

## **ELECTROMETRIC, SPECTROSCOPIC AND THERMOGRAVIMETRIC STUDIES ON LANTHANIDE–ARYLHYDRAZONES OF BENZOYLACETONE AND DIBENZOYLMETHANE COMPLEXES**

Y.M. ISSA and H.A. MOHAMED

*Department of Chemistry, Faculty of Science, Cairo University, Cairo (Egypt)*

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### **ABSTRACT**

The chelate formation reaction of  $\text{La}^{\text{III}}$ ,  $\text{Pr}^{\text{III}}$ ,  $\text{Nd}^{\text{III}}$ ,  $\text{Gd}^{\text{III}}$ ,  $\text{Ho}^{\text{III}}$  and  $\text{Er}^{\text{III}}$  ions with some arylhydrazones of benzoylacetone (BAAH) and dibenzoylmethane (DBMAH) has been investigated by conductimetric and pH-metric titration. The chelates formed have 1:1 and 1:2 stoichiometries ( $\text{M}^{3+}:\text{L}$ ). The stability constants of the metal chelates are correlated to the atomic numbers  $Z$ , the ionic radii  $r$ , the ionization potentials and the electronegativities of the lanthanide ions.

The solid complexes have been isolated and their structures have been assigned on the basis of elemental analysis, IR and NMR spectroscopy and thermogravimetric analysis (TG). It has been determined that the chelation occurs through the  $-\text{NH}$  group and one carbonyl group of the  $\beta$ -diketone, in addition to the  $\text{OH}^-$  group. The coordination number ranges from six to eight according to the number of coordinated water molecules which are confirmed by thermogravimetric analysis. The structural formulae are suggested.

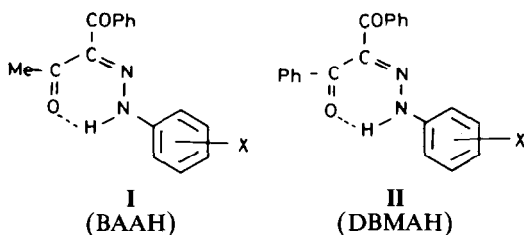
### **INTRODUCTION**

Although arylhydrazones of  $\beta$ -diketones have been applied as anti-diabetics [1], anti-malarial agents [2], potential bactericides [3] and dyes for artificial textiles and polyester fibres [4], the chemistry of benzoylacetone arylhydrazone and dibenzoylmethane arylhydrazone has not yet been thoroughly investigated. Yao [5] has studied the coupling of diazonium ion with  $\beta$ -diketones (acetylacetone, benzoylacetone and dibenzoylmethane). He confirmed the formation of the hydrazo rather than the azo form using IR and NMR spectroscopy. Mitchell and Nonhebel [6,7] have studied the IR and NMR spectra of some 2-arylhydrazones of 1,2,3-tricarbonyl compounds in an attempt to investigate the isolation, the interconversion of the tautomers and the influence of electronic and steric factors on the structure of the preferred tautomer. Picon et al. [8] have investigated the structures and physical properties in solutions of compounds obtained from the con-

denation of aryldiazonium salts with carbanions of  $\beta$ -diketones. Recently, the stability constants, structure and thermogravimetric analyses of  $\text{La}^{\text{III}}$  complexes with some arylhydrazones of benzoylacetone and dibenzoylmethane have been investigated [9].

## EXPERIMENTAL

Benzoylacetone arylhydrazone (BAAH), **I**, and dibenzoylmethane arylhydrazone (DBMAH), **II**, derivatives were prepared as previously reported [10,11]. The resulting arylhydrazones were acidified with diluted (1:1) HCl. The products were filtered and recrystallised from ethanol to constant melting point. The purity of the resulting compounds was confirmed by elemental analysis. The resulting compounds may be represented as shown below, where X = *o*-OH(a), *o*-COOH(b) or *o*-OCH<sub>3</sub>(c).



