Russian Chemical Bulletin, International Edition, Vol. 54, No. 1, pp. 159—164, January, 2005

N,*N*′-Bis(acylvinylated) diaza-18-crown-6 ether as a lanthanide-selective macrocyclic complex-forming agent

P. K. Sazonov,* **V. Yu. Stolyarenko, G. A. Artamkina, and I. P. Beletskaya**

Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 939 3618. E-mail: petr@elorg.chem.msu.ru; beletska@org.chem.msu.ru

Nucleophilic substitution in β-chlorovinyl phenyl ketone with diaza-18-crown-6 ether resulting in displacement of the chlorine atom afforded *N*,*N*′-bis(3-oxo-3-phenylpropen-1-yl)-1,10-diaza-18-crown-6 ether. The ability of the latter to form complexes with a number of metal cations was studied. However, the complex formation occurs only with the rare-earth cations Ln^{3+} and Th^{4+}. This fact was demonstrated by UV and ^1H NMR spectroscopy of solutions, confirmed by isolations of glassy phases of composition $L_3M_2(NO_3)_6 \cdot nH_2O$ (M = La, Y, $n \approx$ 4—7), and supported by IR spectra of these phases in KBr pellets. The formation of complexes with La^{3+} and Y^{3+} leads to an increase in fluorescence intensity of the ligand. The stability constants of the 1 : 1 complexes in methanol were evaluated by spectrophotometry. These constants increase with decreasing ionic radius of the cation.

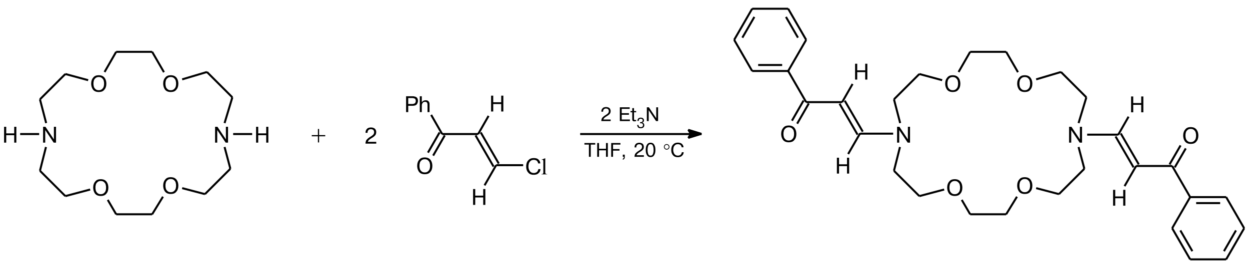
Key words: polyazamacrocycles, azacrown ethers, rare-earth complexes, lanthanides, NMR spectra, IR spectra, UV spectra.

Chemistry of polyazamacrocyclic compounds is being extensively studied because these compounds find use as complex-forming agents.[1—5] Cyclam, cyclen, and various azacrown ether derivatives attract interest due to their ability to coordinate metal cations by both the donor centers (O, N) of the macrocycle and the functional groups introduced at the nitrogen atom (pendant groups). In the case of azacrown ethers, this opens up virtually unlimited possibilities for varying the coordination properties of the macrocyclic ligand, which enables one to perform its "fine tuning," thus achieving selectivity with respect to a particular cation or a group of metal cations.[1,3—14] The chemical nature and conformational flexibility of pendant groups are of particular importance for selective binding of hard lanthanide(III) and actinide cations.[5,10,15—17] We prepared the bis-*N*-(β-acylvinyl) derivative of diaza-18-crown-6 ether by direct acylvinylation of the latter (S_NV-type reaction[18]). In the present study, we report on the ability of this derivative to selectively bind rare-earth (REM) cations.

N,*N*′-Bis(3-oxo-3-phenylpropen-1-yl)-1,10-diaza-18-crown-6 (**1**) was synthesized by the reaction of diaza-18-crown-6 ether with β-chlorovinyl phenyl ketone in the presence of triethylamine in THF at 20 °C. Since Et_3NHCl precipitated within a few seconds after the beginning of the reaction and the mixture slightly warmed up, the reaction was completed almost immediately (Scheme 1).

