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Coordination Compounds of Divalent Lanthanides with Crown Ethers

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Abstract

New complexes $LnI_2 \cdot$18-crown-6 (Ln–Sm, Tm, Dy, Nd) and $LnJ_2 \cdot$dibenzo-18-crown-6 (Ln–Sm, Tm) were synthesized using the solutions of LnI_2 in THF. The compounds obtained oxidize quickly in air, but are relatively stable in an inert atmosphere. The Tm^{2+} complex is decomposed by light. The compounds obtained are poorly soluble in THF, the Sm^{2+} and Tm^{2+} compounds are soluble in CH_3CN, forming solutions with a period of half oxidation of 170 h and 6 min, respectively. Iodide ions of the complexes can be substituted for Cl^- during treatment of the compounds by solution of LiCl in THF. The reflection spectra of the compounds synthesized are similar to the absorption spectra of Ln^{2+} in THF, although a shift of bands towards the short wave region is observed.

The study of the Ln^{2+} oxidation kinetics in H_2O, CH_3CN, THF in the presence of crown ethers has shown that their stability is influenced not only by the type of solvent, relative solubility and stability of complexes Ln^{2+} and Ln^{3+}, but also by phenyl groups, and by decreasing stability of Dy^{2+} and Nd^{2+}.

Introduction

Stability constants of the divalent lanthanide (Yb, Sm) complexes with crown ethers in propylene carbonate are 10^3–10^4 times higher than the constants of corresponding trivalent ions, as shown by competitive potentiometric methods [1]. The Ln^{2+} complexes of stoichiometry 1:1, 1:2 and 1:3 were present in solution, depending upon the dimensions of the internal cavity of crown ethers [1, 2]. Taking into account the higher constants of Ln^{2+} complexations with crown ethers and proceeding from analogous properties of divalent lanthanides (Ln^{2+}) and alkali earth elements, for which the complexes with crown ethers have been known, we isolated compounds of TmI_2 and SmI_2 with crown ethers in tetrahydrofurane (THF) as solvent [3]. The composition of the complexes corresponds to $LnI_2 \cdot$18-crown-6- and $LnI_2 \cdot$dibenzo-18-crown-6. Bünzli *et al* obtained the complexes of Sm^{2+} and Eu^{2+} with 18-crown-6 using methanol and THF as solvents [4]. Although the synthesis and investigation of this compound are difficult, some physico-chemical properties have been studied.

We did not find any information on other complexes of Ln^{2+} with polyethers.

The aim of our work is to investigate the possibility of obtaining the Dy^{2+} and Nd^{2+} complexes with crown ethers and to study some of their properties, both in solutions and in the solid state.

Experimental

Diiodides of Sm, Tm, Dy and Nd were prepared by interaction of corresponding triiodides and metal at 970–1170 K in a sealed Ta crucible in the presence of argon.

THF was purified from peroxides and water by KOH and further distillation over metallic potassium. The resulting solvent was preserved over $LiAlH_4$. Directly before experiments the THF was distilled under new $LiAlH_4$.

Crown ethers were purified from water and oxygen by leaving under vacuum at 300 K for 5–6 h (18-crown-6) or in argon at 390 K during 3–4 h (dibenzo-18-crown-6). Addition of 3–5 mg of fine liquid alloy of potassium with sodium leads to the disappearance of traces of oxidizers in solutions of crown ethers in THF.

Absorption spectra of Ln^{2+} solutions were recorded on an EPS-3T spectrometer in stopped quartz cells of d = 0.01 cm. Reflection spectra were measured on the Specord M40 spectrometer using sealed quartz cells.

In THF LnI_2 dissolves at about 0.04–0.08 mol/l. The solubility of 18-crown-6 in THF exceeds 0.5 mol/l; dibenzo-18-crown-6 dissolves less (~0.01 mol/l).

A quantitative precipitation of Ln^{2+} takes place on mixing crown ethers and LnI_2 solutions in THF at a Ln:crown ratio more than 1:1. This results in a disappearance of colours characteristic for THF

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TABLE I. Colour of Coordination Compounds of Halides of Divalent Lanthanides with Crown Ethers.

