Journal of Inclusion Phenomena and Macrocyclic Chemistry **39:** 65–69, 2001.

The Synergistic Extraction of Lanthanide Ions by a Mixture of Calix[4]resorcinarene or its Dimethylamino-, Piperidyl- or Trimethylammoniummethylated Derivatives and 1,10-Phenanthroline in *n*-Heptanol

LUBOV S. KUZNETSOVA*, ASIYA R. MUSTAFINA, ALBINA YU. ZIGANSHINA, ELLA KH. KAZAKOVA and ALEXANDER I. KONOVALOV
Kazan Scientific Centre of the Russian Academy of Sciences, A.E. Arbuzov Institute of Organic and Physical Chemistry, Arbuzov Str. 8, Kazan 420088, Russia

(Received: 28 October 1999; in final form: 4 April 2000)

Key words: calix[4]resorcinarene, complexes, extraction, lanthanides

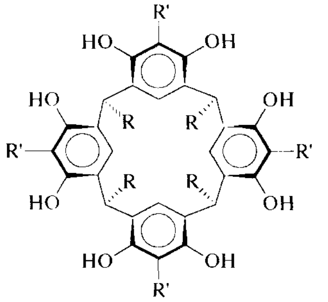
Abstract

The alkylaminomethylated calix[4]resorcinarene derivatives, modified by dimethylamino-, piperidyl- and trimethylammonium moieties, have been synthesised to investigate their extractability towards lanthanide ions and to compare with the extractability of calix[4]resorcinarene. Both calix[4]resorcinarene and its derivatives have been shown to synergistically affect lanthanide ion extraction from neutral aqueous solutions by 1,10-phenanthroline through outer-sphere interaction of lanthanide bis-phenanthrolinate cations with deprotonated forms of calix[4]resorcinarene. The derivatives with dimethylamino- and piperidylmethylated moieties are shown to be more effective extractants in comparison with the unsubstituted one.

Introduction

The similarity of the lanthanides complexing ability is the reason for further research on new extracting agents being selective in the lanthanide series. Most of the extractants, including calix[n]arenes, coordinate lanthanide ions through polycentre inner-sphere coordination. Functionalization of calix[n]arenes with carboxy or amide groups resulted in the growth of their extractability and selectivity in the lanthanide series [1–3]. Calix[4]resorcinarene's "rim" is too large for such encapsulation of the metal ion, hence their acting as "hosts" for bulky cations [4]. Functionalization of calix[4]resorcinarenes with amide or carbamoylphosphine oxide groups leads to the appearance of their extractability toward lanthanide ions [5, 6]. The present report shows that calix[4]resorcinarene's extractability can be also increased by the addition of bidentate nitrogen-containing heterocycles. So, the main goal of this work is to study the extraction of various lanthanides by nonsubstituted calix[4]resorcinarene and its alkylaminomethylated derivatives in the presence of 1,10-phenanthroline.

H_8L with $R = C_{11}H_{23}$ in the presence of 1,10-phenanthroline has been proved [7] to extract La(III) from water to *n*-heptanol media, while neither H_8L nor 1,10-phenanthroline alone extracts La(III) under the same concentration conditions. So, it is rather interesting to investigate whether the extraction extent depend on the lanthanide's atomic number and how the presence of $–N(CH_3)_2$, $–NC_5H_{10}$ and $–N(CH_3)_3^+$ groups on the "host's rim" affects the lanthanide's extraction.