The UV-Vis absorption spectrum of crown ether **1** (Fig. 1) shows an intense maximum at 342 nm ($\varepsilon \approx 3.6 \cdot 10^4$). The changes in the position and intensity of the maximum were used as the primary criterion for com-

Scheme 1



1

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 156—160, January, 2005.

1066-5285/05/5401-0159

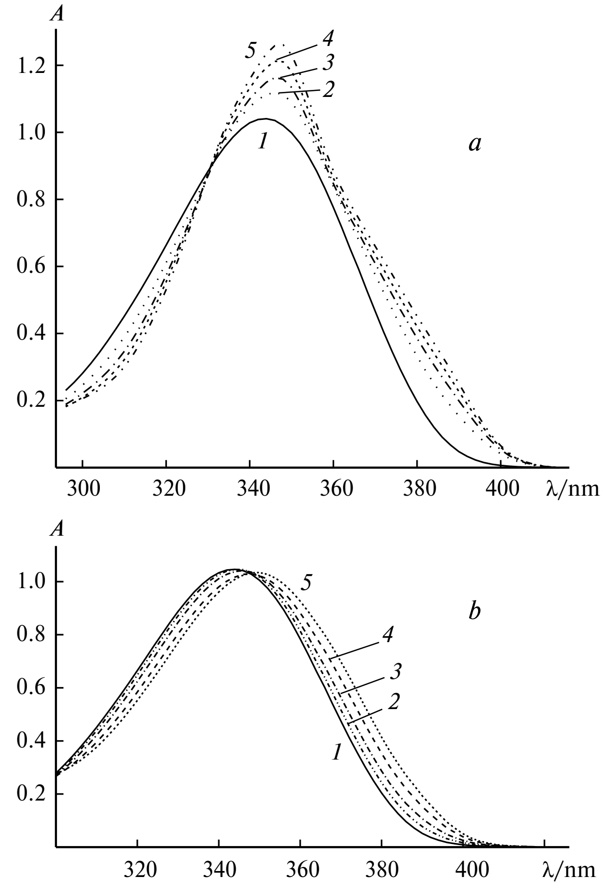
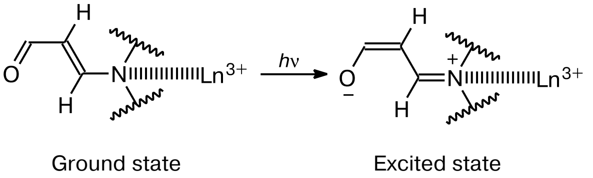


Fig. 1. UV-Vis absorption spectrum of crown ether **1** (a solution in methanol, l = 1 cm, $C = 3 \cdot 10^{-5}$ mol L^{-1}, curve *1*) and its changes in the presence of (*a*) $YbCl_3 \cdot 6H_2O$: $[Yb^{3+}] = 8 \cdot 10^{-4}$ (*2*), $2 \cdot 10^{-3}$ (*3*), $6 \cdot 10^{-3}$ (*4*), and $1.2 \cdot 10^{-2}$ mol L^{-1} (*5*); and (*b*) $Yb(NO_3)_3 \cdot 6H_2O$: $[Yb^{3+}] = 5 \cdot 10^{-4}$ (*2*), $1 \cdot 10^{-3}$ (*3*), $2 \cdot 10^{-3}$ (*4*), and $4 \cdot 10^{-3}$ mol L^{-1} (*5*).

plexation. In the presence of rare-earth salts (La^{III}, Nd^{III}, Y^{III}, and Yb^{III} nitrates and Yb^{III}, Lu^{III}, and Gd^{III} chlorides), a pronounced bathochromic shift of the absorption band was observed (see Fig. 1). In the presence of rare-earth chlorides (Fig. 1, *a*), the absorption band contour also changed and a shoulder at 380 nm appeared. By contrast, the addition of potassium, lithium, barium, zinc, cobalt(II), and indium(III) salts (~10^{-2} mol L^{-1}) caused no changes in the spectra. The appearance of the bathochromic shift was rather unexpected, because coordination of a cation in the cavity of azacrown ether is generally accompanied by a hypsochromic shift of the absorption band of the chromophoric group bound to the nitrogen atom,[19—24] which would be expected according to a simplified model of electron transition accompanied by charge transfer (Scheme 2).