Ln	Solution of LnI_2 in THF	$LnI_2 \cdot$18-crown-6	$LnI_2 \cdot$dibenzo-18-crown-6	$LnCl_2 \cdot$18-crown-6
Sm^{2+}	blue–green	ultramarine blue	ultramarine blue	violet
Tm^{2+}	emerald–green	blue–green	blue–green	crimson
Dy^{2+}	green-brown	green	dark–green	–
Nd^{2+}	dark red–violet	lilac–violet	–	–

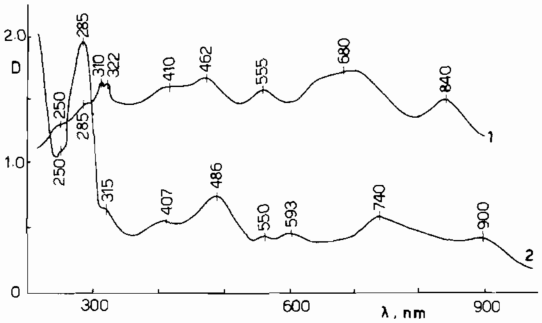

Fig. 1. Reflection spectrum of $DyI_2 \cdot$18-crown-6; (2) absorption spectrum of DyI_2 in THF.

solutions of Ln^{2+}, and formation of coloured precipitates of the complexes (Table I). The composition of resulting compounds was determined by decreasing the quantity of crown ether and Ln in solution after the precipitation of complexes, as well as by the analysis of compounds dried under argon. The Ln^{2+} in the complexes obtained was fixed by titration of the J_2 excess left after reaction of the THF standard solution of iodine, as well as the volume of hydrogen evolved during interaction of the sample with water. The total quantity of Ln was determined by the reverse complexonometric titration of the same aliquot of solution.

Halide ions were titrated by Folgard's method. It was established that the 1:1 complex was formed when the initial ratio of Ln:crown was from 1:1 to 1:4.

Results and Discussion

Since dibenzo-18-crown-6 contains phenyl groups it has been supposed that this polyether will be destroyed at oxidation potentials of Ln^{2+}, as sodium tetraphenyl borate is reduced at potentials less −2.3 V [5]. At Nd^{2+} potential dibenzo-18-crown-6 is destroyed with the formation of brown solutions whose absorption spectra have no bands characteristic for Nd^{2+} [6]. The partial destruction of this polyether takes place at Dy^{2+} potential. This is confirmed by a difference of colours of $DyI_2 \cdot$18-crown-6 and $DyI_2 \cdot$dibenzo-18-crown-6 (Sm^{2+} and Tm^{2+} complexes with both ethers have the same colours). Because of the low solubility of dibenzo-18-crown-6 in THF and its instability it is simpler to deal with 18-crown-6.

Since Dy^{2+} and Nd^{2+} have periods of half oxidation in THF equal to 0.55 and 0.15 h respectively, it is impossible to prepare pure complexes $LnI_2 \cdot$18-crown-6 for them because Ln^{3+} forms $LnI_3 \cdot$18-crown-6 under conditions of synthesis. The content of the divalent form of lanthanide in $DyI_2 \cdot$18-crown-6 was about 40% and in $NdI_2 \cdot$18-crown-6 about 20%.

The pure complexes may be obtained for Sm^{2+}, Tm^{2+} and other lanthanides having higher oxidation potentials, because their solutions in THF are practically stable [6]. However, initial LnI_2 should not contain LnI_3, and the THF and the crown ether should be carefully purified from traces of oxygen.

Since radical-containing products can be formed at low oxidation potentials, the only reliable method for identification of the oxidation state of lanthanide is spectrometry. We recorded reflection spectra of the complexes. The reflection spectrum of DyI_2-18-crown-6 is given in Fig. 1, and the absorption spectrum of DyI_2 in THF is given here for comparison. The reflection spectrum corresponds to the divalent species of the element, although displacement of the bands takes place.

The Ln^{2+} complexes with crown ethers dissolve in water, ethanol and acetonitrile with oxidation, and they have low solubilities in THF. They are destroyed by air and become discoloured. Tm^{2+} compounds are relatively stable in darkness under argon, but are quickly oxidized by light. The Dy^{2+} complex has no such property, although its oxidation potential is lower than that of Tm^{2+}.

It was of interest to study the possibility of obtaining the corresponding chloride complexes of Ln^{2+}. However, it was not possible to prepare these compounds in the way described above, as $LnCl_2$ is practically insoluble in THF. If the precipitation of Ln^{2+} from the LnI_2 solution contained LiCl, then the resulting complexes have other colours than the iodide compounds. For example, there is a crimson–red colour for Tm^{2+} and violet for Sm^{2+} (Table I).

