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THERMOGRAVIMETRIC, POTENTIOMETRIC, CONDUCTIMETRIC AND SPECTROMETRIC STUDIES ON LANTHANIDE COMPLEXES WITH SOME HYDROXYNAPHTHOIC ACID AZO DYES

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ABSTRACT

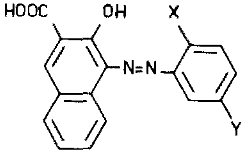
Potentiometric, conductimetric, IR, NMR and TGA studies have been carried out on the complexes of trivalent yttrium, lanthanum, praseodymium, neodymium, samarium, gadolinium and erbium with some azo derivatives of 3-hydroxy-2-naphthoic acid. The ionization constants of the reagents and the formation constants of their metal complexes have been determined potentiometrically by Sarin's method. Complexation has also been studied by a conductimetric titration method and the solid complexes formed were separated, analysed and their structures have been elucidated by IR, NMR and TGA studies.

INTRODUCTION

3-Hydroxy-2-naphthoic acid azo dyes are of interest because of their biological activity [1,2] and dyeing properties for a variety of fabrics [3,4]. They have been used as analytical reagents; values of stability constants of some transition and lanthanide metal complexes have been reviewed [5,6]. The nature of the bond between the central lanthanide ion and the ligand donor groups of some chelating agents was discussed [7]. Necas et al. [8] showed that the thermal stability of substituted phenylazo-3-hydroxy-2-naphthoic acid is correlated with the resonance and inductive effects of the substituent and the azo group.

In the present study, the stability constants of yttrium, lanthanum, praseodymium, neodymium, samarium, gadolinium and erbium trivalent ions with some azo derivatives of 3-hydroxy-2-naphthoic acid have been determined in 50% or 70% ethanol–water medium at 27 ° C ± 0.1 ° C and 0.1 ionic strength using the Sarin and Munshi technique [9]. Conductimetric titrations were carried out to yield further insight into the stoichiometry of the complexes in solutions. IR, NMR and TGA of some solid chelates were performed to throw some light on their structures.

The azo dyes used in this investigation have the general formula:



I

where X and Y are: H, H (**Ia**), COOH, H (**Ib**), OH, H (**Ic**), OH, SO_3Na (**Id**) and $AsO(OH)_2$, H (**Ie**).

EXPERIMENTAL

All chemicals used in this study were of the highest purity available (BDH). The 4-(arylazo)-3-hydroxy-2-naphthoic acid derivatives (**I**) were prepared by coupling 3-hydroxy-2-naphthoic acid with the corresponding diazotized amine in sodium hydroxide [10]. The purities of the resulting azo dyes were confirmed by elemental analyses.

Stock dye solutions (10^{-3} M) were prepared in ethanol. **Ia** and **Ic** were dissolved in 20% dioxane–ethanol and 10% DMF–ethanol solutions, respectively. 10^{-3} M metal perchlorate solutions were prepared [11] and standardized with EDTA using arsenazo I as indicator [12].

Three mixtures of total volume 50 ml were prepared as follows.

(a) 3 ml 0.1 N $HClO_4$ + 5 ml 1 M $NaClO_4$ + X ml ethanol to attain the required alcohol percentage. The volume being completed with distilled water up to 50 ml.

(b) 3 ml 0.1 N $HClO_4$ + 5 ml 1 M $NaClO_4$ + 20 ml ethanolic ligand solution + $X - 20$ ml ethanol and distilled water up to 50 ml.

(c) 3 ml 0.1 N $HClO_4$ + 5 ml 1 M $NaClO_4$ + 20 ml ligand solution + 5 ml metal perchlorate solution + $X - 20$ ml ethanol and distilled water up to 50 ml.

The above three mixtures were titrated potentiometrically against 0.2 N KOH using a pH meter (Orion Research model 701 A digital Ionalyzer) at 27°C ± 0.1°C. Correction of the pH-meter readings for different alcohol percentages was made [13]. The titrations were performed twice to test the reproducibility. The average number of protons $\bar{n}_A$ associated with the ligand 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 the equations given by Sarin [9]. The methods used for calculating successive stability constants were, interpolation at the half $\bar{n}$ value (A), correction term (B), successive approximation (C) and mid-point (D) methods [14]. All calculations were run using a programable calculator (Casio 702 P FX).

