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PHYSICAL METHODS OF INVESTIGATION

Study of Complexation of Alkyl-Substituted 2,2'-Dipyrrolylmethene with Lanthanide Salts by Electronic Spectroscopy

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Abstract—It has been found with the use of electronic spectroscopy that the reaction of alkyl-substituted 2,2'-dipyrrolylmethene with La(III), Pr(III), Sm(III), Dy(III), Ho(III), Er(IIII), and Yb(III) salts leads to the formation of tris(dipyrrolylmethene) complexes. Based on electronic absorption spectroscopy data and formation constants of lanthanide complexes, together with the earlier data, analysis of the nature of M–L bonds in 2,2'-dipyrrolylmethene chelates with *p*, *d*, and *f* elements has been performed. A correlation was found between the complex stability and the polarizing action of the complex-forming ion on the chromophore π system of dipyrrolylmethene, which allows one to classify these heterocyclic ligands with probes highly sensitive to the change in the ratio between the ionic and covalent contributions to coordination interactions.

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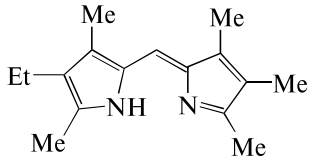
Rare-earth metal complexes with organic ligands provide wide possibilities for synthesis of compounds with various physicochemical properties. They can be used as molecular and ionic precursors, catalysts, analytical agents, thermosensitive dyes, etc. [1, 2]. Lanthanide complexes with linear oligopyrroles, a diverse group of polydentate ligands in which the chelating unit is dipyrrolylmethene, are of considerable interest for obtaining new functional materials. Dipyrrolylmethenes are chromophore molecules in which the high mobility of the conjugated π system is successfully combined with the propensity to form a six-membered chelating rings with metals [3]. In effect, this leads to the appearance of optimal photophysical and spectral properties of metal complexes with dipyrrolylmethenes, which have already used for developing liquid and solid laser dyes [4], photosensitizers [5], and other materials.

Despite considerable progress that has been made in the last two decades in the area of the coordination chemistry of linear dipyrrolylmethenes, none of the works has addressed their lanthanide complexes. In this context, the synthesis and study of such complexes is of practical and theoretical interest. The primary task is to study complexation reactions of dipyrrolylmethenes with lanthanide ions and determine the stability of the resulting coordination compounds. In this paper, we report the results of studying the coordination interactions of La(III), Pr(III), Sm(III), Dy(III), Ho(III), Er(III), and Yb(III) salts with alkylated dipyrrolylmethene (HL),



HL

Dimethylformamide (DMF) was used as a solvent, which was dictated by rather high solubilities of the reaction components and available data in the solvation and dissociation of lanthanide salts in this solvent [6].

EXPERIMENTAL

3,3'4,5,5'-Pentamethyl-4'-ethyl-2,2'-dipyrrolylmethene (HL) was synthesized, purified, and identified as described in [7].

Lanthanide salts of chemically pure grade were recrystallized for aqueous solutions with addition of the corresponding ammonium salts (NH_4Cl, NH_4Br, NH_4NO_3) to suppress hydrolysis. The composition of the resulting hydrates $EX_3 \cdot nH_2O$ ($X = Cl^-, Br^-, NO_3^-$; n = 3–6) was confirmed by elemental analysis and thermogravimetry. Anhydrous salts were obtained by dehydration of the corresponding hydrates on heating in vacuum as described in [8].

DMF of chemically pure grade was dried over molecular sieves 4 Å and distilled at reduced pressure. The water content, determined by the Fisher method, was no higher than 0.02%.