Scheme 2

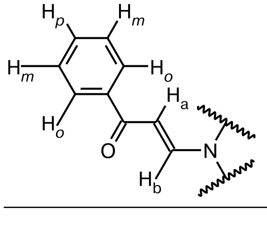


At a substantially higher concentration of the crown ether (c ~10^{-1} mol L^{-1}) and in the presence of an equimolar amount of rare-earth (La, Y) nitrate, the corresponding complex was isolated from a solution as a yellowish oil, which again dissolved upon the addition of one more equivalent of the rare-earth salt. After separation from the mother liquor and vacuum drying, the oil vitrified to form a glassy phase. The REM : crown ether ratio in the glassy phases was estimated by elemental analysis to be substantially smaller than unity. The composition of the yttrium "complex" rather closely corresponds to the $L_3Y_2(NO_3)_6 \cdot 7H_2O$ formula (L is crown ether **1**). The lanthanum content in the sample is somewhat higher due apparently to a smaller degree of hydration.

Complexation with the diamagnetic La^{3+} and Y^{3+} cations in solution for the metal : crown ether ratio of 2 : 1 ($C = 2 \cdot 10^{-2}$ mol L^{-1}) was studied by ^1H NMR spectroscopy. In the presence of an excess amount of KSCN, the ^1H NMR spectrum of crown ether **1** remained unchanged, whereas it is known[25,26] that complexation of disubstituted diaza-18-crown-6 ethers with the potassium cation is accompanied by noticeable shifts of the signals in the ^1H NMR spectra.

The character of changes observed in the ^1H NMR spectrum of crown ether **1** (Table 1) argues against the

Table 1. Influence of the $La(NO_3)_3 \cdot 6H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ additives (2 equiv.) on the chemical shifts of protons in the ^1H NMR spectrum (δ) of compound **1** ($C = 2 \cdot 10^{-2}$ mol L^{-1}, acetone-d$_6$, 20 °C)

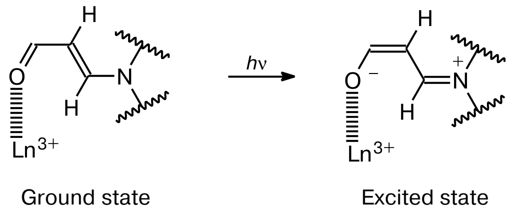


Additives	H_a	H_b	H_o	H_m	H_p	CH_2 groups of the macrocycle
Without additives	5.94	7.75	7.91	7.39	7.44	3.75, 3.65, 3.61
$La(NO_3)_3 \cdot 6H_2O$	6.39	8.31	8.09	7.42	7.52	3.45—3.81
	6.11	~8.35	7.88	7.23	7.41	
$Y(NO_3)_3 \cdot 6H_2O$	6.49	8.37	8.12	7.42	7.54	3.43—3.84
	6.18	~8.40	7.91	7.28	7.43	

symmetric coordination of the rare-earth cation in the cavity of the macrocycle but, nevertheless, it provides evidence for the occurrence of complexation. The changes in the spectrum reflect primarily the breaking of the symmetry of the crown ether, resulting in the nonequivalence of two PhC(O)CH=CH groups. The spectrum of the CH_2 groups of the macrocycle also becomes more complicated; however, the signals of the CH_2 groups are shifted only slightly (see Table 1). By contrast, the signals for the vinylic protons are shifted downfield by 0.15—0.6 ppm, the largest shifts being observed for the protons of the =CH—N fragment.

