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Lanthanide Complexes with *N*,*N*'-Bis(2-hydroxybenzylidene)-2-hydroxyphenylmethanediamine

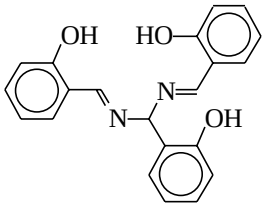
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Abstract—Complexes of lanthanides with *N*,*N*'-bis(2-hydroxybenzylidene)-2-hydroxyphenylmethanediamine (H_3L) were synthesized and investigated by the elemental, IR, magnetochemical, and thermogravimetric methods. Using the data obtained, they were found to have compositions $Ln_2L_2 \cdot nH_2O$ and $La_2L_2 \cdot MCl_2 \cdot 4H_2O$ (Ln = La^{3+}, Pr^{3+}, Nd^{3+}, Dy^{3+}, Er^{3+}; M = Cu^{2+}, Co^{2+}, Ni^{2+}; n = 4, 6). Suggestions on their structures were made. In the interval of 20–140°C, these complexes were shown to be high-resistance semiconductors.

Azomethines are known to contain several donor atoms and to form complexes of different compositions and structures with the *d*- and *f*-element ions [1]. Such azomethine ligands include *N*,*N*'-bis(2-hydroxybenzylidene)-2-hydroxyphenylmethanediamine (H_3L) whose structure was established in [2]:



Synthesis and structures of binuclear complexes of iron(III) and manganese(III) with this ligand of the composition $M_2L_2 \cdot 2DMF$ (M = Fe^{3+}, Mn^{3+}) are described in [3, 4]. An interest in compounds of this class is explained by the fact that they can be used as suitable models for establishing different regularities in magnetic, optical, catalytic, electric, and other properties of the chemical compounds. Such complexes can be used also as the starting compounds in the synthesis of polymetallic materials with the required properties [5, 6].

The aim of this work was to synthesize, study the structure and physicochemical and electric properties of lanthanide complexes with H_3L of the composition $Ln_2L_2 \cdot nH_2O$ (**I**–**V**) and $La_2L_2 \cdot MCl_2 \cdot 4H_2O$ (**VI**–**VIII**) (Ln = La^{3+} (**I**), Pr^{3+} (**II**), Nd^{3+} (**III**), Dy^{3+} (**IV**), Er^{3+} (**V**); M = Cu^{2+} (**VI**), Co^{2+} (**VII**), Ni^{2+} (**VIII**); n = 4 (**I**), 6 (**II**–**V**)).

EXPERIMENTAL

Azomethine H_3L was prepared as described in [2] (mp 435 K).

Synthesis of $[La_2L_2(H_2O)_4]$ (I). Triethylamine was added to a solution of H_3L (3.46 g, 10 mmol) in 50 ml of methanol to bring pH to 9 and then $LaCl_3 \cdot 6H_2O$ (3.72 g, 10 mmol) was added. The mixture was stirred at 40–50°C until the reagents dissolved completely. After cooling, a bright yellow precipitate formed that was filtered off on a glass filter, washed with methanol and ether, and dried in air. Complexes **II**–**V** were synthesized similarly.

Synthesis of $La_2L_2(H_2O)_4 \cdot CoCl_2$ (VII). A solution of $CoCl_2$ (0.134 g, 2.4 mmol) in 30 ml of methanol was added on heating and with continuous stirring to a suspension of compound **I** (2.5 g, 2.4 mmol) in 50 ml of chloroform. The reaction mixture was heated further until homogeneous compound of green color formed. Complexes **VI** and **VIII** were prepared in the same way.

The results of the elemental analysis and physicochemical characteristics of compounds **I**–**VIII** are given in Table 1.

Visual microscopic studies of powders of the synthesized complexes **I**–**VIII** showed that they are single-phase compounds. They do not form single crystals and their structures were determined by IR, magnetochemical, and the combined thermal methods.