H_8L: $R = C_{11}H_{23}$, $R' = H$
H_8X: $R = C_9H_{19}$, $R' = CH_2N(CH_3)_2$ **(I)**
$R = C_9H_{19}$, $R' = CH_2C_5H_{10}N$ **(II)**
H_8Y: $R = C_9H_{19}$, $R' = CH_2N^+(CH_3)_3I^-$

Experimental

The extraction of La(III) from water to *n*-heptanol has been carried out by H_8L, H_8X (**I**, **II**) and H_8Y. The compound H_8L was synthesised according to the procedure [8], the compounds H_8X(**I**, **II**) were synthesised as described in [9]. The synthesis of H_8Y: methyl iodide (0.075 mL) was added to the solution of tetra(dimethylaminomethyl)-calix[4]resorcinarene in 10 mL of DMF. The reaction mix-

---

[*] Author for correspondence. E-mail: lubov@iopc.kcn.ru

ture was stirred at 120 °C for 20 h. The resulting precipitate was separated, washed with cool methanol and dried. Brown crystals mp 151–153 °C; yield (80%), NMR ^1H (ppm) in $CDCl_3$, 8.54 (8H s, OH), 8.03 (4H s, CH aryl), 7.35 (H, DMF), 4.35 (4H, CH ring), 2.94, 2.8, 2.68 (50H m, CH_2N, CH_3N), 2.17 (3H s, CH_3I), 1.26 (64H m, CH_2 ring), 0.88 (12H t, CH_3 ring); found for $C_{80}H_{136}I_4N_4O_8{\cdot}CH_3I{\cdot}(CH_3)_2NCHO$: C, 47.23, H, 7.31, N 3.80; calc.: C, 47.56, H, 7.00, N, 3.26. The extraction of Pr, Ho, Yb and Lu was also investigated for both H_8L and H_8X(**I**).

The extraction procedure was as follows: 5 mL of a *n*-heptanol solution of H_8L or H_8X (4×10^{-4} mol·dm^{-3}) and phen (4×10^{-4} mol·dm^{-3}) were mixed in various quantities of KOH at constant stirring. Then an equal volume of aqueous $LnCl_3$ solution (4×10^{-4} mol·dm^{-3}) was added. The two-phase system was stirred for 60 minutes at 80 ± 0.5 °C. After phase separation, the concentration of the metal ion in the aqueous phase was monitored by the following procedure: the aqueous phase (0.2 mL) was placed in a 5-mL volumetric flask together with 0.6 mL of Xylenol Orange (0.001 mol·dm^{-3}) aqueous solution in 0.01 mol·dm^{-3} HCl. The pH of the solution was adjusted to 6.0 using CH_3COOH and NaOH (0.01 mol·dm^{-3} each) solutions [10]. The concentration of the metal ion in the aqueous phase was determined spectrophotometrically at $\lambda_{max} = 570$ nm using a Specord UV-VIS spectrometer. The error in extraction extent (E) determination is less than 5%. The acidity of the aqueous phase was measured by a pH-meter with an accuracy of 0.05 pH-unit. All pH-metric and spectrophotometric determinations were conducted at 25.0 ± 0.5 °C.

The extraction of $La(phen)_2]Cl_3$ [11] was carried out using a *n*-heptanol solution of H_8L (4×10^{-4} mol·dm^{-3}) with a concentration ratio $[La(phen)_2]Cl_3 : H_8L = 1 : 1$. The change of $[La(phen)_2]Cl_3$ concentration in the aqueous solution through extraction was determined according to the same procedure as for $LnCl_3$. The aqueous solutions were made from bidistilled water. The *n*-heptanol of commercial grade was purified by distillation in vacuum. Xylenol Orange, $LaCl_3{\cdot}7H_2O$, $Pr(NO_3){\cdot}6H_2O$, $HoCl_3{\cdot}6H_2O$, $YbCl_3{\cdot}6H_2O$ and $LuCl_3{\cdot}6H_2O$ were of analytical grade purity.