In our opinion, all the above-mentioned changes in the ^1H NMR spectrum are indicative of coordination of the rare-earth cation by the carbonyl groups of the ligand through the oxygen atoms. This gives an insight into the nature of the bathochromic shift of the absorption band in the UV-Vis spectrum observed upon complexation. The electron transition in compound **1** is accompanied by charge transfer. If coordination to the metal cation occurs through the oxygen atom, the excited state is stabilized to a larger extent, resulting in a decrease in the electron transition energy (Scheme 3).[27,28] This coordination mode of the rare-earth cations through the oxygen atom of the C=O group is additionally supported by a comparison of the IR spectra of the yttrium and lanthanum complexes with the spectrum of free crown ether **1**.

Scheme 3



The spectrum of free crown ether **1** shows two intense bands in the vibration region of the conjugated aminoenone (NCH=CHCO) system at 1640 and 1540 cm^{-1} (Fig. 2), which is in good agreement with the published data on the IR spectra of dialkylaminoenones (adopting the *s-cis* conformation),[29] where the bands at 1640 and 1540 cm^{-1} were assigned to vibrations of the conjugated C=O group and the enaminone CH=CH—N system, respectively. However, quantum-mechanical calculations of the vibrational spectrum* demonstrated that, in fact, these vibrations are strongly coupled and more likely can be characterized as ν_{as} (1640 cm^{-1}) and ν_s (1540 cm^{-1}) of the conjugated NCH=CHCO system. The much less intense narrow band at 1580 cm^{-1} is insensitive to complexation and, apparently, belongs to pulse vibrations of the aromatic ring.

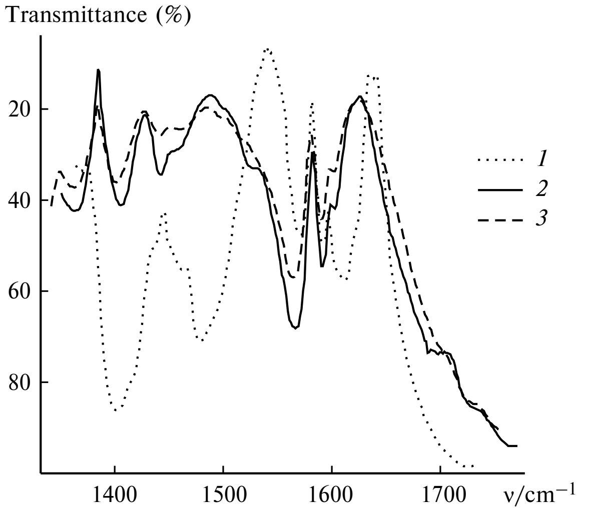


Fig. 2. IR spectra of crown ether **1** (*1*) and its complexes with lanthanum nitrate (*2*) and yttrium nitrate (*3*) (KBr).

As expected, the ν_{as} frequency in the IR spectra of the complexes decreases to 1620—1625 cm^{-1}, whereas the second band, ν_s, is unobservable against the background of δ_{HOH} vibrations of the coordinated water molecules and δ_{HCH} vibrations of the CH_2 groups of the macrocycle (1450—1490 cm^{-1}). This is indicative either of a strong (~50 cm^{-1} or even larger) shift of ν_s(NCH=CHC=O) or, which is more probable, of a substantial decrease in its intensity. The latter may be associated with disruption of conjugation in the CH=CHC=O system due to rotation about the =C—C= bond upon complexation. Disruption of conjugation should even increase ν(C=O) thus compensating for its decrease through coordination with a rare-earth cation. Apparently, the combined action of these two factors is responsible for a relatively small decrease in the ν_{as} frequency (by 20—25 cm^{-1}) in the spectra of the complexes.

The assumption that C=O groups play the key role in coordinating cations provides an insight into high selectivity of acylvinylated crown ether **1** with respect to rare-earth cations. The rare-earth cations are harder acids (in terms of hard and soft acids and bases) than transition metal cations and even alkaline-earth cations and should exhibit high affinity for hard donor centers, such as the C=O group. It is well known[30,31] that rare-earth metals can form stable complexes with carboxamides. Polydentate aminocarboxylate ligands, including those containing amide groups, are widely used for binding rare-earth metals.[5,15,16] It should be noted that the aminoenone fragment in crown ether **1** is a vinylog of the amide function.

