Thermochimica Acta, 143 (1989) 37–49
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

POTENTIOMETRIC, SPECTROMETRIC, THERMOGRAVIMETRIC, CONDUCTIMETRIC AND MAGNETIC STUDIES OF LANTHANUM COMPLEXES WITH SOME NITROSO NAPHTHOLS

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(Received 6 June 1988)

ABSTRACT

Potentiometric, IR, NMR, TG, DTA, molar conductance and magnetic susceptibility studies have been carried out on complexes of the La(III) ion with some nitroso naphthols. The ionization constants of the reagents and the formation constants of their lanthanum complexes were determined potentiometrically using Sarin's method. The lanthanum complexes formed were separated, analysed and their structures elucidated by IR, NMR, TG, DTA, molar conductance and magnetic susceptibility measurements.

INTRODUCTION

Nitroso naphthols are widely used as analytical reagents. They are capable of forming chelates with a number of transition metal ions [1–4]. The chelates formed are characterized by high stability constants, resulting from the formation of a six-membered ring. The stability constants of some lanthanide complexes with nitroso naphthols have been reviewed previously [5,6].

In the present study, the stability constants of the trivalent lanthanum ion with some nitroso naphthol derivatives were determined in water and in a mixture of ethanol and water at 25 °C and 0.1 ionic strength, using the Sarin and Munshi technique [7]. IR, NMR, TG, DTA, molar conductance and magnetic susceptibility measurements of some lanthanum chelates were performed, to throw some light on their structures.

EXPERIMENTAL

All the chemicals used in this study were of the highest purity available. The ligands nitroso Neville Winther's acid (NNWA), nitroso Schaffer's acid (NSA), nitroso-1-hydroxy-2-naphthoic acid (N1HNA) and nitroso-3-hydroxy-2-naphthoic acid (N3HNA) were prepared by nitrosation of the parent compounds. The nitrosation reactions were carried out by acidifying

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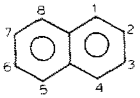
the cooled aqueous solution at 0 °C in sodium hydroxide solution containing an equivalent amount of sodium nitrite with hydrochloric acid [8]. The resulting nitroso compounds were subjected to elemental analysis. These reagents can be represented by the following general formula



Ligand A	1 -OH, 2 -NO, 4 -SO_3Na	NNWA
Ligand B	1 -NO, 2 -OH, 6 -SO_3Na	NSA
Ligand C	1 -OH, 2 -COOH, 4 -NO	N1HNA
Ligand D	2 -COOH, 3 -OH, 4 -NO	N3HNA

Stock nitroso naphthol solutions (10^{-3} M) were prepared. 10^{-3} M lanthanum perchlorate solution was prepared [9] and standardized with EDTA using arsenaso I as the indicator [10]. Three mixtures were prepared according to a method which has been described previously [11], and titrated against standard NaOH solution (0.214 M) using a Chemtrix type 62 pH-meter. For NNWA and NSA, the medium used was water; for N1HNA and N3HNA this was adjusted to be 40% (v/v) with ethanol.

The pH-meter reading was corrected for ethanolic solution [12]. 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 the metal ion, and the free ligand exponent pL were calculated using the equations given by Sarin [7]. Successive stability constants were calculated by (a) interpolation at half $\bar{n}$ value, (b) correction term, (c) successive approximation and (d) mid-point methods [13]. All calculations were performed using a programmable calculator (Casio FX-700 P).

The solid complexes were prepared by reacting 1:1, 1:2 and 1:3 stoichiometric proportions of the lanthanum(III) ion and the ligands. They were then subjected to elemental analysis, IR, NMR spectroscopy, TG, DTA, molar conductance and magnetic susceptibility measurements. The IR spectra of the free ligands and their lanthanum complexes were recorded using a Pye Unicam SP 3-300 spectrometer with KBr discs.

The NMR spectra were obtained using a Varian EM 390–90 MHz NMR spectrometer. The TG and DTA were carried out using an STA 409 Netzsch thermal analyser. Molar conductance was measured using a CM-1K conductivity meter of cell constant 0.975. The magnetic measurements were carried out according to Faraday's methods.

RESULTS AND DISCUSSION

The $\bar{n}_A$ values were calculated, for various levels of pH, from the titration curves. Formation curves relating pH to the corresponding $\bar{n}_A$ values were

TABLE 1

Ionization constants of the nitroso compounds under investigation (A–D)

Compound	1st method [a]		2nd method [b]		Mean pK		Calculated [c]	$-\Delta G^{\ominus}$ (kcal mol^{-1})		Non-nitroso compounds	
	pK_{COOH}	pK_{OH}	pK_{COOH}	pK_{OH}	pK_{COOH}	pK_{OH}	pK_{OH}	COOH	OH	pK_{COOH}	pK_{OH} [d]
A	–	6.56	–	6.59 ± 0.02	–	6.57	6.27	–	8.95	–	8.44 [14]
B	–	7.32	–	7.34 ± 0.05	–	7.33	7.22	–	9.98	–	8.72 [15]
C	4.04	10.82	4.08 ± 0.02	10.82 ± 0.03	4.06	10.82	–	5.51	14.75	4.16 [17]	14.00 [16]
D	3.95	10.50	3.94 ± 0.07	10.50 ± 0.17	3.95	10.50	–	5.39	14.32	3.74 [17]	13.50 [16]

[a] 1st method: proton–ligand formation curve method.