IR spectra of complexes **I**–**VIII** were recorded on a Specord M80 spectrophotometer (with samples suspended in essential and fluorinated oils). The effective magnetic moments (μ_{eff}) were determined by Gouy method at 291 K. The molar magnetic susceptibility with allowance for diamagnetism was calculated using theoretical magnetic susceptibility of organic compounds. The electric conductivity of solutions **I**–**VIII** (20°C, c = 0.001 mol/l) was found by a R-38 slide wire bridge. The derivatograms of the complexes were recorded on a Paulik-Paulik-Erdey derivatograph in the temperature range 20–500°C in air at the rate of 2.5 K/min (with Al_2O_3 as a standard and corundum crucible).

Table 1. Results of elemental analysis and magnetochemical study (291 K) of complexes **I**–**VIII**

Compound	Yield, %	Empirical formula	Content (found/calcd), %				μ_{eff}, μ_B
			Ln	M	N	Cl	
I	72	$C_{42}H_{38}La_2N_4O_{10}$	26.95/26.80		5.19/5.40		
II	75	$C_{42}H_{42}N_4O_{12}Pr_2$	26.48/26.18		5.03/5.20		3.27
III	70	$C_{42}H_{42}N_4Nd_2O_{12}$	26.84/26.63		5.40/5.17		3.34
IV	78	$C_{42}H_{42}Dy_2N_4O_{12}$	28.89/29.02		5.24/5.00		10.21
V	71	$C_{42}H_{42}Er_2N_4O_{12}$	29.42/29.62		5.11/4.96		9.42
VI	80	$C_{42}H_{38}Cl_2CuLa_2N_4O_{10}$	23.54/23.72	5.16/5.43	4.91/4.79	5.89/6.05	1.86
VII	82	$C_{42}H_{38}Cl_2CoLa_2N_4O_{10}$	23.59/23.82	4.84/5.05	4.66/4.80	5.99/6.08	4.86
VIII	85	$C_{42}H_{38}Cl_2La_2N_4NiO_{10}$	23.56/23.82	5.16/5.03	4.71/4.80	5.87/6.08	2.84

The electric properties of pellets of complexes **I**–**VIII** were studied using a ITN-7 electrometer (with the range of the measured resistance from 10^6 to 10^{16} ohm).

RESULTS AND DISCUSSION

The molar conductivity determined for solutions of the synthesized compounds in DMF suggests that they are nonelectrolytes (μ_{1000}^{20} = 2–5 ohm^{-1} cm^2 mol^{-1}).

The magnetochemical studies (Table 1) revealed that the values of μ_{eff} for complexes **II**–**V** are close to those for complexes of the corresponding lanthanide ions [7, 8]. This implies that the oxidation state of the central atom is +3. The magnetochemical parameters of compounds **VI**–**VIII** given in the same table indicate that the introduction of the 3*d* element atom in complex **I** induces their paramagnetic properties. Judging from the values of magnetochemical parameters, the *d* metal ion has pseudooctahedral ligand environment.

The comparison of IR spectrum of the H_3L ligand with those of the synthesized complexes shows that complexation results in disappearance from the latter spectra of the absorption band δ(OH) of the phenolic hydroxyl that appeared in a free ligand at 1240 cm^{-1}. The band ν(C=N) shifts by 40–30 cm^{-1} toward the long-wave region; some new bands appear in the range of 600–400 cm^{-1} that can be assigned, in accordance with the data in [9], to ν(Ln–N) and ν(Ln–O). It thus follows that the ligand is coordinated to the central atom through the phenolic oxygen and azomethine nitrogen atoms. The band ν(C–O) in IR spectra of compounds **I**–**VIII** is splitted in four components: 1173–1171, 1157–1154, 1133–1131, and 1106–1104 cm^{-1}. Such changes in the absorption bands ν(C–O) are known to indicate the bridging nature of the phenolic oxygen atoms in both homonuclear and heteronuclear complexes [9–11]. Since in the range of 1200–1100 cm^{-1}, the IR spectrum of $[Fe_2L_2] \cdot 2DMF$ having the binuclear structure [3, 4] exhibits the splitting of the band due to the ν(C–O) vibration into four analogous components, complexes **I**–**V** are also suggested to have the binuclear structure. Like the described compounds, the spectra of compounds **I**–**V** contain the same bands at 1615 ν(C–O), 1567 ν(C–N), 547 ν(Ln–N), and 324 cm^{-1} ν(Ln–O). Therefore, one can suggest that H_3L is coordinated to the central atoms in the same way and the complexes are supposed to have analogous structure.