Stock hydrazone solutions (0.001 M) were prepared in absolute ethanol. 0.01 M solutions of  $\text{Ln}(\text{ClO}_4)_3$  were prepared and standardised by the recommended method [12] using Arsenazo I as indicator; 0.001 M solutions were then prepared by accurate dilution. Solutions of 0.107 M perchloric acid, 0.293 N NaOH and 1 M sodium perchlorate were also prepared. The potentiometric titrations were performed by the method of Sarin and Munshi [13] using a pH meter (Schott Mainz, model CG 801 digital Ionalyzer) at  $27 \pm 0.1^\circ\text{C}$ . The appropriate correction factor for converting pH-meter readings in 40% (v/v) ethanol-water to pH values amounts to 0.15 [14]; the curves were plotted accordingly.

Conductimetric titrations were performed using a PTI 18 digital conductivity meter at a frequency of 2 kHz. The TG results were obtained on a Du Pont 1090 thermal analyser.

The solid complexes were prepared and characterised on the basis of microanalysis, thermogravimetric analysis and IR and NMR spectroscopy. The IR spectra of the ligands and lanthanide complexes were recorded in KBr using a Pye Unicam SP 1000 IR spectrophotometer, while their NMR spectra were scanned using a Varian EM 360 60 MHz spectrometer.

TABLE 1

Collective data of  $\log \beta_1$ ,  $\log \beta_2$ , ionization potential, electronegativity, ionic radius and atomic number of some trivalent lanthanide ions

Metal ion	Ia		Ib		Ic		IIa		IIb		For metal ion <sup>a</sup>			
	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	$1/r$	EN	Z	$I_2$
La <sup>3+</sup>	4.77	8.97	11.34	19.55	9.02	16.73	10.06	18.51	9.46	18.90	0.98	1.10	57	11.06
Pr <sup>3+</sup>	6.01	10.96	11.36	18.95	10.14	19.05	11.29	20.31	9.62	18.57	0.99	1.13	59	10.55
Nd <sup>3+</sup>	7.32	12.07	11.36	18.95	10.26	20.15	11.74	21.40	9.62	18.57	1.005	1.14	60	10.72
Gd <sup>3+</sup>	9.00	15.48	12.61	23.34	10.32	20.33	15.81	24.85	10.07	19.93	1.07	1.20	64	12.10
Ho <sup>3+</sup>	5.96	10.34	11.30	18.82	10.26	20.15	13.93	21.28	9.44	17.99	1.12	1.23	67	11.80
Er <sup>3+</sup>	6.36	11.54	12.51	22.51	10.32	20.33	12.18	21.84	9.57	18.91	1.135	1.24	68	11.93

<sup>a</sup>  $r$ , Ionic radius (Å); EN, electronegativity (Paulings); Z, atomic number, and  $I_2$ , second ionization potential (kcal mol<sup>-1</sup>).

## RESULTS AND DISCUSSION

The stability constants of the trivalent lanthanide ions La, Pr, Nd, Gd, Ho and Er with BAAH derivatives *o*-OH (Ia), *o*-COOH (Ib), and *o*-OCH<sub>3</sub> (Ic), and with DBMAH derivatives *o*-OH (IIa) and *o*-COOH (IIb), were determined using the method described by Sarin and Munshi [13] and Irving and Rossotti [15,16].

The mean  $\log \beta_1$  and  $\log \beta_2$  for the complexes of the trivalent lanthanide ions La, Pr, Nd, Gd, Ho and Er with derivatives Ia, Ib, Ic, IIa and IIb are listed in Table 1. The maximum  $\bar{n}$  (number of ligand molecules attached per metal ion) values calculated for the metal–ligand systems were found not to exceed two, indicating the formation of 1:1 and 1:2 (M:L) complexes only.

