.90	4.32	2.84	Ho/Eu	1.5	4.57
Ho ³⁺	-3.24	1.56	4.80	3.32	Lu/Ho	2.57	2.75
Lu ³⁺	-2.83	2.00	4.83	3.35			

Notes: The values of the equilibrium constants are calculated on the basis of the 35 experimental points, statistical confidence 95% and standard deviation $\leq \pm 0.05$.

$$\log \beta_{P,S} = \log K_{P,S} - \log K_P \quad (5)$$

The values of the equilibrium constants $K_{P,S}$ and $\beta_{P,S}$ calculated from the experimental data are given in Table 1. The equilibrium constants are based on the assumption that the activity coefficients of the species do not change significantly under the experimental conditions i.e. they are concentration constants. The data presented in Table 1 show that the introduction of the used calix[4]arene into the system Ln³⁺-HP leads to a significant increase of the values of $K_{P,S}$ in comparison with those of K_P as well as that the values of this constant increase from La³⁺ to Lu³⁺ as expected from their decreasing ionic radii. The variation of the equilibrium constants K_P and $K_{P,S}$ versus the atomic number Z of the investigated Ln(III) ions is given in Figure 4. It is seen that the two curves vary practically in the same manner. So, the synergistic agent (phosphorus-containing *tert*-butylcalix[4]arene) causes quantitative but not qualitative changes in the extraction of the lanthanoid(III) ions because of the formation of the same type of complexes (the formation of self-adducts LnP₃·HP when pyrazolone is used as extractant and the formation of mixed adducts LnP₃·S using synergistic mixture of extractants) in both cases.

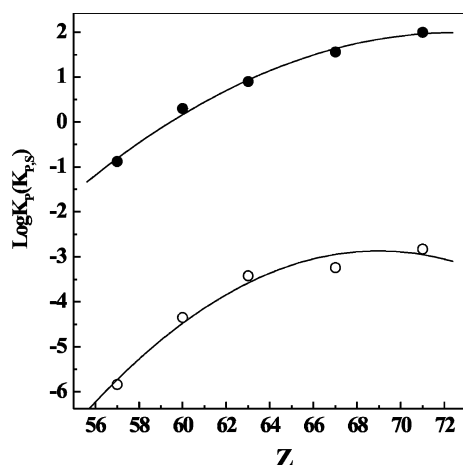


Figure 4. $\log K_P(K_{P,S})$ versus atomic number (Z) of La, Nd, Eu, Ho and Lu. Open circles – $\log K_P$, closed circle – $\log K_{P,S}$.

If the used calix[4]arene is bound to the metal ion through the four P=O groups as noted for 1:1 complexes with Ln(III) ions [10], the coordination number of the lanthanoid(III) ions in the mixed adduct LnP₃·S is ten because the three chelating HP ligands occupy six coordination sites. Such a large coordination number is not unusual for the lanthanoids [22]. However, there is another possibility viz. participation of a part of P=O groups in the donor–acceptor interaction with the metal ion. Then the coordination number would be smaller. Such an opportunity has been supposed by Mathur [23] for the synergistic extraction of Am(III) with mixtures of substituted pyrazolones and crown ethers. He has accepted that not all oxygen atoms of benzo-15-crow-5 are bound to the metal.

The synergistic enhancement produced by HP-S mixtures can be determined using the synergistic coefficients (S.C.). They were calculated according to [24]: $S.C. = \log (D_{1,2}/D_1 + D_2)$ where D_1 , D_2 and $D_{1,2}$ are the distribution coefficients of the metal with the two extractants taken separately and with their mixture. The values of the S.C. are listed in Table 1. It is seen that the lanthanoids are extracted synergistically (S.C. > 0). The addition of 5,11,17,23-*tert*-butyl-25,26,27,28-tetrakis(dimethylphosphino)ethoxy)calix[4]arene to the chelating extractant improves the extraction efficiency of the lanthanoid ions and produces rather large synergistic effects (more than three orders of magnitude in the most cases). The synergistic enhancement established in the present study is higher (2–3 times) as compared to those found in some of our previous investigations dealing with the lanthanoid extraction with the same chelating extractant (HP) and various synergistic agents as dibenzo-18-crown-6, dibenzo-24-crown-8 [25], 1-(2-pyridylazo)-2-naphthol [26] and the perchlorate form of the quaternary ammonium salt Aliquat 336 [27]. Therefore, the complexes of the lanthanoid ions with HP and the used calixarene are more stable in the organic phase than those including HP and the abovementioned synergistic agents. It is probably due to the higher hydrophobicity of the extracted complexes.

