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Synthesis and Characterization of Some New Lanthanide(III) Chelates with 1,4-*bis*-(2′-Hydroxyphenylazomethine) Phenylene

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Summary. The chelates formed between 1,4-*bis*(2′-hydroxyphenylazomethine) phenylene with La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb, and Lu ions have been investigated in solution using conductometric, potentiometric, and spectrophotometric methods. The studies revealed the formation of M_2L and ML complexes. The solid chelates have been characterized by elemental and thermal analysis, molar conductance, IR, ^{1}H NMR (for La and Lu chelates), and electronic spectra. The bonding takes place through the coordination of nitrogen in the –CH=N– group and the oxygen of the hydroxyl group by proton displacement.

Keywords. Synthesis of lanthanide(III) chelates; Conductometry; Potentiometry; Spectrophotometry.

Synthese und Charakterisierung einiger neuer Lanthanid(III)-Chelate mit 1,4-*bis*-(2′-Hydroxyphenylazomethin)-phenylen

Zusammenfassung. Chelate von 1,4-*bis*-(2′-Hydroxyphenylazomethin)-phenylen mit La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb und Lu in Lösung wurden konduktometrisch, potentiometrisch und spektrophotometrisch untersucht. Die Bildung von Komplexen der Form M_2L und ML wurde festgestellt. Die festen Chelate wurden mittels Elementaranalyse. Thermoanalyse, molarer Leitfähigkeit, IR-, UV/Vis- und im Fall von La und Lu-NMR-Spektroskopie charakterisiert. Die Komplexbindung erfolgt durch Koordination des Stickstoffs der –CH=N– Gruppe und des Sauerstoffs der Hydroxylgruppe unter Protonenverschiebung.

Introduction

The coordination phenomena occurring in azomethine derivatives as well as the formation of stable metal complexes were investigated by many authors [1–8] with a view of use *Schiff* bases as metallochromic reagents. The purpose of the present work is to study the stoichiometry and structure of the complexes formed when some lanthanide ions are allowed to react with 1,4-*bis*-(2′-hydroxyphenylazomethine) phenylene. The formation constants of the chelates are determined by potentiometric titration.

Results and Discussion

Studies in solution

The stoichiometry of the chelates liable to be formed on allowing the ligand **1** to react with lanthanide(III) ions was first tested by conductometric titration. Conductometric titration curves of the ligand with all lanthanide ions exhibit two inflections at molar ratios of $\frac{1}{2}$ and 1, indicating the existence of 2:1 and 1:1 (M:L) complex species in solution. The non-existence of 1:3 (M:L) species is due to steric hindrance in accommodating three ligand molecules around a metal ion and the lability of the aquo-ligand on the 1:1 complex.

The molar conductivities of $1 \times 10^{-3}\,M$ solutions of the lanthanide chelates in *DMF* at 25 °C are in the 20.2–31.3 $\text{ohm}^{-1}\cdot\text{cm}^{2}\cdot\text{mol}^{-1}$ range for 1:1 ratios of metal chelates which indicates the lack of ionic character in solution. In the case of 2:1 (M:L) ratios, the molar conductivities lie in the range of 278.2–328.6 $\text{ohm}^{-1}\cdot\text{cm}^{2}\cdot\text{mol}^{-1}$ which indicates the ionic nature of these chelates.

From potentiometric titration data (Fig. 1), the average number of protons $\bar{n}_A$ associated with the reagent at various pH values, the average number of ligands $\bar{n}$ attached to a metal ion, and the free ligand exponent pL were calculated using an equation given by *Mushran et al.* [15]. The formation curves ($\bar{n}_A$ *vs.* pH) for the proton ligand systems are found to extend between 0 and 2 on the $\bar{n}_A$ scale, indicating that the ligand has two dissociable protons. The ionisation constants of **1** were found to be 9.30 and 7.86. From the titration curves, $\bar{n}$ and pL values were calculated [15, 16] and plotted against each other to produce the formation curves of the metal complexes. Table 1 illustrates the overall formation constants of the metal chelates of La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb and Lu ions with **1**. The data show an increase of $\log \beta_{12}$ values from La^{3+} to Sm^{3+} where they reach a maximum and then fall to Dy^{3+}, after which they rise again with increasing atomic number and decrease of the ionic radious of the cations. The relation between the electronegativities of the lanthanide(III) ions and the formation constant of the complexes shows the Sm^{3+} complexes have the highest stability (Table 1).