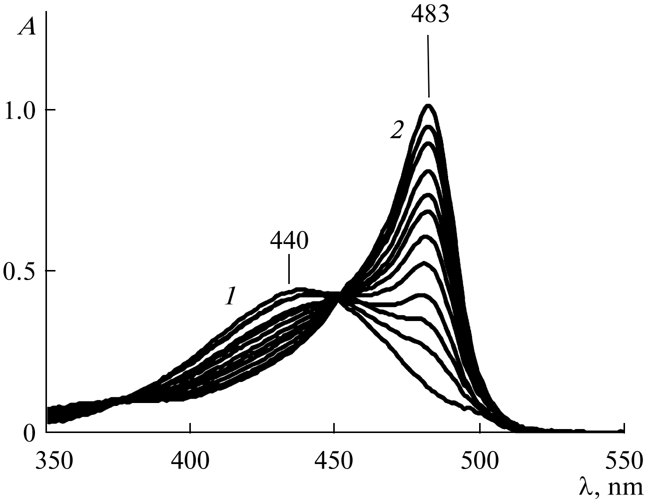


Fig. 1. Changes in the electronic absorption spectra of a solution of HL (c^0_{HL} = 1.33 × 10^{-5} mol/L) as a function of $\tilde{n}^0_{\mathrm{ErCl_3}}$, mol/L: (*1*) 8.1 × 10^{-7} and (*2*) 9.33 × 10^{-6}.

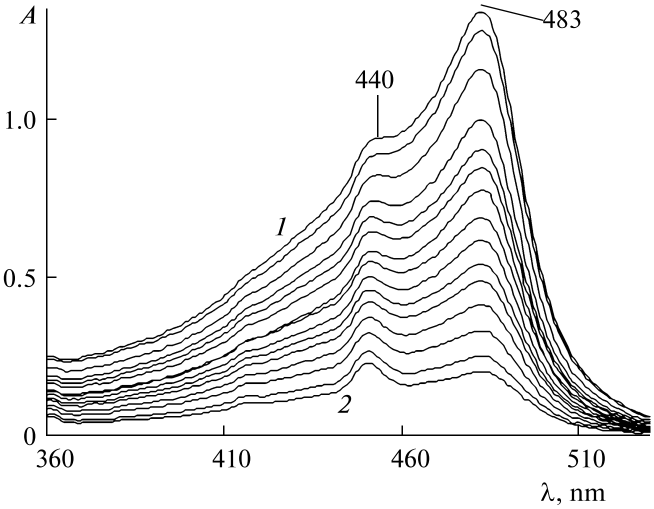


Fig. 2. Changes in the electronic absorption spectra of the reaction mixture at $\tilde{n}^0_{\mathrm{Ho(NO_3)_3}}$ = 1.33 × 10^{-5} mol/L as a function of c^0_{HL}, mol/L: (*1*) 3.29 × 10^{-6} and (*2*) 5.88 × 10^{-5}.

Complexation reactions were studied by spectrophotometry. Electronic absorption spectra of solutions of ligand and their metal complexes were recorded in the range 350–800 nm on an Akvilon SF-103 spectrophotometer (Russia) controlled by personal computer with the Spectr 1.0 software. Studies were carried out in quartz cells with a path length of 2 and 10 mm placed in a temperature-controlled (298.15 K) Peltier cell.

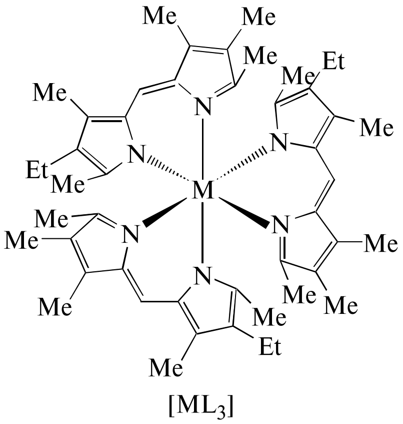
To determine the composition, equilibrium concentrations, and apparent molar extinction coefficients of the metal complexes, the molar ratio method was used. The composition–property diagrams were obtained by plotting as ordinates the measured absorption of the nascent metal complex minus the absorption of the ligand (HL) at a given wave length. The reagent concentrations were varied in the range 10^{-4}–10^{-6} mol/L. Under these conditions, the absorption caused by lanthanide complex solvates was negligible.