Conductimetric titrations of 50 ml 4×10^{-5} M metal ion solution with 10^{-3} M ligand solution were carried out using a D 812 conductivity meter model LBR at a frequency of 3 kHz s^{-1}. The bridge was supported by a platinized platinum black electrode.

The solid complexes were prepared by reacting 1 : 1 and 1 : 2 stoichiometric proportions of lanthanoid(III) ions and the ligands (**Ig**)–(**Ie**). They were subjected to elemental analysis (see Table 6), IR, NMR spectroscopy and TGA.

The IR spectra of free ligands and their metal complexes were recorded using a Pye Unicam SP 1000 spectrophotometer, as KBr pellets.

NMR spectra were performed in dimethyl sulphoxide (DMSO) with the aid of an EM. 390–90 MHz NMR spectrometer. TGA of some samples were obtained using a Du Pont 1090 thermal analyser.

RESULTS AND DISCUSSION

Ligands used in this study did not undergo hydrolysis under the experimental conditions described above. This was indicated by rapid attainment of equilibrium during the titration and by the absence of any significant drift in the pH readings.

$\bar{n}_A$ values were calculated at various pH values from the titration curves using mixtures (a) and (b). The formation curves relating pH and the corresponding $\bar{n}_A$ values are plotted. The ionization constants pK(COOH) and pK(OH) of the ligands were evaluated by the half-integral (i.e. at $\bar{n}_A = 0.5$, 1.5, 2.5 and 3.5) method as well as from the plot of $\log\{\bar{n}_A/(1 - \bar{n}_A)\}$, $\log\{(\bar{n}_A - 1)/(2 - \bar{n}_A)\}$, $\log\{(\bar{n}_A - 2)/(3 - \bar{n}_A)\}$ and $\log\{(\bar{n}_A - 3)/(4 - \bar{n}_A)\}$ vs. pH values for first, second, third and fourth ionization constants respectively. These values are listed in Table 1.

The ionization steps may be assigned to the COOH and OH groups on the naphthalene ring and the OH, COOH and $AsO(OH)_2$ groups on the phenyl moiety when they are present. The sequence of ionization as listed in Table 1 may be attributed to hydrogen bond formation with different OH groups since the difference in pK values and consequently in the free energy change $\Delta G°$ is close to the energy required for hydrogen bond formation.

From the titration curves of mixtures (b) and (c), $\bar{n}$ and pL values were calculated and then plotted against each other; thus the formation curves of the metal complexes are produced. The $\bar{n}$ values extend to 2.0 for all metal complexes at an approximate pH of 7–8 above which the hydrolysis region of the rare earth metal ions starts. Hence 1 : 1 and 1 : 2 (M : L) complexes are formed. The successive stability constants $\log \beta_n$ were calculated using the methods described earlier to refine the values obtained by the half-integral method. Values of $\log \beta_n$ are recorded in Table 2.

TABLE 1

Ionization constant values of 3-hydroxynaphthoic azo dyes (**Ia**–**Ie**) in ethanol–water mixtures

Dye	X	1st method			2nd method			Mean pK		
		p*K*(COOH)	p*K*(OH)	p*K*(X)	p*K*(COOH)	p*K*(OH)	p*K*(X)	p*K*(COOH)	p*K*(OH)	p*K*(X)
Ia	H –	4.65	10.80	–	4.68	10.60	–	4.67	10.70	–
Ib	*o*-COOH	5.85	10.45	4.60	5.88	10.48	4.62	5.87	10.47	4.61
Ic	*o*-OH	3.95	11.45	8.30	3.97	11.49	8.32	3.96	11.47	8.31
Id	2-OH-5-SO_3H	5.50	11.95	9.95	5.54	11.94	10.02	5.52	11.95	9.99
Ie	*o*-AsO(OH_2)	5.70	11.65	3.70, 9.00	5.71	11.74	3.69, 8.98 [b]	5.70	11.69	3.69, 8.99 [b]

1st method: proton-ligand formation curve method.