The electronic absorption spectra of the free ligand in *DMF* solution show absorption bands at 222, 291, and 374 nm which can be assigned to the π-π^* transition for the band at 222 nm corresponding to the ${}^1L_a \leftarrow {}^1A$ state of the phenyl

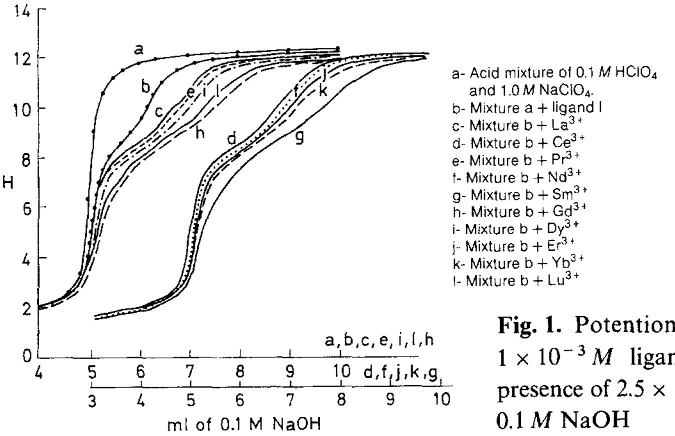


Fig. 1. Potentiometric titration curves of the $1 \times 10^{-3}\,M$ ligand in the absence and in the presence of $2.5 \times 10^{-3}\,M$ lanthanide(III) ions with 0.1 M NaOH

Table 1. Formation constants of lanthanide(III) complexes with **1**

Metal ion	Stepwise formation constant		Overall formation constant	Electro-negativity	Atomic number	Ionic radius (A)	$1/r$
	$\log \beta_1$	$\log \beta_2$	$\log \beta_{12}$				
La^{3+}	3.12	1.30	4.42	1.10	57	1.061	0.943
Ce^{3+}	3.20	1.45	4.65	1.12	58	1.034	0.967
Pr^{3+}	3.30	1.50	4.80	1.13	59	1.013	0.987
Nd^{3+}	3.45	1.87	5.32	1.14	60	0.995	1.005
Sm^{3+}	3.99	3.20	7.19	1.17	62	0.964	1.037
Gd^{3+}	3.90	3.07	6.97	1.20	64	0.938	1.066
Dy^{3+}	3.52	2.30	5.82	1.22	66	0.908	1.101
Er^{3+}	3.58	2.38	5.96	1.24	68	0.881	1.135
Yb^{3+}	3.62	2.59	6.21	1.25	70	0.858	1.166
Lu^{3+}	3.71	2.86	6.57	1.27	71	0.848	1.179

ring, whereas the absorption band at 291 nm corresponds to the low energy π-π^* transition ($^1L_b \leftarrow {}^1A$ state; interaction of aromatic moeties with the CH=N group) and the band at 374 nm is due to the charge transfer interaction within the whole molecule. However, the electronic absorption spectra of lanthanide(III) chelates show a red shift (22–40 nm) in comparison to the CT band of the ligand. This results from the complexation with lanthanide ions. The new absorption band of the chelates lies at 420–495 nm [17].

Studies in solid chelates

The IR spectra of the dehydrated solid complexes M_2L and ML were recorded and compared with those of the free ligand. The IR bands of **1** (ν(OH): 3450–3100 cm^{-1}; ν(C=N): 1638 cm^{-1}) are affected upon complex formation with lanthanide(III) ions indicating that these groups are the active centers for chelation. The OH band disappears on complex formation; the C=N band is shifted to lower frequencies (24–38 cm^{-1}) in the spectra of the chelates suggesting that complex formation takes place through covalent and coordinate bonds with the oxygen atom of the hydroxyl group and the nitrogen atom of the azomethine group, respectively. The OH band at 1345 cm^{-1} in the free ligand exhibits a shift of 5–14 cm^{-1} to lower or higher frequencies values on complexation. This indicates the participation of the OH proton in the reaction with lanthanide ions. The band at 1262 cm^{-1} is assigned to asymm. ν(C–OH) in the ligand. On complexation, this band shifts to higher frequencies (13–34 cm^{-1}). The band at 1590 cm^{-1} which can be attributed to ν(C=C) (aromatic ring of free ligand), suffering a very small shift on complex formation due to higher mesomeric interactions with the aromatic ring in the chelates. In the case of M_2L complexes, a weak broad band is observed at 3490–3580 cm^{-1} which is due to the coordinated water molecule. The new bands for all solid complexes appearing in the ranges 542–510, 436–415, and 375–325 cm^{-1} are assigned to $\nu(M$–O), $\nu(M$–N), and $\nu(M$–Cl), respectively [18].