The conductimetric titration curves for the complexes Ln<sup>3+</sup>–BAAH derivatives and Ln<sup>3+</sup>–DBMAH derivatives show two breaks at molar ratios of 1:1 and 1:2 indicating the formation of two types of complexes in solution with stoichiometric ratios of 1:1 and 1:2 (M<sup>3+</sup>:L). The increase in conductance during titration may be attributed to the imprisonment of the metal ion in different complexes and the release of an equivalent amount of H<sup>+</sup> ions of higher mobility and, hence, a pronounced increase in conductance. The above mentioned stoichiometric ratios, 1:1 and 1:2 (M<sup>3+</sup>:L), are in accordance with the pH-metric titration results.

*Correlation between the properties of the central ion and the stability of the complexes*

*The electronic configuration of the central ion*

The lanthanide ions differ from each other in the number of electrons in the 4f orbitals which are effectively shielded from interaction with the ligand by electrons in the 5s and 5p orbitals. Hybridisation would normally involve unoccupied higher energy orbitals, e.g. 5d, 6s, 6p, and this can only be expected with the most strongly coordinating ligands. Lanthanides, therefore, normally form ionic compounds. The possibility of covalent interaction, however, cannot be completely excluded, as reported in the case of acetylacetonone chelates of lanthanides [17].

If the bonds are ionic, the Born relation,  $E = Z^2/2r[1 - 1/D]$ , should hold for the energy change on complexation of a gaseous ion of charge  $Z$  and radius  $r$  in a medium of dielectric constant  $D$ . Because the stability constant is directly related to this energy, the  $\log K$  values should increase linearly with  $Z^2/r$ . In the present investigation, the plot of  $Z^2/r$  versus  $\log K_1$  ( $\log \beta_1$ ) values of the investigated lanthanide complexes of BAAH and DBMAH derivatives do not exhibit a linear relation. The probable explanation for this non-linearity could be that the assumption concerning the ionic character of the metal–ligand bond on which the linearity is based

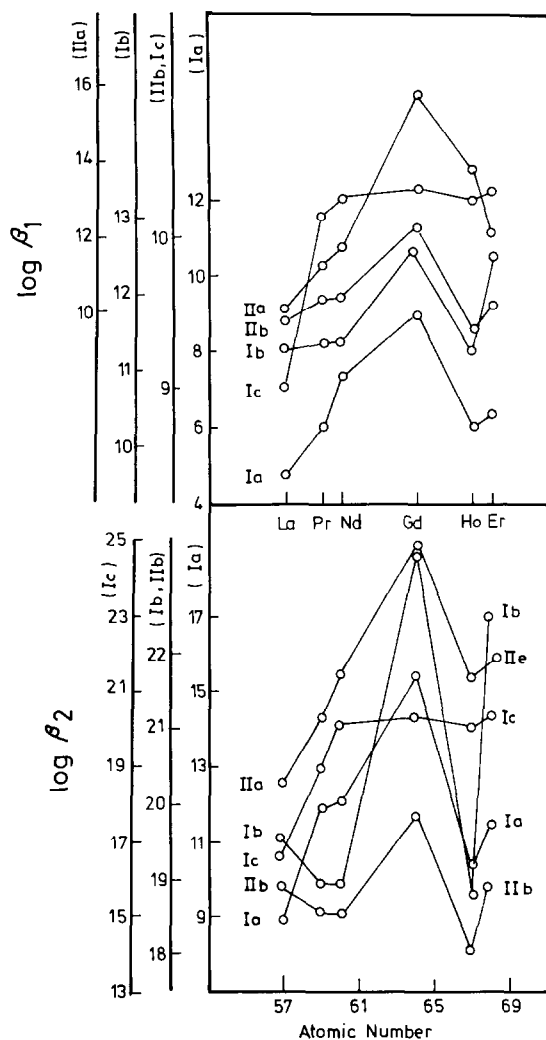


Fig. 1. Relation between the stability constants  $\log \beta_1$  and  $\log \beta_2$  of  $\text{La}^{\text{III}}$ ,  $\text{Pr}^{\text{III}}$ ,  $\text{Nd}^{\text{III}}$ ,  $\text{Gd}^{\text{III}}$ ,  $\text{Ho}^{\text{III}}$  and  $\text{Er}^{\text{III}}$  complexes with Ia, Ib, Ic, IIa and IIb, and the atomic number of the lanthanide ions.

is not valid. The other probable causes are that the coordination number of metal ion is higher than six, and the steric effect.