2nd method: $\log\frac{\bar{n}_A}{1-\bar{n}_A}$, $\log\frac{\bar{n}_A-1}{2-\bar{n}_A}$, $\log\frac{\bar{n}_A-2}{3-\bar{n}_A}$, or $\log\frac{\bar{n}_A-3}{4-\bar{n}_A}$ versus pH method.

[a] For **Ia** and **Ic** 70% ethanol is used, where for **Ib**, **Id** and **Ie** 50% ethanol is used.

[b] 1st and 2nd ionization constants of the arsanilic (OH) groups.

TABLE 2

Collective data of log β_1 and log β_2 values for chelates of 4-phenylazo-3-hydroxy-2-naphthoic acid derivatives (**Ia**–**Ie**) with some lanthanoid metal ions

M(III) ion	log β_1				log β_2				
	A	B	C	Mean	A	B	C	D	Mean
Complexes with **Ia**									
Y	6.92	6.34	6.93	6.73	13.13	13.28	13.25	13.25	13.23
La	7.50	7.41	7.46	7.45	13.75	13.71	13.77	13.80	13.75
Pr	10.00		10.00	10.00	19.50		19.52	18.60	19.21
Nd	9.20	8.89	9.12	9.07	15.95	15.87		16.40	16.07
Sm	9.45	9.50	9.43	9.46	17.35	17.47	17.27	17.80	17.47
Er	8.20	8.01	8.18	8.13	15.30	15.20	15.31	15.00	15.20
Complexes with **Ib**									
Y	9.90	9.22	9.94	9.68	16.65	15.50	16.67		16.27
La	11.60	11.20	11.50	11.43	18.45	18.16	18.33		18.31
Pr	9.90		9.42	9.66	16.30		15.80		16.05
Nd	11.80	11.91	11.76	11.82	19.25	21.17	19.25		19.89
Sm	11.10		11.07	11.08	17.95		17.89		17.92
Gd	11.10			11.10	17.70				17.70
Er	10.80		10.77	10.78	17.85		17.83		17.84
Complexes with **Ic**									
Y	10.40	10.47	10.46	10.44	17.35	17.31	17.34	17.90	17.47
La	10.75	10.80	10.84	10.79	19.85	19.82	19.92	20.00	19.89
Pr	10.20	10.28	10.23	10.23	18.80	18.98	18.91	19.20	18.97
Sm	9.55	9.56	9.52	9.54	17.15	17.15	17.14	17.00	17.11
Gd	9.95	9.92	9.95	9.94	17.55	17.74	17.64	18.20	17.78
Er	9.95	9.75	9.90	9.86	17.30	17.23	17.27	17.30	17.27
Complexes with **Id**									
Y	9.85			9.85					
La	10.00	10.00	10.03	10.01	16.50	16.75	16.58	17.50	16.83
Pr	10.20	10.35	10.24	10.26	16.80	17.46	16.85	17.60	17.17
Nd	10.50	10.50	10.50	10.50	17.25	17.78	17.16	18.70	17.72
Sm	10.50	10.16	10.34	10.33	17.55	17.40	17.36	17.40	17.42
Gd	9.80	9.76	9.88	9.81	17.25	17.27	17.32	17.10	17.23
Er	19.65	10.45	10.58	10.56	17.20	17.32	18.13	17.30	17.48
Complexes with **Ie**									
Y	9.10	9.13	9.11	9.11	15.65	15.71	15.63	15.20	15.54
La	8.10	7.53	8.19	7.94	13.90	13.06	13.98	13.70	13.66
Pr	9.25	8.81	9.33	9.13	15.60	15.48	15.80	15.50	15.59
Nd	8.85	8.37	8.83	8.68	14.65	14.17	14.73		14.51
Sm	9.65		9.65	9.65	16.25		16.25		16.25
Gd	8.20	8.01	8.14	8.11	14.85	14.04	14.30	14.00	14.17

At 30 °C and $U = 0.10$ M.