The separation of the lanthanoids using HP-S mixtures can be assessed by the separation factors (S.F.) calculated as a ratio of the distribution coefficients of two adjacent lanthanoids (the heavier and the lighter

one). When the metal ions form complexes of the same type (as in the present case), the S.F. can be determined as a ratio of the equilibrium constants $K_{P,S}$. Their values are also given in Table 1. It is seen that the S.F. obtained for the extraction of the investigated lanthanoid ions with HP alone and those with HP-S combination do not differ in large extent. However, the use of the present combination of extractants propose the advantage of much higher extraction in comparison with HP alone. Another advantage of this extractants mixture to similar combinations [13], including calyx[4]resorcinarene or its dimethylamino-, piperidyl- or trimethylammoniummethylated derivatives and 1,10-phenanthroline is that the extraction process is carried out at rather lower pH values of the aqueous phase.

IR and ^1H NMR spectra of the complexes

The characteristic bands of the IR spectrum of HP are: a band at 1285 cm^{-1} typical for O-C=C group and a broad band at around 3100 cm^{-1} for intramolecular hydrogen bond. Such band is not observed in the complex of Eu(III) with HP as HO group is deprotonated as a results of the complex formation. The band at 1285 cm^{-1} in the free HP is shifted to 1296 cm^{-1} in the spectrum of the complex of HP with EuCl_3 . The position of the bands typical for aromatic rings do not move: they are at the same place in the IR spectra of HP and its complex with Eu(III).

It was noted above that from a mixture of S, HP and EuCl_3 (mol ratio of the compounds respectively 1:3:1) a crystal compound with m.p. $308\text{--}309\text{ }^\circ\text{C}$ has been isolated. Its IR spectrum shows some shift of the band for P=O group at 1160 cm^{-1} in the free S to 1142 cm^{-1} in the crystal compound prepared from the S, HP and EuCl_3 . In the IR spectrum of this compound a band at 1653 cm^{-1} for C=O group have been observed.

The ^1H NMR spectra of the mixture of HP and S, and of the synthesized complex of Eu with them were measured in MeOH-d_6 at 300, 320, 335 and 338 K. At the highest temperature the signals are sufficiently resolved (Figure 5) and on the basis of their integral

intensity the ratio of the ligands in the synthesized $[\text{EuP}_2\text{S}]^+$ complex was calculated as HP:S = 2:1. The proposed structure of the complex is presented in Figure 6.

The ^1H NMR spectral data of the free ligands and complex in CD_3OD at 338 K are summarized in Table 2. The expected resonances are shifted in some degree to higher field upon coordination, except the signal for *tert*-butyl group. On the other hand only *o*-Ph protons from one of the phenyl ring in HP are significantly shifted to higher field (Figure 5) indicating proximity to the metal ion. There is no change in the symmetry of ligand S upon coordination and all resonances of S remain in the same form as for free S ligand, which indicates uniform interaction of all P=O with Eu^{3+} ion. This complex will be an object of additional investigations.

The different composition of the mixed complex in solution (LnP_3S) and in solid state ($[\text{EuP}_2\text{S}]^+$) could be due to the different experimental conditions.

Conclusion

Selected lanthanoid(III) ions (La, Nd, Eu, Ho, Lu) are synergistically extracted by HP-S combination as LnP_3S species. The addition of the phosphorus-containing *p-tert*-butylcalix[4]arene (S) produces a large synergistic effect. The synergistic enhancement factors for the various lanthanoids do not change significantly. The values of the overall equilibrium constant $K_{P,S}$ increase with increasing atomic numbers of the metals. The values of the separation coefficient obtained for the lanthanide extraction with HP alone and with mixtures of HP and the used calix[4]arene do not vary in great extent.

The IR and NMR spectra show that the composition of the complex in solid state is $[\text{EuP}_2\text{S}]^+$. It is suggested that the different composition of the mixed complex in solution and in solid state is a result of the different experimental conditions.