In the ^{1}H NMR spectra of the solid La(III) and Lu(III) chelates in *DMSO*-d$_6$ the disappearance of the signals of the OH protons of the ligand at 10.9 and 12.52 ppm can be observed. This confirms that the bonding to the ligand takes place through displacement of the two protons from the OH groups. The signal characteristic for the azomethine group is observed at 8.48–9.4 ppm for the free ligand and shifts downfields by ~0.6 ppm on chelation. The signals of the aromatic protons of the free ligand show some shifts of varied magnitude towards lower fields in chelates. In case of the La_2L and Lu_2L chelates, the new strong signal found at 4.23 ppm is due to water molecules coordinated to the lanthanum ion in the complex.

For TGA and DTA curves for solid chelates of La, Pr, Sm, Dy, and Lu with **1** from ambient temperature up to 900 °C at a rate of 10 °C min^{-1}, see Fig. 2.

From the thermographs, the initial weight loss of the chelates within the range of 115–200 °C and therefore the number of water molecules in the complexes can be calculated (Table 2). It is followed by the removal of chloride atoms from the chelates in the temperature range of 240–320 °C. The metal content was calculated from the residual weight after decomposition of the chelate applying the method of *MacDonald et al.* [19] (Table 2). Above 340 °C, decomposition of the chelate species takes place in two stages with an inflection in the range of 400–700 °C, indicating the transformation to another type of chelates at this temperature. The formation of metal oxides (Ln_2O_3) as a final product starts above 800 °C.

The DTA curves of the *Ln*(III) complexes consist of a broad endothermic peak at a temperature range of 140–190 °C, assigned to the loss of coordinated water

Table 2. Thermogravimetric analysis of lanthanide(III) complexes with **1**

Chelate	Ratio (M:L)	Metallic residue (%)	Decomp. temp. (°C)	ΔE_a (KJ·mol^{-1})	%*M*		%H_2O		No. of H_2O molecules
					calcd.	found	calcd.	found	
La^{3+}-**1**	1:1	30.4	370	13.30	26.47	25.92	6.87	6.8	2
	2:1	38.5	410	33.24	32.99	32.83	12.84	12.9	6
Pr^{3+}-**1**	1:1	30.6	391	36.01	26.75	26.15	6.84	6.7	2
	2:1	45.8	435	44.32	39.96	39.13	15.33	15.5	6
Sm^{3+}-**1**	1:1	32.4	382	53.18	28.04	27.94	6.72	6.6	2
	2:1	40.5	398	59.56	34.77	34.93	12.50	12.7	6
Dy^{3+}-**1**	1:1	33.2	365	43.63	29.64	28.93	6.57	6.4	2
	2:1	42.0	415	55.40	36.55	36.6	12.16	12.2	6
Lu^{3+}-**1**	1:1	35.2	360	37.77	31.2	30.95	6.43	6.3	2
	2:1	43.6	385	45.71	38.28	38.34	11.82	12.0	6

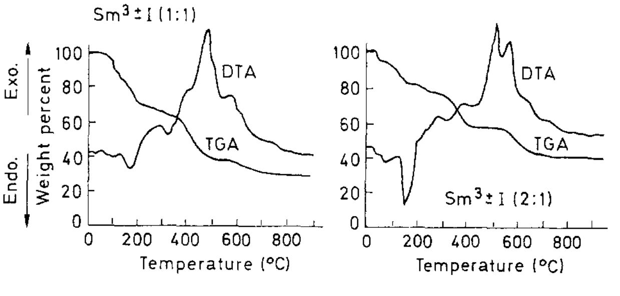


Fig. 2. TGA and DTA for chelates of Samarium(III) (*ML* and M_2L)