Results and discussion

The extraction by nonsubstituted calix[4]resorcinarene

Due to our previous data the extraction of lanthanium from aqueous solutions of $LaCl_3$ to *n*-heptanol solutions of H_8L and phen in a concentration ratio $LaCl_3 : H_8L : phen = 1 : 1 : 2$ occurs in the pH-range 5.5–7.5 (Table 1). The pH-values required were obtained by adding alkali to the organic phase, just as using aqueous acetate buffers with the same pH-values leads to the lack of extraction. The extraction of Pr, Ho, Yb and Lu occurs in the same pH-range ($pH_{50} \sim 6.0$–6.2). The whole extraction was obtained through adding alkali in a molar ratio $H_8L : KOH = 1 : 4$ (Table 1). The log q (q – extraction coefficient) dependence on pH (equation (1)) is linear with n = 3 for La and Pr (Figure 1a, b).

$$\beta = \log q - n\ \mathrm{pH} + \log([\mathrm{phen}]^2/[H_8L]), \qquad (1)$$

where β is a constant of extraction, n is the quantity of protons deprotonated. The log q/pH dependence for Lu and Yb is divided into two linear regions with n-values of 1 and 2 (Figure 1c,d). Thus, the extraction of Yb and Lu can be proposed to occur through two steps with dissociation of one and two protons. The graphic solution of equation (1) for La and Pr resulted in $n = 3$, possibly indicating that the extraction of La and Pr occurs in one step with dissociation of three protons from H_8L. The extraction scheme for all ions investigated may be written as Equation (2):

$$\begin{aligned} &Ln^{3+} + 2\mathrm{phen} + H_8L \\ &\quad = [Ln(\mathrm{phen})_2]^{3+}\,[H_5L]^{3-} + 3H^+. \end{aligned} \qquad (2)$$

The interaction of La(III) bis-phenanthrolinate with $[H_5L]^{3-}$ can be proposed to be the main driving force of the La(III) extraction. The extraction of La(III) bis-phenanthrolinate from aqueous solutions by a *n*-heptanol solution of H_8L at the same pH-conditions through adding alkali to the organic phase by the same quantities of alkali is confirmation of the $[Ln(phen)_2]^{3+}$ outer-sphere interaction with $[H_5L]^{3-}$.

The extraction by functionalized calix[4]resorcinarenes

The presence of dimethyl- and piperidyl moieties on the upper "rim" may be proposed to affect the lanthanide extraction through realization of additional coordination bonds with lanthanide ions. It is evident from the pH-metric data, that H_8X is protonated in neutral and acidic solutions, but dissociates in alkaline water-alcohol solutions [12]. According to their UV-spectra (the detectable shoulder at 350 nm) dialkylaminomethylated derivatives of calix[4]resorcinarene, H_8X, maintain deprotonated centres on the "rim" even in neutral water-isopropanol solutions due to intramolecular proton transfer from hydroxy- to dialkylamino-groups [12].

H_8X itself also does not extract lanthanides. The extraction by H_8X in the presence of 1,10-phenanthroline occurs under the same concentration conditions (molar ratio of $LaCl_3 : H_8X : phen = 1 : 1 : 2$) as H_8L but in more acidic media: pH = 5.0–7.0, $pH_{50} \sim 6.0$–6.5 (Table 1). Unlike H_8L, H_8X noticeably extracts without adding any alkali to the organic phase, the same extraction percentage by H_8X requires less alkali, than H_8L (Table 1). Moreover, the extraction takes place even through acidifying the organic phase by HCl. So, the whole suppression of extraction can be achieved by addition of 2–2.5 equivalents of HCl, just as only 1–1.5 equivalents of KOH is required to obtain nearly the whole extraction of lanthanides by H_8X(**I**) and 2 equivalents – by H_8X(**II**) (Tables 1, 2).

It is evident from the dependence of log q on pH (Figure 2), that Pr and Ho are extracted by H_8X(**I**) in two steps with deprotonation of one and two protons, while the two steps are indistinguishable in the case of La and Lu. The n-value obtained for La and Lu was 3, indicating their extraction

Table 1. The values of the extraction extent (E) of La, Pr, Ho, Yb, Lu from water (c = 4 × 10^{-4} mol·dm^{-3}) to *n*-heptanol solution of H_8L or H_8X(**I**) (c = 4 × 10^{-4} mol·dm^{-3}) and phen (c = 8 × 10^{-4} mol·dm^{-3}) for different quantities of KOH (HCl) added to the organic phase