Unfortunately, the role of the donor centers (O, N) of the macrocycle in coordination of cations remains an

---

* Calculations were carried out at the B3LYP/6-31G(d) level for the model *E*-Ph(CO)CH=CHNR$_2$ compounds.

open question. In this case, an approach based on analysis of conformationally sensitive vibrations (ν_{COC}, ν_{CNC}, *etc.*) in the IR spectra of complexes is inapplicable, because the assignments of the corresponding vibrations in the spectrum of free crown ether **1** are lacking. In this connection, let us mention the structure of the complex of the neodymium cation with bis-*N*,*N′*-phosphorylated diaza-18-crown-6 ether, in which (X-ray diffraction data) the cation is coordinated only by the oxygen atoms of two phosphoryl groups, whereas the donor N- and O-centers remain uncoordinated.[32]

The absorption bands in the IR spectra of the complexes are broadened compared to the corresponding bands in the spectrum of free crown ether **1**, which is, apparently, attributable to polymeric structures of the complexes.

The stability constants of the rare-earth complexes with crown ether **1** were determined spectrophotometrically. The stability constant of the only representative of the actinide group, *viz.*, of Th^{IV} nitrate, which simulates, to some extent, the behavior of Pu^{IV}, was also measured. To estimate the group selectivity of crown ether **1** with respect to rare-earth metals, we carried out analogous measurements for barium perchlorate, because it is known[3,4,9] than many azacrown ethers containing pendant groups at the nitrogen atom form the most stable complexes with the Ba^{2+} cation. Although the spectra did not cease to change even at the maximum concentration of the rare-earth salt (~10^{-2} mol L^{-1}) and the well-defined isobestic points were absent, which is additional evidence for the complexity of equilibria occurring in solution, the results of measurements show no significant deviations ($r > 0.99$) from a linear dependence in terms of a simplified model (Eq. (1))[20] of the formation of equimolar complexes (L : M = 1 : 1).

$$\frac{A_L}{A_L - A_i} = \frac{\varepsilon_L}{\varepsilon_L - \varepsilon_{ML}}\left(\frac{1}{\beta[M]_i} + 1\right), \qquad (1)$$

where A_L is the absorbance of the starting solution of the ligand, A_i is the absorbance of the *i*-th solution containing a metal salt at the concentration $[M]_i$, and β is the concentration stability constant of the complex.

In any case, the calculated stability constants β (Table 2) with dimensionality of inverse concentration, are convenient parameters for comparing with the published data on other macrocycles and podands, which, as a rule, form 1 : 1 complexes.

Although stability of the complexes under consideration is low, it is comparable, for example, with that of complexes of many known chromoionophores based on *N*-substituted monoazacrown ethers with alkali and alkaline-earth metals.[19,21,23,24] The stability constant of the complexes increases as the ionic radius of the cation decreases in going from La^{3+} (r_{eff} = 1.22 Å) to Yb^{3+} (r_{eff} = 1.04 Å) and then to Th^{4+} (r_{eff} = 0.98 Å). The bathochromic shift of the absorption band increases in the same series.

Table 2. Stability constants (β/L mol^{-1}) of the complexes of compound **1** with the Ln^{3+}, Th^{4+}, and Ba^{2+} cations in methanol at 20 °C

Metal salt[a]	logβ[b]
$Th(NO_3)_4$	4.0
$YbCl_3$	3.0
$Nd(NO_3)_3$	2.6
$La(NO_3)_3$	2.2
$Ba(ClO_4)_2$	≤0

[a] Rare-earth salts were used as hexahydrates.

[b] The values of logβ were calculated by averaging the results of processing of the experimental data according to Eq. (1) at several wavelengths in a range of 365—390 nm. The 95% confidence intervals for logβ are no larger than ±0.2 log units.