This fact demonstrates that substitution of iodide ions for chloride ions takes place. The substitution of the iodide ions for chloride also takes place at processing of $LnI_2 \cdot$18-crown-6 by the THF solution of LiCl. The reflection spectrum of $SmCl_2 \cdot$18-crown-6 is given in Fig. 2, compared with the absorption spectrum of $SmI_2 \cdot$18-crown-6 in CH_3CN. Both spectra are in a good agreement with each other. The chloride complexes are likely to be more stable.

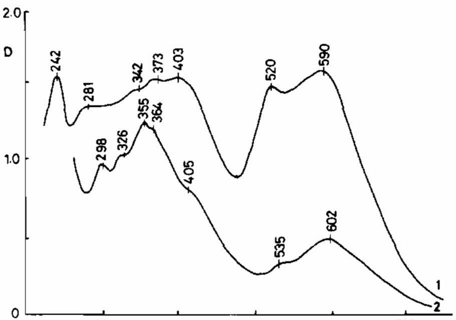

Fig. 2. Reflection spectrum of $SmCl_2 \cdot$18-crown-6; (2) absorption spectrum of $SmI_2 \cdot$18-crown-6 in acetonitrile.

The study of the influence of the crown ethers on the Ln^{2+} stability in solutions was of special interest. As was mentioned above, in propylene carbonate Ln^{2+} forms with crown ethers complexes that are more stable than the Ln^{3+} complexes.

As was reported, an addition of 18-crown-6 to a methanolic solution of $LnCl_3$ increases the yield of photochemical production of Eu^{2+} and Sm^{2+} [7]. However, Bünzli and Wessner have shown that the addition of 18-crown-6 to solutions of $EuCl_2$ in methanol catalyzes the oxidation of Eu^{2+} [4]. Such contradictory results require further investigation of Ln^{2+} properties in solutions.

By spectrophotometry we studied the Ln^{2+} stabilization in water, acetonitrile and THF in the presence of 0.01–0.1 mol/l of 18-crown-6. Figure 3 shows the absorption spectrum of Sm^{2+} in water in the presence of crown ether. The shape of the spectrum is a little different from that in pure solvent [6]. The oxidation reaction of Sm^{2+} in the presence of crown ether is first order and its rate constant is equal to 1.82×10^{-4} s^{-1} (the period of half oxidation, $t_{1/2}$, is 1.05 h), that is 3 times less than without ether (6.0×10^{-4} s^{-1} and 0.32 h, correspondingly). Thus, crown ethers promote the stabilization of Sm^{2+} in aqueous solutions. Larger effects were expected from the difference of the values of the complexation constants of Ln^{2+} and Ln^{3+} in propylene carbonate [1]. Obviously, the relative stability of Ln^{2+} and Ln^{3+} complexes and their species in water and propylene carbonate differ very much.

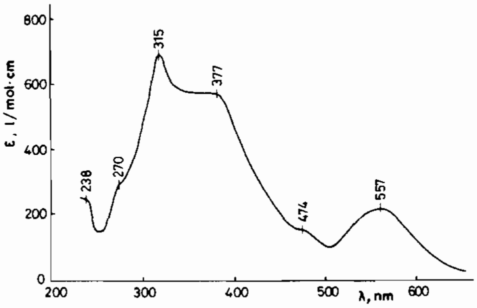

Fig. 3. Absorption spectrum of the solution of $SmI_2 \cdot$18-crown-6 in water (~0.01 mol/l).

It was expected that the presence of crown ether in CH_3CN leads to stabilization of Ln^{2+}. However, it turned out that the rate constant of the oxidation reaction of Sm^{2+} in the presence of 18-crown-6 did not decrease, but it increased 1.5 times as compared with a pure solvent (1.1×10^{-6} s^{-1} and 0.7×10^{-6} s^{-1}, respectively). This fact can be explained by the formation of the precipitated Sm^3 complexes, which are hardly soluble in THF. This fact in turn causes a right shift of the reaction $Sm^{2+} \rightarrow Sm^{3+} + e^-$ and acceleration of the Sm^{2+} oxidation. We observed the same phenomenon during our investigation of the oxidation kinetics of Ln^{2+} in aqueous solutions. At the moment of forming hydrolyzed products of Ln^{3+} the quick increase of the oxidation rate constants of Ln^{2+} took place.