Where A, interpolation at half n values method; B, correction-term method; C, successive approximations method; D, mid-point method.

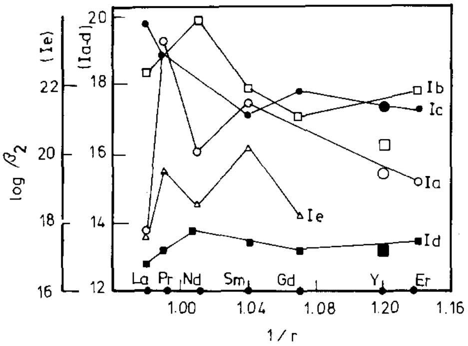


Fig. 1. Relationship between the stability constants (log β_2) and the ionic radii of complexes of yttrium, lanthanum, praseodymium, neodymium, samarium, gadolinium and erbium with (**Ia**–**Ie**).

Correlations between atomic number Z, ionic radius r, electronegativity EN and the second ionization potential I_2 of the lanthanoids under investigation with the stability constants of their complexes [Figs. (1–3)] revealed the following relationships.

(1) For one and the same ligand, the general increase in the stability constants with decrease in crystal radius that we predicted is verified. However, the data show that this increase is invariable in the region from lanthanum through samarium with a break or discontinuity occurring at gadolinium which may be interpreted as corresponding to either the stability of the half-filled orbital ($4f^7$) arrangement of the gadolinium(III) ion or the changes in ionic radii [15] centring at the gadolinium(III) ion which allows a change in coordination number of the cations.

(2) The stability constants of the complexes increase with increasing EN for **Ia, Ib, Id** and **Ie** till samarium, then decrease for gadolinium and erbium. Lanthanum and praseodymium complexes with **Ic** show higher stability

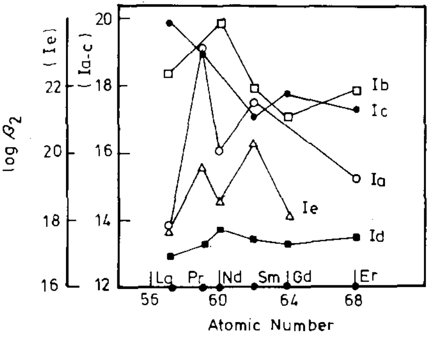


Fig. 2. Relationship between the stability constants (log β_2) of complexes and the atomic number of lanthanum, praseodymium, neodymium, samarium, gadolinium and erbium with (**Ia**–**Ie**).

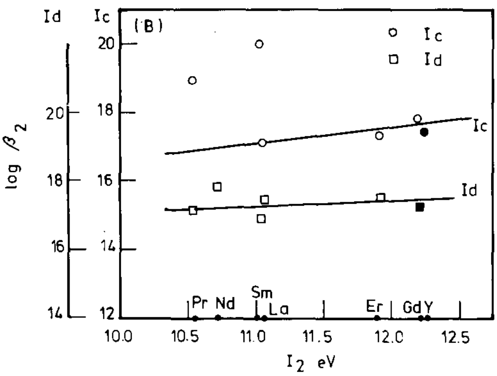


Fig. 3. Relationship between the stability constants log β_2 of complexes and the second ionization potentials I_2 of metals.

constants with respect to their complexes with other ligands. This may be attributed to the introduction of the phenolic OH group in the *ortho* position with respect to the azo group.

(3) Correlations between stability constants and the basicity of the ligands (Fig. 4) give straight lines of non-unit slopes.

(4) The plots of Z^2/r vs. log β_n values do not exhibit linear increases. A probable explanation of the non-linearity could be that the assumption of an ionic character for the metal–ligand bond on which the linearity relation depends is not valid. Other possible causes are (i) the coordination number of the metal ion being greater than six, and (ii) a steric factor being present.