The thermal analysis of complexes **I**–**V** (Table 2) showed that their thermolysis occurs in stages attended by the mass loss and terminating in their complete decomposition at 380–440°C. The introduction of *d* metal in compound **I** lowers the full decomposition temperature by 20–60°C. In the temperature interval 50–70°C, the derivatograms of complexes **II**–**V** have endothermic effect that corresponds to removal of water of crystallization. The mass loss in the second endothermic effect observed at 140–150°C corresponds

Table 2. Results of thermal analysis of complexes **I–VIII**

Compound	No. of endo-effect on DTA curve	Temperature, °C	Mass loss			Kinetic parameters		Full decomposition temperature, °C
			found, %	calcd. %	*n**	*E**, kJ/mol	log*Z*	
I	1	150	6.7	7.0	4	130.0	24.2	440
II	1	60	3.0	3.3	2	48.5	5.1	410
	2	140	7.0	6.7	4	115.6	20.8	
III	1	50	3.5	3.3	2	57.8	7.4	420
	2	145	6.5	6.6	4	118.5	22.6	
IV	1	70	3.0	3.2	2	63.3	6.8	410
	2	140	6.5	6.4	4	122.4	21.9	
V	1	60	3.0	3.2	2	60.7	7.5	425
	2	150	6.5	6.4	4	126.3	23.1	
VI	1	120	6.0	6.1	4	120.4	22.5	400
VII	1	130	6.0	6.2	4	112.0	22.3	380
VIII	1	125	6.5	6.2	4	119.7	20.6	420

* *n* is the number of eliminated water molecules.

Table 3. Range of working temperatures, resistance changes, temperature sensitivity of resistance (*B*), and temperature coefficient of resistance (TCR) of compounds **I–VIII**

Complex	Range of working temperatures, °C	Resistance changes, ohm	*B*, K	TCR, 1/K (373 K)
I	20–140	1.3×10^6–2.6×10^4	4211.4	0.03025
II	88–126	1.4×10^7–2×10^6	2723.4	0.01956
III	23–120	3.1×10^6–5×10^5	2220.4	0.01595
IV	80–140	1.4×10^7–3.5×10^5	10584	0.07601
V	82–140	1.4×10^7–6.3×10^5	10455	0.07509
VI	34–138	1.4×10^8–9×10^2	13817	0.00923
VII	20–128	1.6×10^5–3×10^4	2080.8	0.01494
VIII	30–126	2.5×10^6–1.3×10^4	4824.5	0.03465