The complex with the Ba^{2+} cation is almost nonexistant: a very weak bathochromic shift of the absorption band of crown ether **1** was observed only at very high concentrations of barium perchlorate (0.1—1 mol L^{-1}).

In conclusion, it should be noted that crown ether **1** not only exhibits the properties of a chromoionophore selective with respect to rare-earth cations but also has weak fluorescence (λ_{max} = 425 nm), the intensity of which increases several times in the presence of lanthanum or yttrium salts (Fig. 3).

Due to high electrophilicity of β-chlorovinyl ketones, the CH=CHC(O)R fragment can easily be introduced into various macrocyclic and acyclic compounds containing N- or O-nucleophilic centers. Hence, crown ether **1** can be considered as a prototype for the promising class of chromo- and fluoroionophores selective with respect to hard lanthanide and actinide cations.

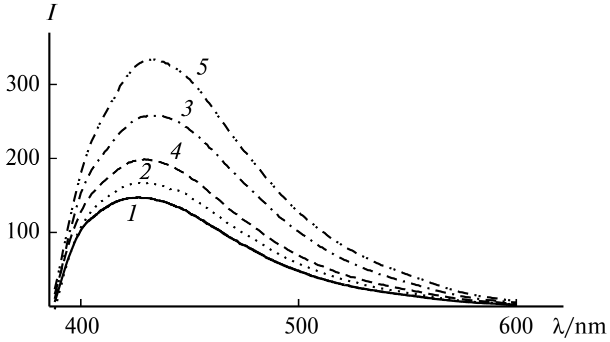


Fig. 3. Fluorescence spectra of crown ether **1** ($C = 1 \cdot 10^{-5}$ mol L^{-1}, λ_{exc} = 344 nm, methanol, 20 °C) without additives (*1*) and in the presence of $Y(NO_3)_3$ (*2*, *3*) and $La(NO_3)_3$ (*4*, *5*) at concentrations of $6 \cdot 10^{-4}$ (*2*, *4*) and $6 \cdot 10^{-3}$ mol L^{-1} (*3*, *5*).

Experimental

Diaza-18-crown-6 ether* was additionally purified by vacuum sublimation (10^{-2} Torr). β-Chlorovinyl phenyl ketone was synthesized by Kondakov's reaction.[33] Rare-earth nitrates and chlorides were used as hexahydrates.

The ^{1}H NMR spectra (400 MHz) were recorded on a Varian VXR-400 spectrometer. The IR spectra were measured on UR-20 and Thermo Nicolet IR-200 spectrophotometers in KBr pellets. The UV-Vis absorption spectra were recorded on a Hewlett—Packard-8452A spectrophotometer in methanol, in which salts of various metals are readily soluble. The fluorescence spectra were measured in methanol on a Shimadzu RF-5301PC spectrofluorometer.

***N,N´*-Bis(3-oxo-3-phenylpropen-1-yl)-1,10-diaza-18-crown-6 ether (1).** Triethylamine (101 mg, 1 mmol) was added to a solution of diaza-18-crown-6 ether (131 mg, 0.50 mmol) in THF (2 mL) and then a solution of β-chlorovinyl phenyl ketone (267 mg, 1 mmol) in THF (0.5 mL) was added dropwise for 5 min. The reaction solution was filtered off from the triethylammonium chloride precipitate, the precipitate was washed with benzene, the filtrate was evaporated, and the residue was chromatographed on a column with silica gel (Merck, 40/63) using a mixture of benzene, acetone, and light petroleum (5 : 3 : 1) as the eluent. The yield was 80%. Compound **1** was additionally purified by precipitation from a benzene solution with light petroleum. M.p. 117—119 °C. Found (%): C, 68.54; H, 7.36; N, 5.41. $C_{30}H_{38}N_2O_6$. Calculated (%): C, 68.94; H, 7.33; N, 5.36. The ^{1}H NMR spectroscopic data are given in Table 1. The IR spectrum is shown in Fig. 2.