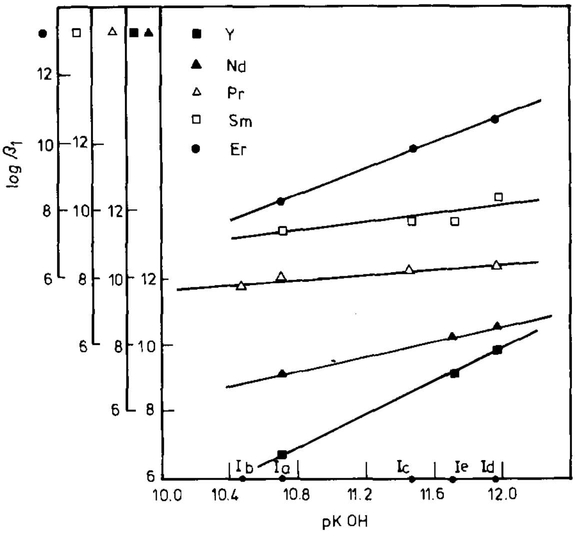


Fig. 4. Relationship between log β_1 and pK(OH) for the complexes investigated.

(5) Yttrium lies in its expected position with respect to its EN value for **Ic**, **Id** and **Ie** (between gadolinium and erbium ions), but for **Ia** and **Ib** complexes, it shows low stability constant values similar to lighter lanthanoids.

Conductimetric titration curves of all ligands (**Ia**–**Ie**) with all metal ions under investigation exhibit inflexion points indicating the formation of 1 : 1 and 1 : 2 (M : L) complex species, except that for yttrium and lanthanum ions with **Ib** and **Ie** only 1 : 1 complex species are formed. The increase in conductance during titration is attributed to the displacement of the H^+ of the ligand with the metal ion [16].

INFRARED SPECTRA

The IR spectral bands of some solid chelates of (**Ia**–**Ie**) are given in Table 3. A comparison of those of the ligands and the complexes indicate that a lot of changes are observed on complexation with lanthanoid(III) ions. Some important changes are described below.

TABLE 3

Assignment of IR bands of some solid chelates of (**Ia**–**Ie**) ligands

Complex	C=O	ν OH	δ OH	N=N	M–O
La–**Ia** 1:1		3500 b	1125 vw	1490 b	585
La–**Ia** 1:2		3400 b	1135	1475 b	595 w
La–**Ib** 1:1		3500 vb	1090 w	1425	595 s
La–**Ib** 1:2		3500 vb	1105 w	1425	595 s
La–**Ic** 1:1		3450 b	1115 w	1480	600 s
La–**Ic** 1:2		3500 b	1120 w	1480	600 w
La–**Id** 1:1	1665 vw	3450 b	1110 vw	1450	
La–**Id** 1:2	1665 vw	3450 b	1110 vw	1450	
La–**Ie** 1:1		3400	1125 vw	1450	595
La–**Ie** 1:2		3500		1445	590
Y–**Ic** 1:1		3450 b	1120 sp	1450 sh	600, 630 sp
Y–**Ic** 1:2		3500 vb		1450	
Pr–**Ic** 1:1		3200 b	1100		600 w, sp
Pr–**Ic** 1:2		3500 b	1095		
Nd–**Ic** 1:1		3500 vb	1110	1450 sh	600 w
Nd–**Ic** 1:2			1110	1450 sh	600 s, 425 m
Sm–**Ic** 1:1		3500 b	1095 s	1460 w, sp	
Sm–**Ic** 1:2		3400 vb	1110 w, sp	1460 sh	595, 430
Gd–**Ic** 1:1		3475 b	1110	1470	600
Gd–**Ic** 1:2		3500	1195	1460	
Er–**Ic** 1:1		3400 vb	1110 vw	1470	600 w
Er–**Ic** 1:2		3500 b	1110	1470	600 m

Key: vb, very broad; b, broad; s, strong; m, medium; w, weak; sh, shoulder; sp, split.