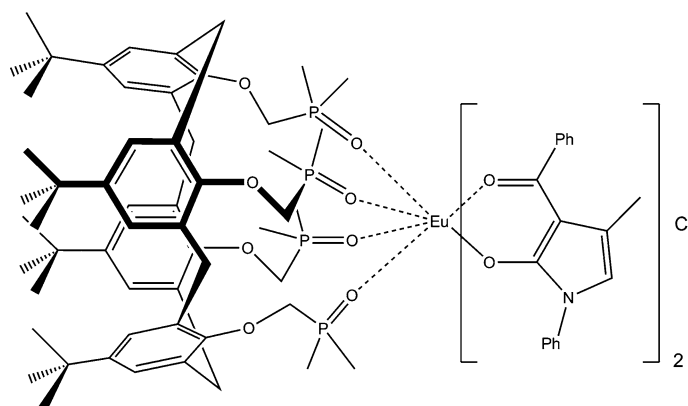


Figure 5. The ^1H NMR spectra of the $\text{EuP}_2\text{S}\text{Cl}$ complex in MeOH-d_6 at 300, 320, 335 and 338 K. The assignment of signals in spectrum at 338 K is done by running 2D COSY spectrum at the same temperature. The belonging of signal to S or P ligand is given in paranthesis.

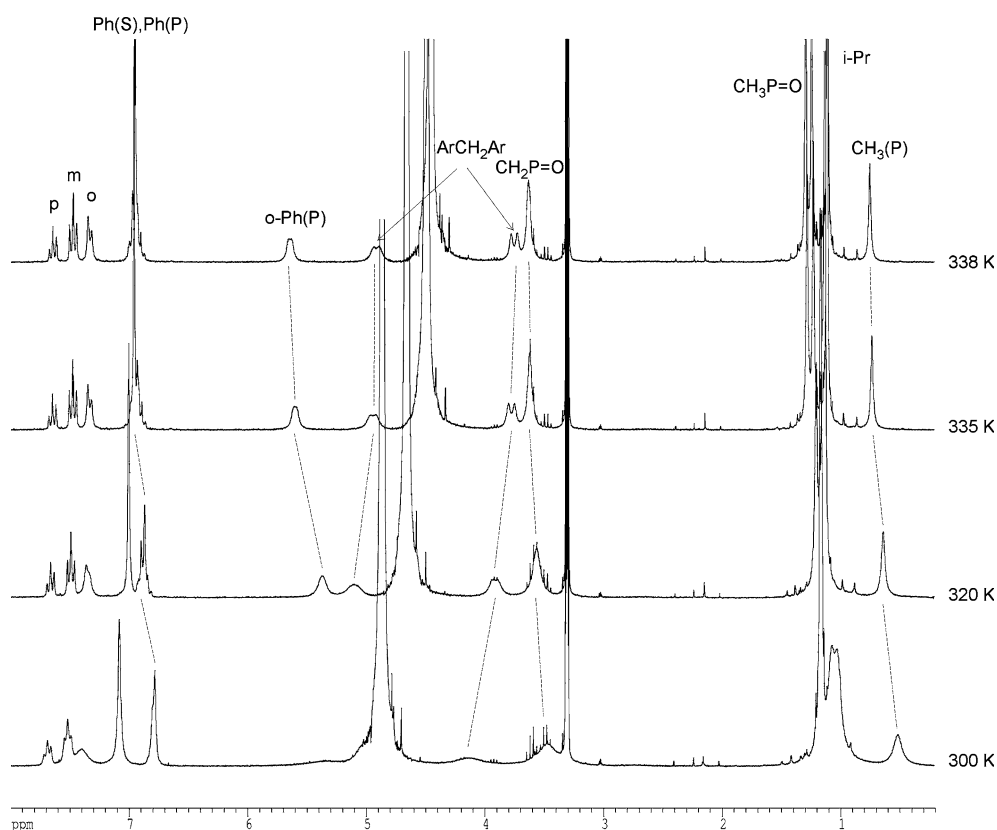


Figure 6. Proposed structure of the extracted complexes. During the solvent extraction of Eu^{3+} ion $n = 3$, while in the synthesized solid complex $n = 2$.