Complexes of crown ether 1 with rare-earth nitrates were prepared by the addition of a solution of rare-earth nitrate hexahydrate (0.06 mmol) in methanol (0.2 mL) to a solution of crown ether **1** (30 mg, 0.057 mmol) in acetone (0.5 mL). After several minutes, the yellow oil that formed was separated by decantation and dried *in vacuo* (10^{-2} Torr) to prepare a yellowish glassy substance.

Complex with lanthanum(III) nitrate. Found (%): C, 47.13; H, 5.62; N, 7.37; La, 13.07. $C_{90}H_{122}La_2N_{12}O_{40}$ ($L_3La_2(NO_3)_6 \cdot 4H_2O$). Calculated (%): C, 47.21; H, 5.37; N, 7.34; La, 12.13.

Complex with yttrium(III) nitrate. Found (%): C, 48.20; H, 5.83; N, 7.90; Y, 7.96. $C_{90}H_{128}N_{12}O_{43}Y_2$ ($L_3Y_2(NO_3)_6 \cdot 7H_2O$). Calculated (%): C, 48.18; H, 5.75; N, 7.49; Y, 7.92. The IR spectra of the complexes are shown in Fig. 2.

Determination of the stability constants of complexes of crown ether 1 with metal cations in methanol was performed in a series of spectrophotometric experiments, in which the concentration of a metal salt was gradually increased, while the concentration of the crown ether was kept constant. Working solutions were prepared as follows: a solution (3 g) of crown ether **1** ($5.7 \cdot 10^{-5}$ mol L^{-1}) and a weighed sample of the corresponding metal salt were placed in a 10-mL measuring flask and methanol was added to the mark. In all experiments, an excess amount (5—10^5-fold) of the metal salt was used. Therefore, it can be assumed that $[M]_{total} \approx [M]_{free}$ ($[M]_{total}$ is the total concentration of the metal, and $[M]_{free}$ is the concentration of the metal, which is not involved in the complex with crown ether), which is a necessary condition for experimental data processing by Eq. (1). Calculations were carried out with the use of the data obtained in a wavelength range of 365—390 nm, where rather large, both relative and absolute, changes in the absorbance are observed upon complexation.

We thank B. N. Tarasevich (Department of Chemistry, M. V. Lomonosov Moscow State University) and I. S. Ivanova (N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences) for help in recording IR spectra and helpful discussion. We also acknowledge E. M. Rekharskaya (Department of Chemistry, M. V. Lomonosov Moscow State University) for measuring fluorescence spectra.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-33331) and the Foundation of the President of the Russian Federation (Program for the Support of Leading Scientific Schools, Grant NSh-1611.2003.03).

References

1. G. W. Gokel, W. M. Leevy, and M. E. Weber, *Chem. Rev.*, 2004, **104**, 2723.
2. J.-M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives,* VCH, Weinheim, 1995.
3. R. M. Izatt, K. Pawlak, and J. S. Bradshaw, *Chem. Rev.*, 1991, **91**, 1721.
4. R. M. Izatt, K. Pawlak, J. S. Bradshaw, and R. L. Bruening, *Chem. Rev.*, 1995, **95**, 2529.
5. V. Alexander, *Chem. Rev.*, 1995, **95**, 273.
6. R. D. Hancock and A. E. Martell, *Chem. Rev.*, 1989, **89**, 1875.
7. C.-T. Chen and W.-P. Huang, *J. Am. Chem. Soc.*, 2002, **124**, 6246.
8. T. Novak, P. Bako, T. Imre, and G. Keglevich, *J. Inclusion Phenom. Macrocycl. Chem.*, 2000, **38**, 435.
9. X. X. Zhang, A. V. Bordunov, J. S. Bradshaw, N. K. Dalley, X. L. Kou, and R. M. Izatt, *J. Am. Chem. Soc.*, 1995, **117**, 11507.
10. C. Platas, F. Avecilla, A. De Blas, T. Rodriguez-Blas, R. Bastida, A. Macias, A. Rodriguez, and H. Adams, *J. Chem. Soc., Dalton Trans.*, 2001, 1699.
11. E. Yamamoto, K. Kubo, and A. Mori, *Heterocycles*, 2002, **56**, 305.
12. A. Thaler, R. Bergter, T. Ossowski, B. G. Cox, and H. Schneider, *Inorg. Chim. Acta*, 1999, **285**, 1.
13. H. Tsukube, J. I. Uenishi, H. Higaki, K. I. Kikkawa, T. Tanaka, S. Wakabayashi, and S. Oae, *J. Org. Chem.*, 1993, **58**, 4389.
14. E. Sonveaux, *Tetrahedron*, 1984, **40**, 793.
15. M. Meyer, V. Dahaoui-Ginderey, C. Lecomte, and R. Guilard, *Coordination Chemistry Reviews*, 1998, **178—180**, 1313.
16. G. R. Choppin and K. M. Schaab, *Inorg. Chim. Acta*, 1996, **252**, 299.
17. P. Caravan, J. J. Ellison, T. J. Mcmurry, and R. B. Lauffer, *Chem. Rev.*, 1999, **99**, 2293.