“host”			La		Pr		Yb		Lu	
c/mol dm^{-3}	KOH (HCl)	m^a	pH$_{aq.phase}$	E (%)	pH$_{aq.phase}$	E (%)	pH$_{aq.phase}$	E (%)	pH$_{aq.phase}$	E (%)
H_8L	0	0	4.54	0	4.14	0	4.45	4.4	4.5	6.4
	$0.0004^{(KOH)}$	1	6.10	22.8	6.14	17.4	5.64	22.6	5.91	20.7
	$0.0006^{(KOH)}$	1.5	6.11	29.5	6.13	26.7	5.72	38.1	5.92	28.1
	$0.0008^{(KOH)}$	2	6.19	43.5	6.23	44.2	6.12	35.7	5.95	64.3
	$0.0012^{(KOH)}$	3	6.44	72.4	6.40	75.6	6.35	82.1	6.53	70.7
	$0.0016^{(KOH)}$	4	6.85	94.1	6.74	100	6.6	95.2	6.89	100
	$0.0018^{(KOH)}$	4.5	7.11	100	–	–	6.79	100	–	–
“host”			La		Pr		Ho		Lu	
c/mol dm^{-3}	KOH (HCl)	m^a	pH$_{aq.phase}$	E (%)	pH$_{aq.phase}$	E (%)	pH$_{aq.phase}$	E (%)	pH$_{aq.phase}$	E (%)
H_8X(**I**)	$0.0010^{(HCl)}$	2.5	4.55	0	–	–	–	–	4.19	0
	$0.0008^{(HCl)}$	2	4.88	1.2	3.99	0	4.29	0	5.63	8.6
	$0.0004^{(HCl)}$	1	6.39	25.0	4.88	10.2	5.33	20.3	6.05	24.3
	0	0	6.30	90.1	6.09	37.2	6.13	57.6	6.29	48.6
	$0.0002^{(KOH)}$	0.5	6.40	92.3	6.14	61.2	6.29	73.6	6.44	91.7
	$0.0004^{(KOH)}$	1	6.70	100	6.46	84.7	7.21	100	6.67	100
	$0.0008^{(KOH)}$	2			6.62	100				

[a] Number of KOH (HCl) equivalents with reference to concentration of H_8L or H_8X(**I**).