The stability constants of trivalent La, Pr, Nd, Gd, Ho and Er ions with BAAH and DBMAH derivatives *o*-OH (Ia), *o*-COOH (Ib), *o*-OCH<sub>3</sub> (Ic), *o*-OH (IIa) and *o*-COOH (IIb), exhibit an increase with the increase in atomic number and the decrease in ionic radius, up to gadolinium, and then a decrease in the stability constant takes place for  $\text{Ho}^{\text{III}}$  and  $\text{Er}^{\text{III}}$  (Figs. 1 and 2). The relative increase in stability constants of the lanthanide-ion complexes from La to Gd is in agreement with the expected trend of the

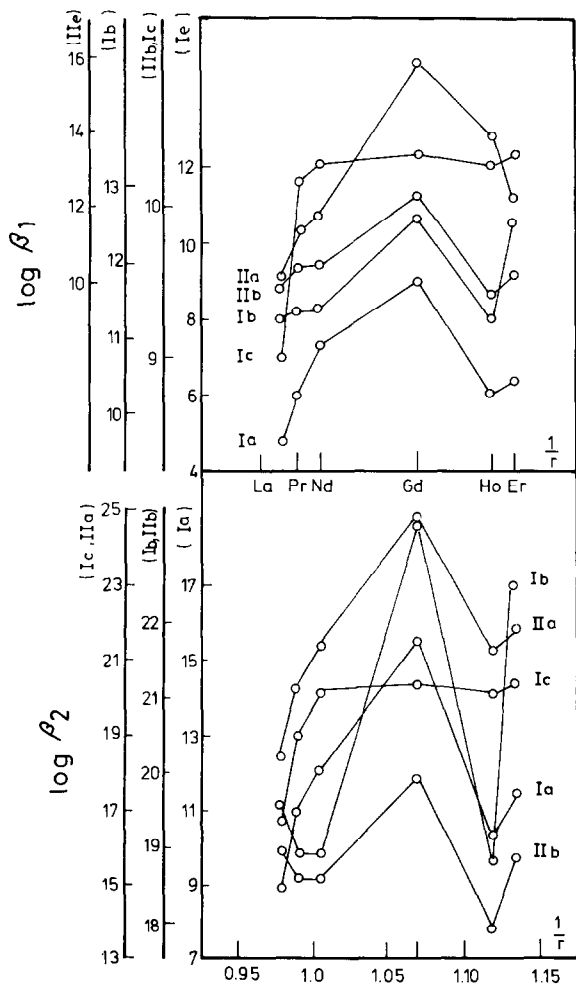


Fig. 2. Relation between the stability constants  $\log \beta_1$  and  $\log \beta_2$  of  $\text{La}^{\text{III}}$ ,  $\text{Pr}^{\text{III}}$ ,  $\text{Nd}^{\text{III}}$ ,  $\text{Gd}^{\text{III}}$ ,  $\text{Ho}^{\text{III}}$  and  $\text{Er}^{\text{III}}$  complexes with Ia, Ib, Ic, IIa and IIb, and the ionic radius of the lanthanide ions.

simple electrostatic model [18]. The situation for the heavier lanthanides, Ho and Er, is different and cannot be explained by the possible existence of the crystal-field effect. The relative order of stability constants is found, in general, to be:  $\text{La}^{\text{III}} < \text{Pr}^{\text{III}} < \text{Nd}^{\text{III}} < \text{Gd}^{\text{III}} > \text{Ho}^{\text{III}} < \text{Er}^{\text{III}}$ .