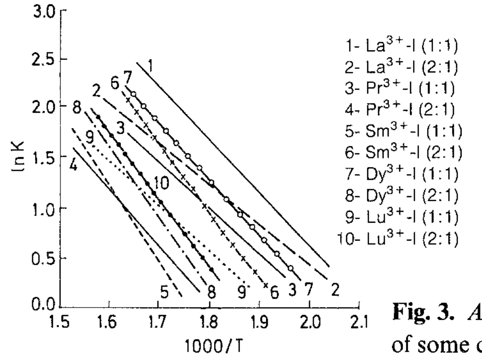
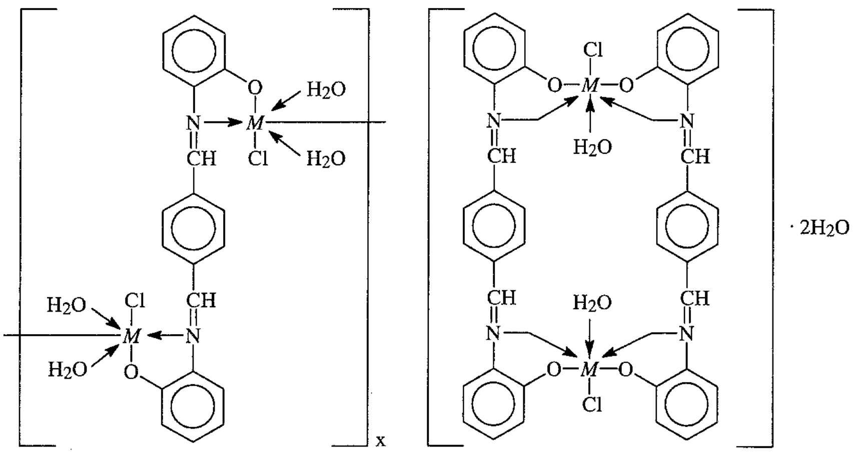


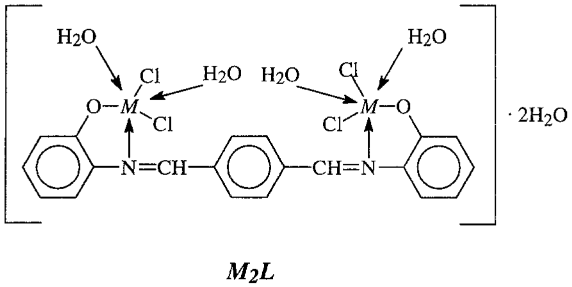
Fig. 3. *Arrhenius* plots constructed from the DTA thermogram of some chelates

molecules. The appearance of medium exothermic peaks at 260–330 °C may be assigned to the elimination of chloride atoms. The two strong broad exothermic peaks at 400–700 °C include the decomposition; combustion starts, followed by decarbonization of the organic material in presence of oxygen, leaving oxide Ln_2O_3 as residue. The energy of activation (ΔE_a) of the thermal decomposition of the complexes is evaluated from the thermograms as previously [20, 21]. An *Arrhenius* plot was constructed (Fig. 3), and ΔE_a was obtained from the slope (Table 2).

Based on the knowledge gained from the present investigation, the bonding of the lanthanum ions to **1** can be formulated as follows:



ML (x = 2 or infinity)



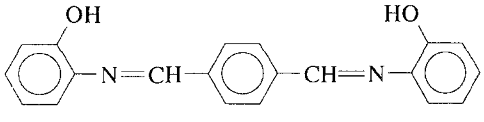
M2L

Table 3. Elemental analysis and molar conductance for some lanthanide(III) chelates (x = 2 or ∞)