(a) Bands at 3500 cm^{-1} in the ligand spectra, which are assigned to the ν_{OH} mode of the ligands disappear from the spectra of the complexes indicating deprotonation of the OH group and coordination through the oxygen atom. Very broad bands are observed in the region 3200–3500 cm^{-1} which may be assigned to the ν_{OH} of water molecules coordinated to the central metal ion. Other bands appearing in the spectra of the ligands at 1230–1210 cm^{-1} for ν_{C-O} asymmetric vibration, 1120–1110 cm^{-1} for δ_{OH} and 805–820 cm^{-1} for γ_{OH} also suffer great change on chelation where the first splits, the second shifts and the third disappears.

(b) Disappearance of the band at 1720–1760 cm^{-1} which is assigned to the stretching frequency of the C=O group indicates the participation of the COOH group in chelation. In the case of **Ib** (*o*-COOH) the disappearance of the unified intense band at 1760 cm^{-1} corresponding to the two COOH groups is explained by participation of one of them in chelation and conversion of the second to a salt characterized by a new band at 1590 cm^{-1}.

(c) No, or slight, shift is associated with the N=N stretching frequency band position in the solid chelates appearing at 1430–1450 cm^{-1}. This can be taken as a criterion of non-participation of the azo group in chelation. These slight changes in the N=N band in the spectra of chelates may be attributed to the change in the electronic charge distribution resulting from chelation with the OH group lying ortho to the azo group.

(d) All the complexes investigated show a band at 585–600 cm^{-1} characteristic of the M–O dative bond [17], which is not obviously present in the spectra of the free ligands, resulting from the interaction between the carboxylic and hydroxylic oxygen atoms and the metal ion. However, no bands due to an M–N bond could be assigned.

NUCLEAR MAGNETIC RESONANCE SPECTRA

Substantial support for the results obtained from the IR spectra is gained by considering the changes in the NMR spectra of some chelates in comparison with those of the ligands. The study was limited to lanthanoid complexes being paramagnetic.

The spectra of all ligands exhibit a single band at δ 2.5 ppm which is assigned to the CH_3 of the solvent. Aromatic protons of the phenyl and naphthyl nuclei display a multiplet signal at 7.2–8.2 ppm. Integration curves show 10 protons for **Ia**, 9 protons for **Ib, Ic** and **Ie** and 8 protons for **Id**. Signals due to OH and COOH are shifted down field because of intermolecular and intramolecular hydrogen bonding [18] and hence display signals at 8.5–8.7 ppm (Table 4).

For the metal chelates studied, the disappearance of the multiplet signal of aromatic naphthyl protons and the remaining of the phenyl proton

TABLE 4

Data obtained for NMR spectra of some naphthoic acid derivatives and their lanthanum chelates in DMSO

Compound	δ (ppm)	
	Multiplet	Singlet
Ia	8.2–7.4	2.5, 8.6
Ib	8.2–7.6	2.5, 8.5
Ic	8.2–7.2	2.5, 8.6
Id	8.2–6.8	2.5, 8.7
Ie	8.3–7.3	2.5, 8.6
La–**Ia** (1 : 1)	–	2.5,–, 3.3
La–**Ib** (1 : 1)	singlet at 8.0	2.5,–, 3.3
La–**Ic** (1 : 1)	singlet at 8.7	2.5,–
La–**Id** (1 : 1)	8.7–7.5	2.5,–

signals at 7.9 ppm indicate that the centre of chelation is the naphthyl moiety. This is supported by the disappearance of the proton signals of the COOH and OH groups present on the naphthyl ring.

THERMOGRAVIMETRIC ANALYSIS

TGA of some chelates was performed. The weight loss was measured from the ambient temperature up to 600–800 °C at a rate of 10 °C min^{-1}.