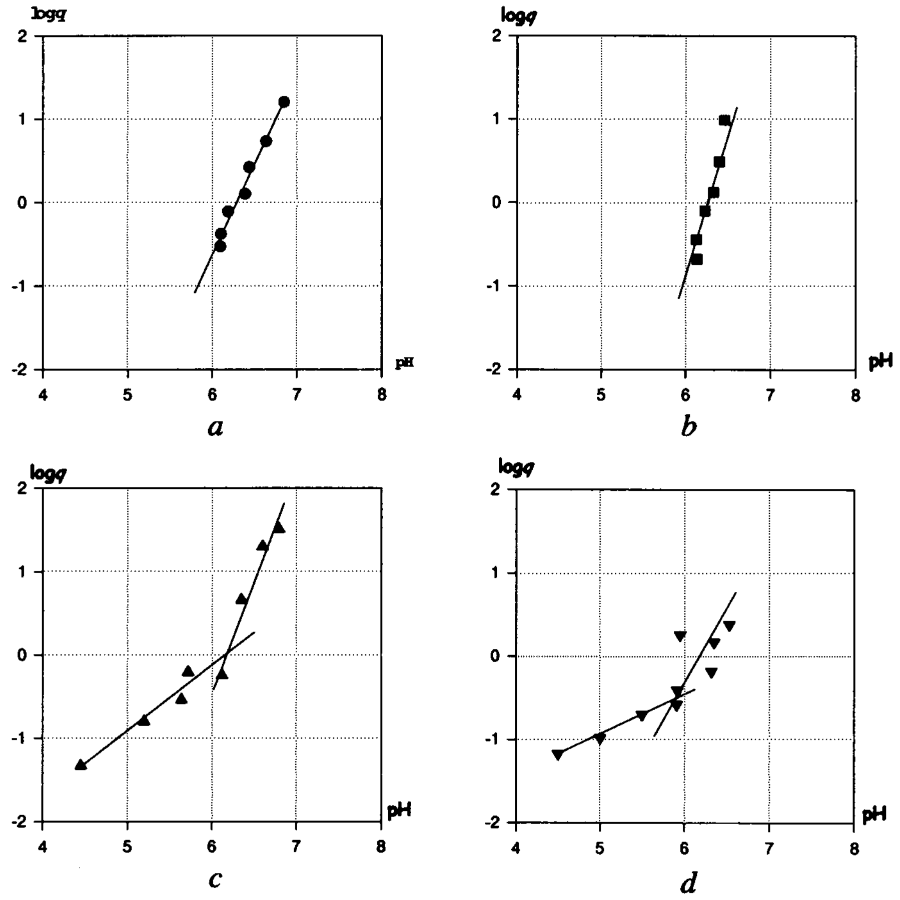


Figure 1. The dependence of log q on the pH of the aqueous phase for the extraction systems $LnCl_3$–H_8L-phen, Ln = La (a), Pr (b), Yb (c), Lu (d).

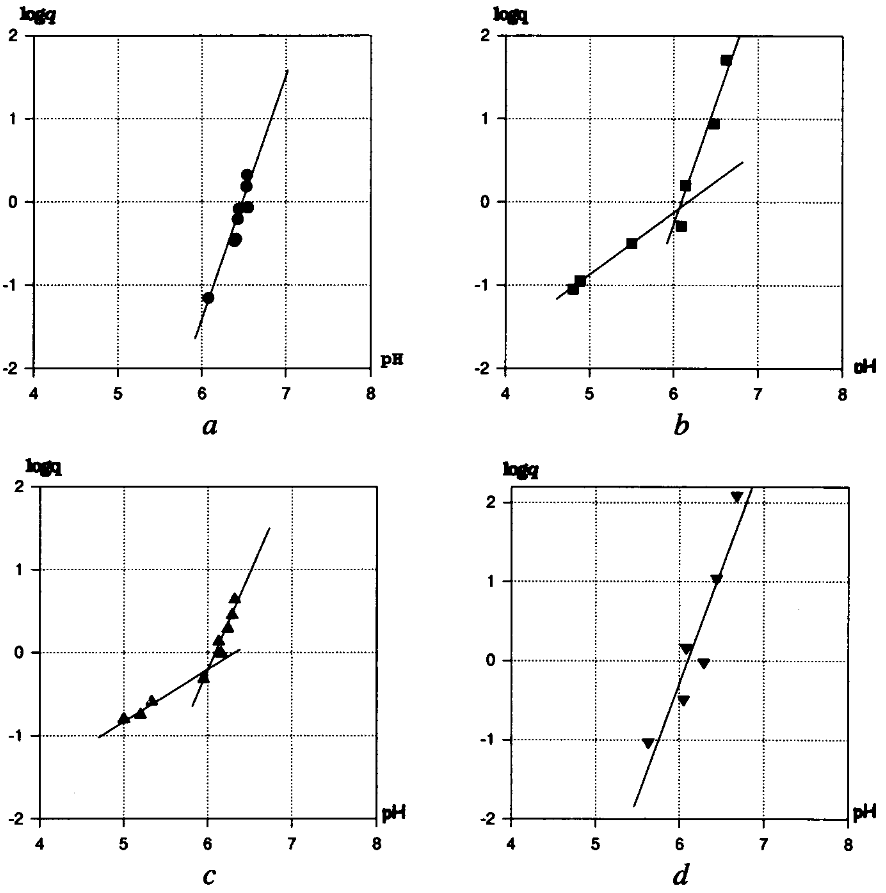


Figure 2. The dependence of log q on the pH of the aqueous phase for the extraction systems $LnCl_3$- H_8X(**I**)-phen, Ln = La (a), Pr (b), Ho (c), Lu (d).