#### *Ionization potential and electronegativity of the central ion*

In complex formation, the electrons lost in the ionization process are gained from the donor atoms. The ionization potential can therefore be regarded as a direct measure of the electron affinity of the metal ion and a correlation could be expected between the stability of the complexes and the

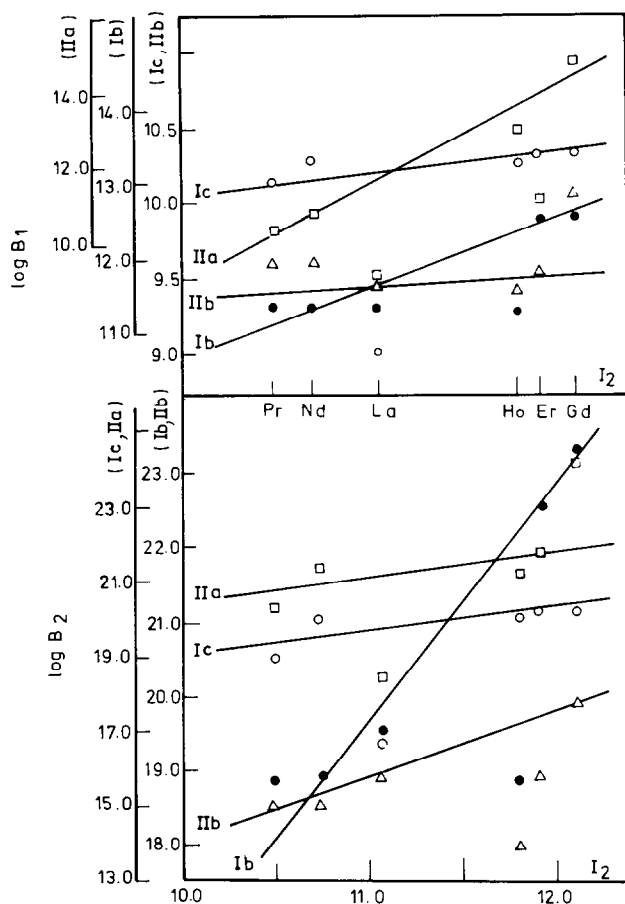


Fig. 3. Relation between the stability constants  $\log \beta_1$  and  $\log \beta_2$  of the trivalent  $\text{La}^{\text{III}}$ ,  $\text{Nd}^{\text{III}}$ ,  $\text{Gd}^{\text{III}}$ ,  $\text{Ho}^{\text{III}}$  and  $\text{Er}^{\text{III}}$  complexes with Ib, Ic, IIa and IIb, and the second ionization potential  $I_2$  of the lanthanide ions.

ionization potential of the metal. The relation between  $\log \beta_1$  and  $\log \beta_2$  of the tripositive lanthanide ion (La, Pr, Nd, Gd, Ho and Er) complexes with *o*-OH (Ia), *o*-COOH (Ib), *o*-OCH<sub>3</sub> (Ic), *o*-OH (IIa) and *o*-COOH (IIb), and the ionization potential are represented in Fig. 3, where straight lines are obtained indicating the increase of  $\log \beta_1$  or  $\log \beta_2$  as the second ionization potential increases.

Many authors have established relationships between the electronegativities of the metal ions and the stability of the complexes [19–22]. The stability constants ( $\log \beta_1$  and  $\log \beta_2$ ) of the complexes as a function of the electronegativities of the metal ions have been studied. The trend indicates that the stability constants of the investigated complexes mostly increase with the increase in the electronegativities of the metal ions (La–Gd).

TABLE 2

Elemental analyses of **Ib**, **IIb** and **Ic** complexes with some lanthanide ions