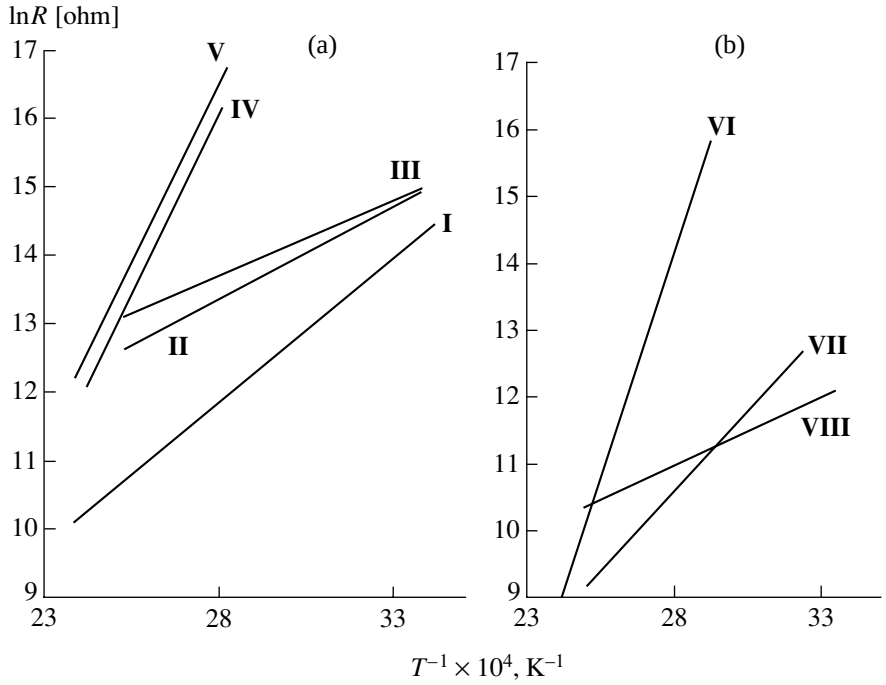
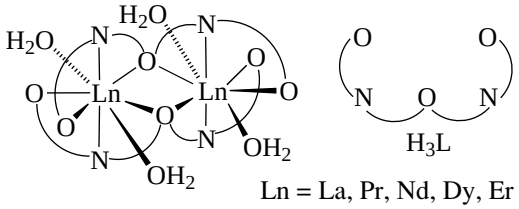


Fig. 1. Temperature dependence of specific resistance of (a) complexes **I–V** and (b) complexes **VI–VIII**.

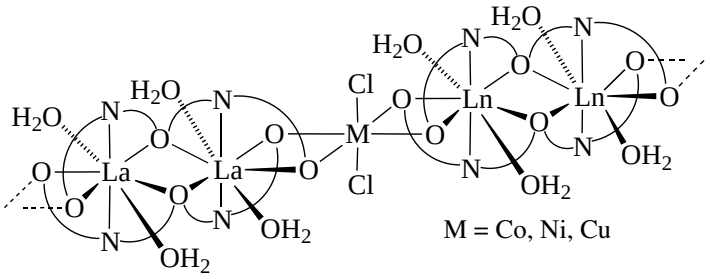
to elimination of four inner-sphere water molecules. In order to obtain the quantitative estimates of dehydration and deaquation of complexes **I–V**, their kinetics was studied by the Horowitz–Metzger–Topor method [12, 13]. The results obtained are given in Table 2. One can see that the values of the activation energy (E^*) and preexponential factor (Z) characterizing the removal of inner-sphere water are mainly determined by the nature of lanthanide and change in the series La > Er > Dy > Nd > Pr. At the same time, the determined values of E^* and log$Z$ are close to analogous parameters describing similar topochemical reactions [14, 15].

The above data of physicochemical studies provide grounds for considering complexes **I–V** as binuclear complexes as $M_2L_2 \cdot 2DMF$ [3, 4]. In these complexes, L acts as a bridging ligand; coordination number of Ln is 8; two additional coordination sites are occupied by water molecules:



Ln = La, Pr, Nd, Dy, Er

Heterometal complexes **VI–VIII** are likely to have polymeric structures.



M = Co, Ni, Cu

The final solution of the question on their structures requires additional investigation.

Many heterometal complexes are known to have specific electric properties (dielectric, semiconducting, or conducting properties) [16–18]. In this connection, it was of interest to study the electrochemical properties of the synthesized complexes **I–VIII**. In the temperature interval of 20–140°C, they were found to be high-resistance semiconductors (see figure, Table 3).

The temperature dependence of resistance of complexes **I**–**VIII** plotted in the figure shows that the nature of lanthanide influences both the range of the working temperatures and the temperature sensitivity of resistance (*B*) and the temperature coefficient of resistance (TCR) of the investigated material. For complexes **I**–**V**, the temperature sensitivity of resistance changes in the series: *B*(Dy) > *B*(Er) > *B*(La) > *B*(Pr) > *B*(Nd), while in the case of heterometal La complexes **VI**–**VIII**, this value changes in the order *B*(Cu) > *B*(Ni) > *B*(Co). The introduction of *d* metal in complex **I** improves its semiconducting properties.

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