The spectra of Sm^{2+} in CH_3CN are given in Fig. 4. It can be seen that presence of the crown ether results in some shift of bands into higher-energy regions, as well as some decrease of the band widths because of the limiting interaction of Sm^{2+} with solvent molecules. Splitting of the absorption bands might be caused by the lower symmetry of direct environment of Sm^{2+} ions inside the polyether cavity. The displacement of the absorption bands and some

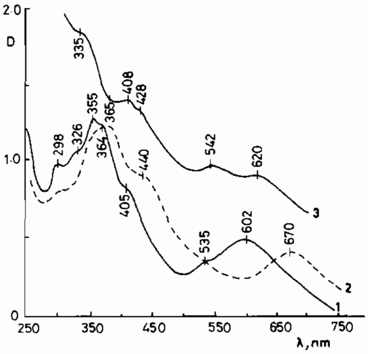

Fig. 4. (1) Absorption spectrum of $SmI_2 \cdot$18-crown-6 in acetonitrile. (2) Absorption spectrum of SmI_2 in acetonitrile. (3) Absorption spectrum of $TmI_2 \cdot$18-crown-6 in acetonitrile.

TABLE II. Influence of 18-crown-6 on Energetic Parameters of Sm^{2+} and Tm^{2+} in Various Media.

Ln	Medium	Anion	Gravity centres of absorption bands, 10^3 cm^{-1}			Δ 10^3 cm^{-1}	E_{fd} 10^3 cm^{-1}	E°_{fd} 10^3 cm^{-1} [10]
			I	II	III			
Sm^{2+}	H_2O + 18-crown-6	Cl^-	17.95	21.09	29.13	11.18	23.85	23.48
	H_2O	Cl^-	17.85	21.14	32.25	14.40	25.05	
	CH_3CN + 18-crown-6	I^-	17.60	24.39	28.16	10.56	25.88	
	CH_3CN	I^-	14.92	22.72	27.39	12.47	21.15	
Tm^{2+}	CH_3CN + 18-crown-6	I^-	17.21	24.50	29.85	12.64	23.53	23.12
	THF	I^-	16.26	23.80	32.13	14.54	23.53	

decrease of the extinction coefficients indicate the decrease of the metal–iodide interaction.

It was not possible to prepare the relatively stable solutions of TmI_2, DyI_2 and NdI_2 in water and CH_3CN, because of the instability of these solvents to low oxidation potentials. However, the green coloured solutions of Tm^{2+} ($t_{1/2}$ $\simeq$ 6 min) can be prepared if the complex $TmI_2 \cdot$18-crown-6 is dissolved in CH_3CN. In this case the stabilization effect of Tm^{2+} takes place. The spectrum of the Tm^{2+} solution in CH_3CN is shown in Fig. 4. The results of the influence of 18-crown-6 on some energy parameters of Sm^{2+} and Tm^{2+} in various media are listed in Table II. These parameters were calculated on the basis of J_1 γ-coupling scheme [6, 8, 9]. Energies of the first unsplitting level of f–d configuration (E_{fd}) of Sm^{2+} and Tm^{2+} in the system under study are close to free ion energies (E°_{fd}). In aqueous solutions with crown ether present, where Sm^{2+} is stabilized, E_{fd} is smaller than in pure water, but in CH_3CN solutions E_{fd} is a little more than in pure solvent. The crystal field splitting parameters, Δ, of Ln^{2+} in solution are smaller by 2000–3000 cm^{-1} in the presence of crown ether than in pure solvents. This fact points to the decrease of electrostatic intensity of the field caused by encapsulation of Ln^{2+} into the cavity of crown ether.

The possibility of Dy^{2+} and Nd^{2+} stabilization was of particular interest. However, it was impossible to use the solutions of these elements in THF, the only solvent in which they were obtained in 2^+ oxidation state, because the low soluble compounds $LnI_2 \cdot$18-crown-6 were precipitated by adding crown ether to the THF solutions of LnI_2. Nd^{2+} and Dy^{2+} are more stable than in THF solutions, as these solid compounds contained some THF. For example, $t_{1/2}$ for Dy^{2+} in a damp $DyI_2 \cdot$18-crown-6 is about 3 h, greater than in THF solutions by 6 times. Hence the effect of stabilization also takes place.

The stabilization of Ln^{2+} in solution represents a difficult problem. The utilization of solvents stable to low oxidation potentials does not always give a chance to prepare stable solutions of Ln^{2+}. Furthermore, we need to take into account such factors as relative stability and solubility of complexes of di- and trivalent elements, the stability to low oxidation potentials of ligands used, and their stabilizing effect.

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