Table 2. ^1H NMR spectra of the free ligands and complex in CD_3OD at 338 K

Group	P (ppm)	S (ppm)	EuP_2S (ppm)
CH_3		1.09(s)	1.10(s)
CH_3P		1.52(d)	1.26(d)
CH_3	2.18(s)		0.74(s)
CH_2P		4.64(d)	3.62(d)
CH_2Ph		3.29(d), 4.75(d)	3.74(d), 4.91(d)
Ph(S)		6.88(s)	6.95(s)
Ph(P)		7.30–7.73(m)	5.65–7.67(m)

Acknowledgements

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References

- Z. Asfari, V. Bohmer, J. Harrowfield, and J. Vincens: *Calixarenes 2001*, Kluwer, Dordrecht (2001).
- R. Ludwig: *Fres. J. of Anal. Chem.* **376**, 103 (2000).
- R. Ludwig, K. Kunogi, N. Dung, and S. Tachimori: *Chem. Commun.* 1985 (1997).
- R. Ludwig, D. Lentz, and T. Nguyen: *Radiochim. Acta* **88**, 335 (2000).
- F. Arnaud-Neu, M.A. McKerver, and M.-J. Schwing-Weil: Metal-Ion Complexation by Narrow Rim Carbonyl Derivatives. In Z. Asfari, V. Böhmer, J. Harrowfield and J. Vincens (eds.), *Calixarenes 2001*, Kluwer, Dordrecht, (2001) p. 385.
- F. Arnaud-Neu, M.-J. Schwing-Weil, and J.F. Dozol: Calixarenes for Nuclear Waste Treatment. In Z. Asfari, V. Böhmer, J. Harrowfield and J. Vincens (eds.), *Calixarenes 2001*, Kluwer, Dordrecht (2001), pp. 642–662.
- F. Arnaud-Neu, S. Cremin, S. Harris, M.A. McKerver, M.J. Schwing-Weill, P. Schwinte, and A. Walker: *J. Chem. Soc., Dalton Trans.* 329 (1997).
- F. Arnaud-Neu, J.K. Brown, D. Byrne, D.J. Marra, M.A. McKerver, P.O. Hagan, M.J. Sewing-Weill, and Walker: *Chem. Eur. J.* **5**(1), 175 (1999).
- D. Roundhill and J. Shen: Phase Transfer Extraction of Heavy Metals. In Z. Asfari and Böhmer (eds.), *Calixarenes 2001*, Kluwer, Dordrecht (2001), pp. 407–420.
- L. Saulnier, S. Varbanov, R. Scopelliti, M. Elhabiri, and J.C.G. Bünzli: *J. Chem. Soc., Dalton Trans.* 3919 (1999).
- F. Ramirez, S. Varbanov, C. Cecile, G. Muller, N. Rouge, R. Scopelliti, and J. Bunzli: *J. Chem. Soc., Dalton Trans.* 4505 (2002).
- L. Kuznetsova, A. Mustafina, C. Podjatchev, E. Kazakova, A. Buzirilova, and M. Pudovik: *Russ. Coord. Chem.* **24**(8), 623 (1998).
- L. Kuznetsova, A. Mustafina, A. Ziganshina, E. Kazakova, and A. Konovalov: *J. Incl. Phenom.* **39**, 65 (2001).
- L. Kuznetsova, G. Pribylova, A. Mustafina, I. Tananaev, B. Myasoedov, and A. Konovalov: *Radiochemistry* **46**, 277 (2004).
- M. Kyrš, K. Svoboda, P. Lhotak, and J. Alexova: *J. of Radioanal. Nucl. Chem.* **254**, 455 (2002).
- M. Kyrš, K. Svoboda, P. Lhotak, and J. Alexova: *J. of Radioanal. Nucl. Chem.* **258**, 497 (2003).
- K. Shimojo and M. Goto: *Sep. Purif. Technol.* **44**, 175 (2005).
- I. Natatou, M. Burgard, Z. Asfari, and J. Vincens: *J. Incl. Phenom. Mol. Recogn. Chem.* **22**, 107 (1995).
- S.B. Savvin: *Arsenazo III*, Atomizdat, Moskva, (1966) p. 172 (in Russian).
- M. Atanassova and I. Dukov: *Separ. Purif. Technol.* **40**, 171 (2004).

21. Yu. Zolotov and N. Kuzmin: *Ekstraktsia acylpirazonomi*, Nauka, Moskva (1977) p. 14 (in Russian).
22. G.R. Choppin: *Separ. Sci. Technol.* **16**(9), 1113 (1981).
23. J.N. Mathur: *Solvent Extr. Ion Exch.* **8**(4, 5), 629 (1990).
24. J.N. Mathur: *Solvent Extr. Ion Exch.* **1**(2), 349 (1983).
25. M. Atanassova and I. Dukov: *Acta Chim. Slovenika* (2006) in press.
26. M. Atanassova and I. Dukov: *Separ. Purif. Technol.* **49**, 101 (2006).
27. I. Dukov and M. Atanassova: *Separ. Sci. Technol.* **39**, 227 (2004).