(M:L)	Formula	C%	H%	N%	M%
		Calc. (found)	Calc. (found)	Calc. (found)	Calc. (found)
<b>Complexes of Ib</b>					
(1:1)	La(C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> )(H <sub>2</sub> O) <sub>3</sub> (OH)	39.39 (39.56)	3.67 (4.00)	5.40 (5.21)	26.81 (27.10)
(1:1)	Pr(C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> )(H <sub>2</sub> O) <sub>5</sub> (OH)	36.69 (35.20)	4.14 (4.50)	5.03 (4.75)	25.34 (24.88)
(1:1)	Nd(C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> )(H <sub>2</sub> O) <sub>4</sub> (OH)	37.69 (37.50)	3.90 (4.50)	5.17 (5.10)	26.64 (26.68)
(1:1)	Gd(C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> )(H <sub>2</sub> O) <sub>3</sub> ·3H <sub>2</sub> O (OH)	34.56 (34.60)	4.22 (4.00)	4.73 (4.55)	26.64 (26.24)
(1:1)	Er(C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> ·4H <sub>2</sub> O (OH)	33.98 (33.50)	4.16 (4.00)	4.65 (4.32)	27.86 (27.20)
<b>Complexes of IIb</b>					
(1:2)	La(C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O)	58.73 (58.90)	3.66 (4.10)	6.22 (5.90)	15.45 (15.20)
(1:2)	Pr(C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub>	56.35 (56.60)	3.85 (4.20)	5.97 (5.60)	15.03 (14.70)
(1:2)	Nd(C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub>	56.15 (56.30)	3.83 (4.30)	5.96 (5.70)	15.34 (15.60)
(1:2)	Gd(C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O)	55.85 (57.90)	3.60 (4.40)	5.92 (5.80)	17.69 (17.50)
(1:2)	Er(C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	55.85 (55.70)	3.60 (3.70)	5.92 (5.70)	17.69 (17.90)
<b>Complexes of Ic</b>					
(1:2)	La(C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (OH)	51.98 (51.80)	4.58 (4.10)	7.13 (6.9)	17.70 (18.00)
(1:1)	Gd(C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> )(OH) <sub>2</sub>	42.04 (43.20)	3.71 (3.80)	6.17 (5.80)	34.69 (35.00)
(1:1)	Er(C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> )(H <sub>2</sub> O)(OH) <sub>2</sub>	39.40 (39.20)	4.25 (4.10)	5.41 (5.20)	32.33 (32.50)
(1:2)	Tm(C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ·(H <sub>2</sub> O)(OH)	51.19 (51.40)	4.40 (4.80)	7.03 (6.80)	21.19 (21.30)
(1:2)	Lu(C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ·(H <sub>2</sub> O) <sub>2</sub> (OH)	48.63 (47.40)	4.76 (4.50)	6.67 (6.30)	20.85 (20.60)

The solid complexes were prepared by reacting 1:1 and 1:2 stoichiometric proportions of Ln<sup>3+</sup> and the ligands **Ib**, **Ic** and **IIb**. The hot mixture was stirred and left for 30 minutes on a steam bath, then dilute ammonium hydroxide was added dropwise with stirring. At pH values in the range 8–9.50, the solid complexes precipitated, and were collected and washed with cold ethanol. The resulting complexes were analysed for C, H, N and



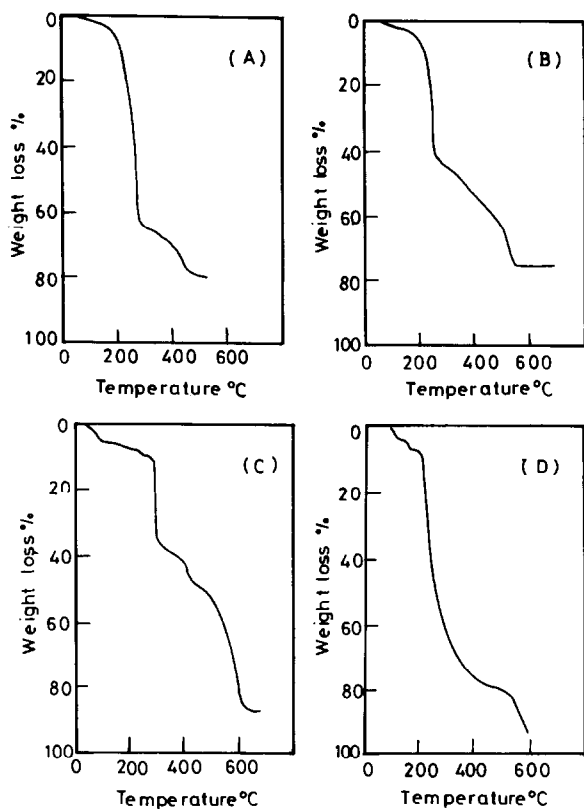


Fig. 4. Thermogravimetric analysis curves of the complexes La-Ic (A), Lu-Ic (B), Gd-Ib (C) and Er-Ib (D).