---

* Diaza-18-crown-6 ether was kindly supplied by Yu. G. Gorbunova (N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences).

18. Z. Rappoport, *Rec. Trav. Chim.*, 1985, **104**, 309.
19. Yu. V. Fedorov, O. A. Fedorova, S. P. Gromov, M. V. Bobrovskii, E. N. Andryukhina, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 727 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 789].
20. J. Bourson and B. Valeur, *J. Phys. Org. Chem.*, 1989, **93**, 3871.
21. K. Rurack, J. L. Bricks, G. Reck, R. Radeglia, and U. Resch-Genger, *J. Phys. Chem. A,* 2000, **104**, 3087.
22. I. K. Lednev, T.-Q. Ye, R. E. Hester, and J. N. Moore, *J. Phys. Chem.*, 1997, **101**, 4966.
23. L. Antonov, M. Vladimirova, E. Stanoeva, W. M. F. Fabian, L. Ballester, and M. Mitewa, *J. Inclusion Phenom. Macrocycl. Chem.*, 2001, **40**, 23.
24. N. Mateeva, L. Antonov, M. Mitewa, and S. Miteva, *Talanta*, 1996, **43**, 275.
25. A. J. Pearson and W. J. Xiao, *J. Org. Chem.*, 2003, **68**, 5369.
26. A. V. Bordunov, J. S. Bradshaw, X. X. Zhang, N. K. Dalley, X. L. Kou, and R. M. Izatt, *Inorg. Chem.*, 1996, **35**, 7229.
27. J. Bourson, J. Pouget, and B. Valeur, *J. Phys. Chem.*, 1993, **97**, 4552.
28. J. S. Kim, O. J. Shon, S. H. Yang, J. Y. Kim, and M. J. Kim, *J. Org. Chem.*, 2002, **67**, 6514.
29. J. Dabrowski and K. Kamienska-Trela, *Spectrochim. Acta*, 1966, **22**, 211.
30. H. A. Alvarez, J. R. Matos, P. C. Isolani, G. Vicentini, E. E. Castellano, and J. Zukerman-Schpector, *J. Coord. Chem.*, 1998, **43**, 349.
31. K. L. Nash, *Solvent Extr. Ion Exch.*, 1993, **11**, 729.
32. L. Kh. Minacheva, I. S. Ivanova, I. K. Kireeva, V. E. Baulin, V. G. Sakharova, A. Yu. Tsivadze, and V. S. Sergienko, *Zh. Neorg. Khim.,* 2000, **45**, 346 [*Russ. J. Inorg. Chem.,* 2000, **45** (Engl. Transl.)].
33. N. K. Kochetkov, A. Yu. Khorlin, and M. Yu. Karpeiskii, *Zh. Obshch. Khim.*, 1956, **26**, 595 [*J. Gen. Chem. USSR,* 1956, **26** (Engl. Transl.)].

Received September 14, 2004;
in revised form December 29, 2004