chelate	Empirical formula	Yield (%)	Calcd. (found) (%)						Λ_m ($ohm^{-1} \cdot cm^2 \cdot mol^{-1}$)
			C	H	N	M	Cl	H_2O	
[(La*L*) Cl·$2H_2O]_x$	$C_{20}H_{18}O_4N_2Cl$ La	91.2	45.78 (45.6)	3.46 (3.4)	5.34 (5.2)	26.47 (26.2)	6.76 (6.7)	6.87 (6.8)	20.5
(La_2*L*) 4Cl·$6H_2O$	$C_{20}H_{26}O_8N_2Cl_4La_2$	88.4	28.53 (28.5)	3.11 (3.0)	3.33 (3.3)	32.99 (32.7)	16.84 (16.6)	12.84 (12.9)	278.2
[(Pr*L*) Cl·$2H_2O]_x$	$C_{20}H_{18}O_4N_2Cl$ Pr	87.5	45.61 (45.5)	3.44 (3.3)	5.32 (5.3)	26.75 (26.5)	6.73 (6.7)	6.84 (6.7)	20.2
(Pr_2*L*) 4Cl·$6H_2O$	$C_{20}H_{26}O_8N_2Cl_4Pr_2$	80.6	34.07 (34.0)	3.72 (3.7)	3.97 (3.9)	39.96 (39.7)	20.11 (20.0)	15.33 (15.4)	281.8
[(Nd*L*) Cl·$2H_2O]_x$	$C_{20}H_{18}O_4N_2Cl$ Nd	93.5	45.32 (45.1)	3.42 (3.3)	5.28 (5.2)	27.21 (27.0)	6.69 (6.6)	6.80 (6.7)	25.6
(Nd_2*L*) 4Cl·$6H_2O$	$C_{20}H_{26}O_8N_2Cl_4Nd_2$	89.8	28.17 (28.0)	3.07 (3.0)	3.29 (3.3)	33.83 (33.7)	16.63 (16.5)	12.68 (12.8)	320.3
[(Sm*L*) Cl·$2H_2O]_x$	$C_{20}H_{18}O_4N_2Cl$ Sm	81.9	44.80 (44.7)	3.38 (3.2)	5.22 (5.2)	28.04 (28.0)	6.61 (6.5)	6.72 (6.7)	30.8
(Sm_2*L*) 4Cl·$6H_2O$	$C_{20}H_{26}O_8N_2Cl_4Sm_2$	78.8	27.77 (27.7)	3.03 (3.0)	3.24 (3.2)	34.77 (34.6)	16.39 (16.3)	12.50 (12.7)	298.6
[(Gd*L*) Cl·$2H_2O]_x$	$C_{20}H_{18}O_4N_2Cl$ Gd	84.2	44.23 (44.2)	3.34 (3.1)	5.16 (5.1)	28.96 (28.7)	6.53 (6.4)	6.63 (6.5)	29.6
(Gd_2*L*) 4Cl·$6H_2O$	$C_{20}H_{26}O_8N_2Cl_4Gd_2$	76.9	27.34 (27.1)	2.98 (2.8)	3.19 (3.2)	35.79 (35.6)	16.14 (16.1)	12.30 (12.5)	288.5
[(Dy*L*) Cl·$2H_2O]_x$	$C_{20}H_{18}O_4N_2Cl$ Dy	92.3	43.81 (43.5)	3.31 (3.2)	5.11 (5.1)	29.64 (29.5)	6.47 (6.3)	6.57 (6.6)	31.3
(Dy_2*L*) 4Cl·$6H_2O$	$C_{20}H_{26}O_8N_2Cl_4Dy_2$	90.8	27.01 (26.9)	2.95 (3.0)	3.15 (3.1)	36.55 (36.3)	15.95 (15.8)	12.16 (12.4)	328.6
[(Lu*L*) Cl·$2H_2O]_x$	$C_{20}H_{18}O_4N_2Cl$ Lu	90.9	42.84 (42.7)	3.24 (3.2)	5.00 (4.9)	31.20 (31.1)	6.32 (6.1)	6.43 (6.5)	27.9
(Lu_2*L*)4Cl·$6H_2O$	$C_{20}H_{26}O_8N_2Cl_4Lu_2$	85.3	26.28 (26.2)	2.87 (2.8)	3.06 (3.0)	38.28 (38.2)	15.51 (15.3)	11.82 (11.9)	311.4

Experimental

The *Schiff* base used in the present investigation (**1**) is given below. The compound was prepared as previously reported [9–11].



1

Stock solutions (0.1 *M* of **1** or lanthanide(III) chlorides) were prepared in absolute ethyl alcohol.

The lanthanide(III) complexes were prepared by refluxing an ethanolic mixture of lanthanide(III) chloride (0.01 or 0.025 mole) and the organic reagent (0.01 mole) for about 4 h on a water bath to form 1:1 or 2:1 (*M*:*L*) complexes. On cooling, the solid complexes were separated as fine precipitates which were then filtered, washed with ethanol, dried and kept in a desiccator over dry calcium chloride. The decomposition point for all chelates was found above 340 °C. They were subjected to analyses for carbon, hydrogen, and nitrogen (carried out in the microanalytical laboratory, Cairo University, Cairo, Egypt). Lanthanides and chloride ions were analysed by *EDTA* titration after decomposition of the chelates according to a reported procedure [12, 13]. The analytical data along with the electrolytic conductance in *DMF* are given in Table 3.

Physical measurements and apparatus were as given before [14, 15].

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