RESULTS AND DISCUSSION

The changes in the electronic absorption spectra at various ligand-to-lanthanide salt concentration ratios point to the formation of one metal complex species. An increase in the lanthanide salt concentration at the constant ligand concentration in a solution leads to the appearance and gradual buildup of the intensity of one absorption maximum at 483 nm with concurrent decrease of the ligand band at 440 nm (Fig. 1). In the near-UV region, a weak charge transfer band is observed (372–377 nm). The use of the molar ratio method with variation in the ligand concentration at the constant metal salt concentration (Fig. 2) also leads to the only complexation product. In this case, an increase in the HL concentration is accompanied by the simultaneous increase in the intensity of the absorption bands at 440 and 482–483 nm. In the molar ratio diagram at c_{M} = const, a well-pronounced bend is observed at $c_{\mathrm{L}}/c_{\mathrm{M}} = 3$, and at c_{L} = const, the bend is observed at $c_{\mathrm{M}}/c_{\mathrm{L}} = 1/3$ (Fig. 3), which is evidence of the formation of the single stable complex $[\mathrm{ML_3}]$ by the reaction

$$\mathrm{M^{3+} + 3HL = [ML_3] + 3H^+}.$$

Thus, the above data point to the substitution of three dipyrrolylmethene ligands for all acido ligands in the initial lanthanide salt, which leads to the formation of tris(dipyrrolylmethene) complexes $[\mathrm{ML_3}]$.



$[\mathrm{ML_3}]$

The apparent equilibrium constants (*K*) were calculated from the spectral data obtained at $c_{\mathrm{L}}/c_{\mathrm{M}} > 3$ by the equation

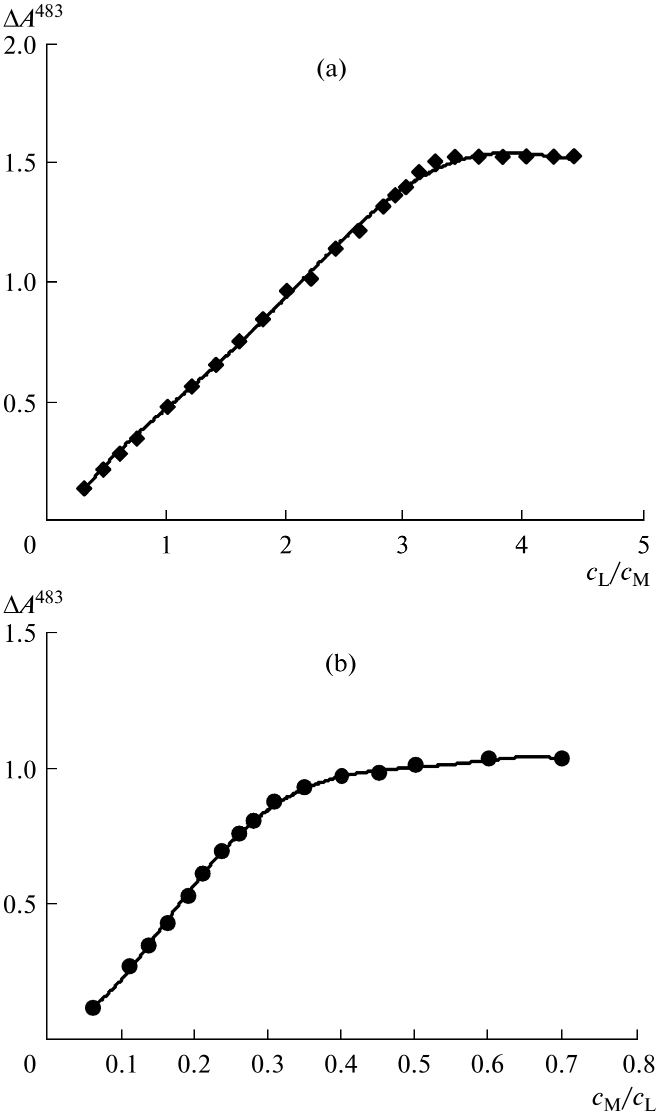


Fig. 3. Molar ratio diagrams for the system HL–$ErCl_3$–DMF at (a) $\tilde{n}^0_{ErCl_3}$ = const and (b) c^0_{HL} = const.

$$K = \frac{[ML_3][H^+]^3}{[M^{3+}][HL]^3} = \frac{27[ML_3]^4}{(c^0_{M^{3+}} - [ML_3])[HL]^3},$$

where $[ML_3]$ and [HL] are the equilibrium concentrations of the metal complex and ligand (mol/L) directly determined from electronic spectra, and $c^0_{M^{3+}}$ is the initial concentration of the lanthanide salt (mol/L).