metal content [23]. The results are listed in Table 2. It should be noted that only 1:2 complexes of trivalent lanthanide ions La, Pr, Nd, Gd, Ho and Er with *o*-COOH (IIb) were isolated even when mixed with the ratio required for 1:3 complexes, while only 1:1 lanthanide complexes of *o*-COOH (Ib) were isolated even when mixed with the ratio required for 1:2 complexes. Both 1:1 and 1:2 complexes could be isolated for *o*-OCH<sub>3</sub> (Ic) with trivalent lanthanide ions La, Gd, Er, Tm and Lu.

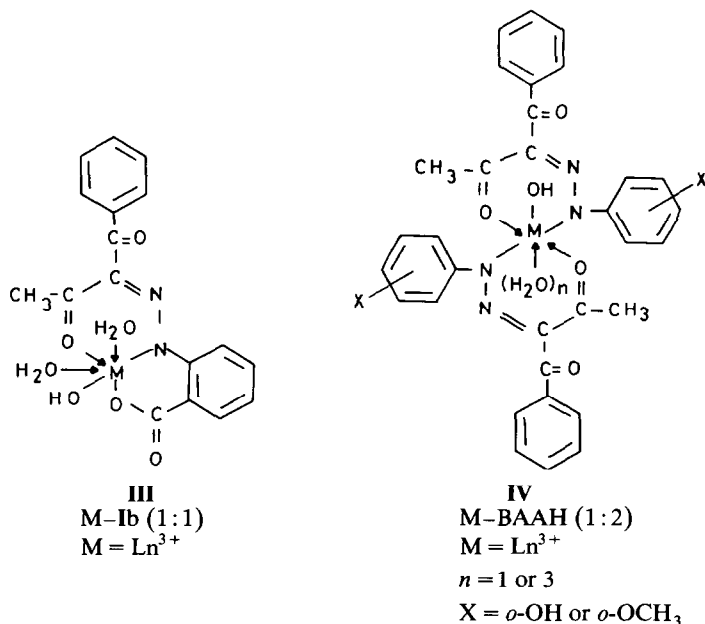
The thermogravimetric curves (Fig. 4) exhibit a weight loss of 9.20% (Gd<sup>3+</sup>-Ib), 6.0% (Er<sup>3+</sup>-Ib), 4.4% (La<sup>3+</sup>-Ic) and 4.00% (Lu-Ic) equivalent to 3, 2, 2 and 2 molecules of water, respectively, within the temperature range 125–250 °C (Table 3) which indicates the presence of coordinated water molecules. On the other hand, the weight loss below 125 °C, in Gd<sup>3+</sup>-Ib and Er<sup>3+</sup>-Ib, corresponds to the water molecules of hydration.

The nature of the bonding of the ligands to the Ln<sup>3+</sup> ions was explored by investigating the IR spectra of the complexes compared to those of the free ligands. The spectra of the lanthanide chelates of BAAH and DBMAH