TABLE 5

TGA results of solid chelates of lanthanum

Complex	Weight loss(%)		Temperature range (°C)	Number of H_2O molecules [a]	Metallic residue (%)
	Calculated	Found			
La–**Ia**(1 : 1)					
$La(C_{17}H_{10}N_2O_4)\cdot(OH)\cdot 3H_2O$	10.79	10.80	120–335	3.0	17.00
La–**Ia**(1 : 2)					
$La(C_{17}H_{10}N_2O_4)_2\cdot 2H_2O$	4.76	5.00	120–280	2.0	16.00
La–**Ib**(1 : 1)					
$La(C_{18}H_{12}N_2O_5)\cdot(OH)\cdot 3H_2O$	9.92	9.20	115–350	3.0	33.50
La–**Ib**(1 : 2)					
$La(C_{18}H_{12}N_2O_5)_2\cdot 2H_2O$	4.26	4.20	110–300	2.0	20.00
La–**Ic**(1 : 1)					
$La(C_{17}H_{10}N_2O_4)\cdot(OH)\cdot 3H_2O$	10.46	10.50	100–330	3.0	31.00
La–**Ic**(1 : 2)					
$La(C_{17}H_{10}N_2O_4)_2\cdot 2H_2O$	4.57	5.00	130–280	2.0	25.00
La–**Id**(1 : 2)					
$La(C_{17}H_{10}N_2O_7S)_2\cdot 2Na\cdot 2H_2O$	3.80	4.00	125–240	2.0	28.00
La–**Ie**(1 : 2)					
$La(C_{17}H_{11}N_2O_4As)_2\cdot 2Na\cdot 2H_2O$	4.92	5.00	110–290	2.0	44.00

[a] Coordinated water molecules.

TABLE 6

Elemental analysis of solid complexes

La chelate with	Formula	C (%)		H (%)		N (%)		M (%)	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
La(III) complexes									
Ia (1 : 1)	$La(C_{17}H_{10}N_2O_2)\cdot OH\cdot 3H_2O$	40.79	40.97	3.42	4.30	5.60	5.55	27.78	27.90
Ia (1 : 2)	$La(C_{17}H_{10}N_2O_2)_2\cdot 2H_2O$	54.03	55.50	3.20	4.30	7.42	7.33	18.39	18.45
Ib (1 : 1)	$La(C_{18}H_{12}N_2O_5)\cdot OH\cdot 3H_2O$	39.73	39.50	3.15	3.00	5.15	5.21	25.52	25.30
Ib (1 : 2)	$La(C_{18}H_{12}N_2O_5)_2\cdot 2H_2O$	51.26	49.40	2.99	3.12	6.64	6.60	16.47	16.31
Ic (1 : 1)	$La(C_{17}H_{10}N_2O_4)\cdot OH\cdot 3H_2O$	39.53	39.70	3.32	3.20	5.43	5.36	26.92	26.45
Ic (1 : 2)	$La(C_{17}H_{10}N_2O_4)_2\cdot 2H_2O$	51.88	51.70	3.07	3.10	7.11	7.02	17.63	17.00
Id (1 : 1)	$La(C_{17}H_{10}N_2O_7S)\cdot Na\cdot OH\cdot 3H_2O$	33.00	33.4	2.77	3.20	4.53	4.60	22.44	23.50
Id (1 : 2)	$La(C_{17}H_{10}N_2O_7S)_2\cdot 2Na\cdot 2H_2O$	41.11	40.90	2.44	2.58	5.64	5.70	13.99	14.32
Ie (1 : 1)	$La(C_{17}H_{11}N_2O_4As)\cdot Na\cdot OH\cdot 3H_2O$	31.56	33.90	2.80	2.91	4.33	4.42	21.47	22.00
Ie (1 : 2)	$La(C_{17}H_{11}N_2O_4As)_2\cdot 2Na\cdot 2H_2O$	38.93	37.80	2.50	3.80	5.34	5.25	13.24	13.44
Ic(o-OH) complexes									
Y (1 : 1)	$Y(C_{17}H_{10}N_2O_4)\cdot OH\cdot 3H_2O$	43.77	44.50	3.67	3.70	6.01	5.95	19.08	20.30
Y (1 : 2)	$Y(C_{17}H_{10}N_2O_4)_2\cdot 2H_2O$	55.40	54.90	3.28	3.90	7.61	7.53	12.08	12.12
Pr (1 : 1)	$Pr(C_{17}H_{10}N_2O_4)\cdot OH\cdot 3H_2O$	39.38	39.72	3.31	4.00	5.41	5.35	27.20	28.20
Nd (1 : 1)	$Nd(C_{17}H_{10}N_2O_4)\cdot OH\cdot 3H_2O$	39.13	39.60	3.28	3.10	5.37	5.25	27.66	26.90
Nd (1 : 2)	$Nd(C_{17}H_{10}N_2O_4)_2\cdot 2H_2O$	51.48	49.90	3.05	3.20	7.07	6.95	18.20	19.20
Sm (1 : 1)	$Sm(C_{17}H_{10}N_2O_4)\cdot OH\cdot 3H_2O$	38.67	39.20	3.24	2.50	5.31	5.40	28.51	27.30
Sm (1 : 2)	$Sm(C_{17}H_{10}N_2O_4)_2\cdot 2H_2O$	51.09	51.21	3.03	3.70	7.01	6.94	18.83	19.20
Gd (1 : 1)	$Gd(C_{17}H_{10}N_2O_4)\cdot OH\cdot 3H_2O$	38.18	38.90	3.21	3.60	5.42	5.61	29.43	30.01
Gd (1 : 2)	$Gd(C_{17}H_{10}N_2O_4)_2\cdot 2H_2O$	50.65	49.70	3.00	2.90	6.95	6.88	19.49	20.20
Er (1 : 1)	$Er(C_{17}H_{10}N_2O_4)\cdot OH\cdot 3H_2O$	37.47	37.67	3.14	3.90	5.15	5.22	30.73	29.50
Er (1 : 2)	$Er(C_{17}H_{10}N_2O_4)\cdot 2H_2O$	50.03	49.20	2.97	3.10	6.86	6.75	20.49	21.20