In the working concentration ranges, the changes in the ionic strength of solutions caused by the complexation reaction are less than 1×10^{-4} mol/L. At constant $c^0_{M^{3+}}$, the values of the complexation equilibrium constants are independent of the salt concentration in the solution. Therefore, the $\log K^\circ$ values (table), average of the series of concentration $\log K$. values, can be considered standard.

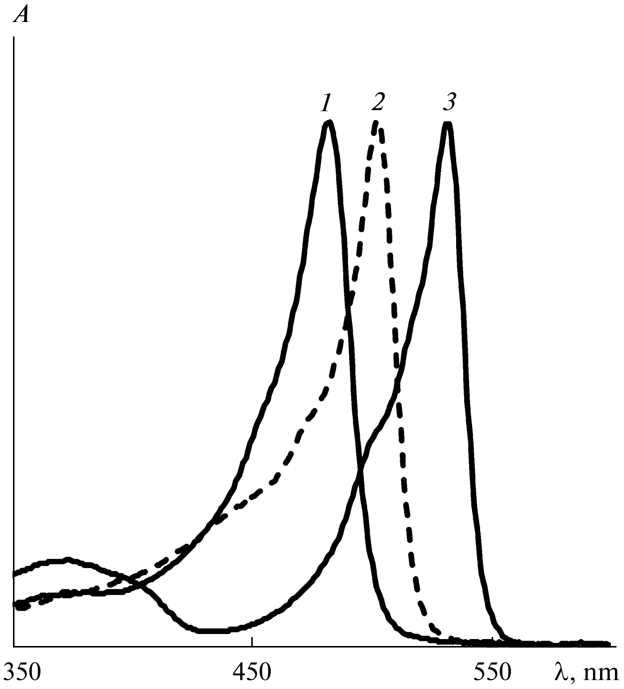


Fig. 4. Typical electronic absorption spectra of solutions of dipyrrolylmethene complexes with *f*-, *d*-, and *p* elements: (*1*) [ErL3], (*2*) $[ZnL_2]$, and (*3*) $[BF_2L]$ (*2* and *3* taken for [9, 10], respectively).

Previously [3, 9], for *d*-metal complexes with dipyrrolylmethenes, it was noticed that the thermodynamic stability of chelates increases with an increase in the degree of polarization of the π system of the chromophore by the auxochrome estimated from the bathochromic shift of the strong band in the electronic absorption spectrum of the complex as compared with the free ligand. Comparison of these results with our data allows us to analyze the nature of the M–L bonds in the dipyrrolylmethene complexes. Figure 4 shows typical spectra of complexes of 2,2'-dipyrrolylmethenes with *p*-, *d*-, and *f* elements. As is seen, the strongest polarization of the π system of the chromophore appears at the maximal overlap of the orbitals of the central atom and the donor nitrogen atoms of the ligand, which is realized for B(III) complexes with dipyrrolylmethene [10]. A decrease in the contribution of the orbitals of the *d*-metal ion to the formation of the complex with dipyrrolylmethene leads to the hypsochromic shift of the intraligand band. The smallest bathochromic shift is observed for the complexes with lanthanides, which points first of all to the predominance of the ionic character of coordination bonds and is confirmed by the dependence of $\log K^\circ$ of formation of $[ML_3]$ complexes on the inverse radius of Ln(III) (Fig. 5). The monotonic character of this dependence is evidence of strengthening of the M–L bonds with a decrease in the Ln(II) ionic radius, as it follows from the simple Fajans polarization theory [11]. Nevertheless, the contribution of the 4*f* orbitals to the formation of coordination bonds in lanthanide complexes with dipyrrolylmethenes cannot be ignored. This is reflected by the deviation from the straight line of the $\log K°–1/r$ plot, which is a result of a superposition of the covalent contribution and the effect of steric hindrances [12]. Despite the fact that elucidation of this problem as applied to the dipyrrolylmethene complexes calls for additional studies, the following circumstance is noteworthy. Two linear segments can be discerned in the $\log K°–1/r$ curve. The intersection of these straight lines gives the limiting radius of the Ln ion (r_{lim} = 0.91 Å); for larger lanthanide ions, the electrostatic interaction of M^{3+} with the L^- anion remains almost constant and the $\log K°$ values are constant. This fact is consistent with the conclusions in [12] for lanthanide complexonates.