derivatives are compatible with the structure that would result if the chelated hydrogen of the ligand is replaced by the lanthanide ion. Thus the position of the free carbonyl bands of the ligand is marginally altered in the spectra of their lanthanide chelates: instead of being at  $1620\text{ cm}^{-1}$  (due to the hydrogen-bonded carbonyl), it is observed at around  $1550\text{ cm}^{-1}$ , assignable to  $\nu_{\text{C=O}\cdots\text{M}}$  [20]. In addition to these metal–oxygen stretching and vibrational modes, coupled with ring deformation,  $\nu_{\text{M-O}} + \delta$  (ring), observed at about  $650\text{ cm}^{-1}$ , both  $\text{BAAH-Ln}^{3+}$  and  $\text{DBMAH-Ln}^{3+}$  complexes exhibit a broad band within the wavenumber range  $3500\text{--}3400\text{ cm}^{-1}$ , attributed to the stretching frequency of water molecules, while the bands observed in the ranges  $1110\text{--}1075\text{ cm}^{-1}$  and  $860\text{--}830\text{ cm}^{-1}$  were attributed to  $\delta_{\text{OH}}$  and  $\gamma_{\text{OH}}$  of the bonded water molecules.

Confirmation of the results obtained from the IR spectra was obtained by considering the changes in the NMR spectrum of  $\text{La}^{3+}\text{-Ic}$  compared with that of Ic. The NMR spectrum of Ic exhibits a singlet in the range  $11\text{--}12.70$  ppm with an integration equivalent to 1 proton. This band is assigned to the ionizable proton of the  $\text{-NH}$  group; this is demonstrated by its disappearance following deuteration. The NMR spectrum of the  $\text{La-Ic}$  complex does not show this low-field signal, thus confirming that the chelated hydrogen is replaced by  $\text{La}^{3+}$  ion.

Thus the structure of the 1 : 1 and 1 : 2 ( $\text{M}^{3+} : \text{L}$ ) complexes of  $\text{Ln}^{3+}$  with Ib and IIb may be represented as shown below.

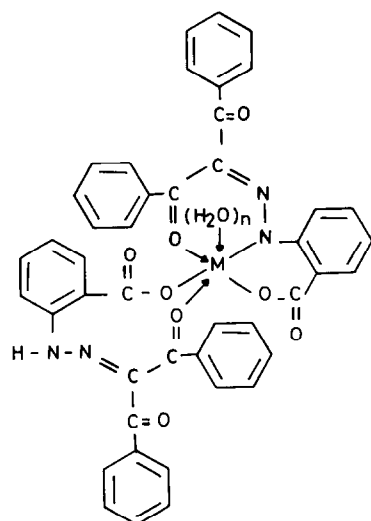


The structure of the 1 : 2 ( $\text{M} : \text{L}$ ) complexes of  $\text{Ln}^{3+}$  with BAAH and

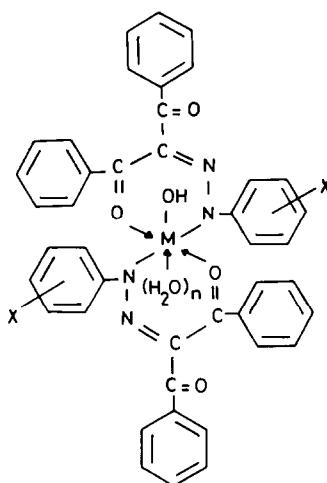
TABLE 3  
Thermogravimetric analysis of some solid complexes

Complex [M:L]	Weight loss (%)		Temperature range (°C)	No. of coordinated H <sub>2</sub> O molecules
	Calc.	Found		
Gd <sup>3+</sup> (Ib) (H <sub>2</sub> O) <sub>3</sub> (1:1)	9.18	9.20	110–250	3.00
Er <sup>3+</sup> (Ib) (H <sub>2</sub> O) <sub>2</sub> (1:1)	6.17	6.00	125–225	2.00
La <sup>3+</sup> (Ic) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (1:2)	4.59	4.40	125–210	2.00
Lu <sup>3+</sup> (Ic) (H <sub>2</sub> O) <sub>2</sub> (1:2)	4.49	4.00	110–225	2.00

DBMAH derivatives may be represented as shown below.



**V**  
M-IIb (1:2)  
M = Ln<sup>3+</sup>  
n = 1 or 3



**VI**  
M-DBMAH (1:2)  
M = Ln<sup>3+</sup>  
n = 1 or 3  
X = o-OH

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