From the TGA curves obtained, the weight loss for each chelate was used in the calculation of the number of water molecules present in each chelate molecule (Table 5).

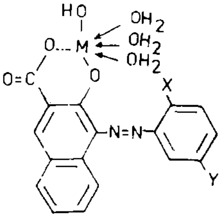
The loss below 100 ° C is attributed to moisture and hygroscopic water. The number of these water molecules ranges from 2 to 3 per chelate molecule.

For the 1 : 1 chelates, three H_2O molecules are coordinated to the metal ion to fulfil the coordination number six and they are expelled within the temperature range of 100–350 ° C, but for 1 : 2 chelates, two H_2O molecules are coordinated per chelate molecule and they are expelled in a temperature range of 100–250 ° C.

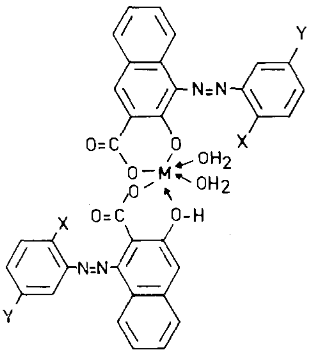
The results obtained are in good agreement with the theoretical values and with those obtained by determination of the metal ion after decomposition of the chelate applying the method described by Macdonald [19], and with the result of elemental analysis (Table 6).

Based on the above results, it can be concluded that, all lanthanoid(III) metal ions show a coordination number of six. For 1 : 1 chelates the first two coordination sites are occupied by the replacement of hydroxyl and carboxyl hydrogen atoms of the naphthalene nucleus. The remaining four sites are occupied by three water molecules and one OH^- ion to achieve electrical neutrality of the complex. For 1 : 2 chelates, the coordination sites are occupied by three covalent bonds supported by the two carboxyl groups and one of the hydroxyl groups and the other three are filled by three coordinate bonds supported by two water molecules and a non-ionized hydroxyl group.

In the light of these findings, the structures of the 1 : 1 and 1 : 2 chelates may be represented by the following formulae:



1:1



1:2

where M≡Y, La, Pr, Nd, Sm, Gd, and Er; X, Y≡H, H (**Ia**), COOH, H (**Ib**), OH, H (**Ic**), OH, SO_3Na (**Id**), AsO_3H Na, H (**Ie**).

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