proceeds with dissociation of three protons. The data presented in Table 1 show, that in spite of n being equal to 3 for both H_8L and H_8X(**I**) the latter extracts lanthanides in the monodeprotonated form. As the dimethylamino-groups are protonated in neutral and acidic media, H_8X(**I**) extracts lanthanides with dissociation of three protons from two dimethylamino- moieties and one from the hydroxy-group according to equilibrium (3):

$$Ln^{3+}+2phen + H_8X{\cdot}2H^+ = [Ln(phen)_2]^{3+}[H_7X]^- + 3H^+. \quad (3)$$

The *n*-value obtained from the dependence of logq on pH in the case of La extraction by H_8X(**II**) was 4 (Figure 3). So, H_8X(**II**) can be proposed to extract La(III) in the dianion form according to equilibrium (4):

$$Ln^{3+}+[2phen + H_8X{\cdot}2H^+ = [Ln(phen)_2]^{3+}[H_6X]^{2-} + 4H^+. \quad (4)$$

The extraction of La by H_8Y proceeds with deprotonation of four protons (n ≈ 4) (Figure 3b), but requires the same quantities of KOH as H_8L (Tables 1, 2). Thus, $–N(CH_3)_3^+$ groups being incapable of capturing the proton from hydroxy groups make the extraction by H_8Y very similar to those by H_8L. Consequently, the presence of $(CH_3)_2N$- and $C_5H_{10}N$-groups on the "host's rim" leads to H_8X being a more efficient extractant than H_8L and H_8Y. This effect is the result of additional negative charge on the "rim" due to intramolecular proton transfer from hydroxy to basic alkylamino- groups of the "host".

Table 2. The values of the extraction extent (E) of La^{3+} from water (c = 4 × 10^{-4} mol·dm^{-3}) to *n*-heptanol solution of H_8X(**II**) or H_8Y (c = 4 × 10^{-4} mol·dm^{-3}) and phen (c = 8 × 10^{-4} mol·dm^{-3}) for different concentrations of KOH (HCl) added to the organic phase

"host" *c*/mol dm^{-3}	KOH (HCl)	m[a]	$pH_{aqueous\ phase}$	E(%)
	0.0008$^{(HCl)}$	2	6.00	0
	0.0006$^{(HCl)}$	1.5	6.33	34.2
	0.0004$^{(HCl)}$	1	6.43	49.0
H_8X(**II**)	0	0	6.45	66.0
	0.0002$^{(KOH)}$	0.5	6.69	73.8
	0.0004$^{(KOH)}$	1	6.70	92.3
	0.0008$^{(KOH)}$	2	7.14	100
	0	0	4.30	0
H_8Y	0.0008$^{(KOH)}$	2	6.58	30.3
	0.0012$^{(KOH)}$	3	6.74	62.9
	0.0016$^{(KOH)}$	4	6.69	85.4
	0.0018$^{(KOH)}$	4.5	7.22	100

[a] Number of KOH (HCl) equivalents with reference to concentration of H_8X or H_8Y.

In summary, both H_8L, H_8X and H_8Y in the presence of 1,10-phenanthroline extract lanthanide ions from