The formation of [ML_3] complexes is characterized by the constants that are 8–13 orders of magnitude smaller than the corresponding values for the *d*-metal complexes [3, 9], which is also a direct result of the predominantly ionic character of the bond between the central Ln atom and the dipyrrole ligand. Taking into account the correlation between the stability and the strength of the polarizing action of the metal ion on the chromophore system of the dipyrrole ligand (Fig. 4), we should note that electronic spectroscopy not only reveals the character of coordination bonds but also allows one to predict the stability of complexes in series of structurally related compounds. Thus, because of the high sensitivity of the π-electron system of the dipyrrolylmethene ligands to coordination interactions, they are suitable probes that indicate the ratio between the ionic and covalent contributions to the M–L bonds.

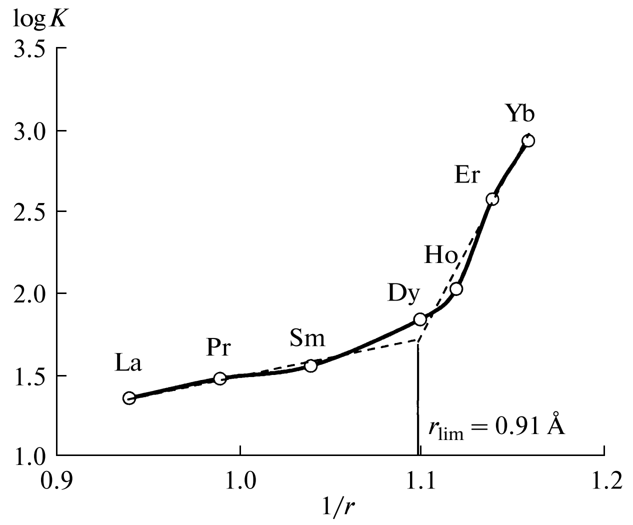


Fig. 5. Plot of $\log K°$ of formation of the tris(dipyrrolylmethene) complexes of lanthanides in DMF vs. the inverse radius of the M^{3+} ion (Å). r_{lim} is the limiting radius of the Ln ion (see text for details).

Characteristics of electronic spectra ($\lambda_{\max}$, nm ($\log\varepsilon$) and formation constants ($\log K°$) of the complexes of 3,3',4,5,5'-pentamethyl-4'-ethyl-2,2'-dipyrrolylmethene (HL) with La(III), Pr(III), Sm(III), Dy(III), Ho(III), Er(IIII), and Yb(III) in DMF at 298.15 K

Complex	$\lambda_{\max}$, nm ($\log\varepsilon$)	$\log K°$
[LaL_3]	372 (3.63), 482 (4.74)	1.37 ± 0.10
[PrL_3]	374 (3.65), 483 (4.93)	1.49 ± 0.09
[SmL_3]	375 (3.71), 483 (4.95)	1.56 ± 0.25
[DyL_3]	375 (3.65), 483 (4.95)	1.84 ± 0.30
[HoL_3]	375 (3.65), 483 (4.95	2.02 ± 0.25
[ErL_3]	376 (3.65), 483 (4.95)	2.57 ± 0.51
[YbL_3]	377 (3.71), 483 (5.00	2.93 ± 0.64

A crucial result of the ionic character of the bond in Ln complexes is a high and variable coordination number of the central atom. Our findings and data on dipyrrolylmethene complexes with triply charged *d* metals [13] point to the possibility of arrangement of three dipyrrolylmethene ligands in the octahedral coordination sphere. Taking into account the structural rigidity of dipyrrolylmethene molecules, we can assume that, in the [ML_3] complexes, the structure of the coordination polyhedron is also close to octahedral and involved DMF molecules as extra ligands (according to [6], the number of DMF molecules coordinated to the lanthanide ion changes depending on the nature of the lanthanide from 7 to 9).

Thus, our results are the benchmark for studying dipyrrolylmethene complexes with lanthanides as functional components of new materials.

ACKNOWLEDGMENTS

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