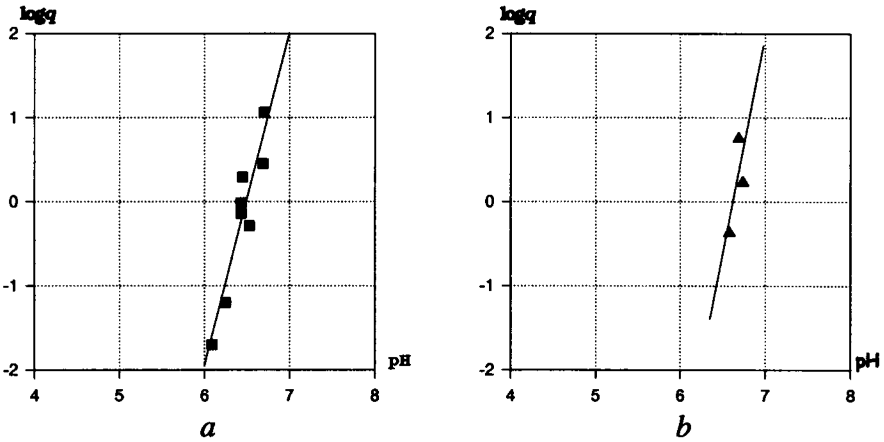


Figure 3. The dependence of log q on the pH of the aqueous phase for the extraction systems $LaCl_3$- H_8X(**II**)-phen (a), and $LaCl_3$- H_8Y-phen (b).

their chloride or nitrate aqueous solutions at pH = 5.0–7.5 through outer-sphere interaction of the lanthanide's bisphenanthrolinate cations with the negatively charged deprotonated "rim" of calix[4]resorcinarene. Unfortunately, H_8L and H_8X do not appear to be selective extractants with the lanthanide ions investigated. The comparison of H_8L, H_8X and H_8Y extractability makes it evident that the dimethylamino- and piperidyl moieties of H_8X do not take part in lanthanide coordination, but affect the lanthanide extraction through intramolecular proton transfer from hydroxy-to alkylamino- groups. Thus, calix[4]resorcinarene's affinity for bulky cations is the reason for its complexation with metal complexes which leads to its effective extractability towards metal ions.

Acknowledgement

This work was supported by the Russian Foundation for Basic Research (Grants Nos. 98-03-32760 and 98-03-33051).

References

1. N. Sabbatini, M. Guardigli, A. Mecati, V. Balzani, R. Ungaro, E. Ghidini, A. Casnati and A. Rochini: *J. Chem. Soc. Chem. Commun.* 878 (1990).
2. F. Arnaud-Neu: *Chem. Soc. Rev.* **23**, 235 (1994).
3. F. Arnaud-Neu, S. Cremin, S. Harris, M.A. McKervey, Weill M.-J. Schwing, P. Schwinte and A. Walker: *J. Chem. Soc., Dalton Trans.* 329 (1997).
4. H.-J. Schneider, D. Guttes and U. Schneider: *J. Am. Chem. Soc.* **110**, 6449 (1988).
5. J.R. Fransen and P.J. Dutton, *Can. J. Chem.* **73**, 2217 (1995).
6. H. Boerrigter, W. Verboom and D.N. Reinhoudt: *J. Org. Chem.* **62**, 7148 (1997).
7. L.S. Kuznetsova, A.R. Mustafina, S.N. Pod'yachev, E. Kh. Kazakova, A.R. Burilov and M.A. Pudovik: *Koord. Khim.* **24**, 623 (1998); *J. Coord. Chem.* (Engl. trans.) **24**, 582 (1998).
8. L.M. Tunstad, J.A. Tucker, E. Dalcanale, J. Weiser, J.A. Bryant, J.C. Sherman, R.C. Helgerson, C.B. Knobler and D.J. Cram: *J. Org. Chem.* **54**, 1305 (1989).
9. J. Matsuskita and T. Matsui: *Tetrahedron Lett.* **46**, 7433 (1993).
10. L.S. Serdyuk and V.S. Smirnaya: *Zh. Analit. Khim.* **19**, 451 (1964): *J. Anal. Chem. USSR* (Engl. trans.) **20**, 161 (1965).
11. D.M. Czakis-Sulikowska and J. Radwanska-Doszekalska: *Monatsh. Chem.* **118**, 1243 (1987).
12. Yu.E. Morozova, L.S. Kuznetsova, A.R. Mustafina, E.Kh. Kazakova, V.I. Morozov, A. Yu. Ziganshina and A.I. Konovalov: *J. Incl. Phenom.* **35**, 397 (1999).