[b] 2nd method: log $\bar{n}_A/(1-\bar{n}_A)$, log$(\bar{n}_A-1)/(2-\bar{n}_A)$ vs. pH method.

[c] The pK_a values were calculated from the Debye–Hückel equation.

[d] References are given in square brackets.

then plotted. The ionization constants pK_{COOH} and pK_{OH} of the ligands were evaluated according to the half-integral method (i.e. $\bar{n}_A = 1.5$ and 0.5), as well as being calculated from the plot of $\log \bar{n}_A/(1 - \bar{n}_A)$ and $\log(\bar{n}_A - 1)/(2 - \bar{n}_A)$ vs. pH values for the first and second ionization constants, respectively. The values are listed in Table 1.

For NNWA and NSA one ionization step was observed, corresponding to the OH group; while for N1HNA and N3HNA two ionizations were detected, corresponding to COOH and OH groups. The relatively low pK_{OH} values for the NNWA and NSA derivatives compared with those of the naphthoic derivatives can be attributed to the effect of the electrostatic charge of the negative sulphonate group, and to mesomeric and inductive effects [18]. The electrostatic effect of the negative sulphonate group retards the ionization of the OH group, and mesomeric and inductive effects both increase the acid strength. The mesomeric effect is especially prominent when the sulphonate group is located in the para-position to the hydroxyl group. This shows why NNWA has the lowest pK_{a} value. The ionization constants can be calculated by applying the Debye–Hückel equation

$$\log k_1 = \log k_1^0 - \frac{A\sqrt{I}}{1 + \alpha\sqrt{I}} + \beta I$$

where $\log k_1^0$ is the protonation constant at zero ionic strength and A is equal to 2.036 [8] for nitroso naphthol monosulphonic acids. The parameters α and β are 1.08 and 0.46 for NNWA [18] and 1.87 and 0.24 for NSA [8]. The calculated results were close to those obtained potentiometrically (Table 1). Generally, the introduction of a nitroso group to the ligands under investigation led to decreased ionization constants as compared with those of the non-nitroso ligands (Table 1). This may be due to the electron-withdrawing character of the nitroso group increasing the likelihood of hydrogen bonding between the hydroxy and nitroso groups. It is worthy of mention that there is a good correlation between the nitroso and non-nitroso compounds, i.e. they have the same trend of variation (Table 1). Values of $\bar{n}$ and pL were also calculated from the titration curves, and then plotted against each other to give the formation curves of the metal complexes. The $\bar{n}$ values extend to 2.0 for complexes of La(III) with the nitroso naphthoic acids (N1HNA and N3HNA), indicating the formation of 1 : 1 and 1 : 2 complexes. In the case of NNWA and NSA, however, $\bar{n}$ is of the order of 3.0, indicating the formation of 1 : 3 complexes. Also, the $\bar{n}$ values reach their maxima at approximate pH values of 4.0–7.7, above which hydrolysis of the rare earth metal ion begins. Thus 1 : 1, 1 : 2 and 1 : 3 (M–L) complexes are formed, the successive stability constants $\log \beta_n$ of these being calculated using the methods described earlier. Values of $\log \beta_n$ are recorded in Table 2. Comparing the values of $\log \beta_1$ and $\log \beta_2$ of NNWA (A) and NSA (B), it is clear that NSA forms much stronger chelates with the lanthanum ion than does NNWA. Similarly, the conjugate base of the former is stronger than

TABLE 2

Collective data of log β_1, log β_2 and log β_3 values for chelates of the ligands under investigation (A–D) with lanthanum metal ion, at 25 °C and $\mu = 0.1$ M

M(III) ion	log β_1				log β_2					log β_3
	a	b	c	mean	a	b	c	d	mean	a
NNWA–La	4.54	4.57	4.53	4.55	8.26	8.37	8.39	8.64	8.42	11.58
NSA–La	5.01	4.99	4.97	4.99	8.96	9.01	9.00	9.10	9.02	12.50
N1HNA–La	7.70	7.78	7.91	7.80	14.74	14.83	14.94	14.36	14.72	–
N3HNA–La	8.68	8.47	8.65	8.60	15.12	14.89	15.10	14.28	14.85	–

where a is interpolation at half $\bar{n}$ values method, b is correction term method, c is successive approximation method, d is mid-point method.

that of the latter; this is supported by the pK_{OH} values obtained potentiometrically for the free ligands. For complexes of nitroso naphthoic acid (N1HNA and N3HNA) with lanthanum, the values of log β_n were not much different from each other. Their acid strengths, and consequently their conjugate bases, were also comparable, i.e. of the same order.

IR spectra

The IR spectral bands of lanthanum chelates with the ligands under investigation are given in Table 3. A comparison of the IR spectra of the ligands (Table 4) with those of their lanthanum complexes indicates that some changes are occurring as a result of the involvement of ligands at different coordination sites on the La(III) metal ion. Among these changes are the following.

(a) The bands at 3500 cm^{-1}, assigned to naphthalenic νOH of the ligands, disappear from the spectra of the complexes, indicating deprotonation of the OH group and its participation in chelation. Broad bands

TABLE 3

Assignments of IR bands of lanthanum chelates of ligands A–D [a]

Complex	νOH	δOH	N=O	M–O
La–A 1:1	3420 b	1110 s	–	600 s
La–A 1:2	3420 b	1110 s	–	600 s
La–B 1:1	3400 b	1125 s	–	600 s
La–B 1:2	3420 b	1125 s	–	600 s
La–C 1:1	3420 b	1110 s	1410 s	620 s
La–C 1:2	3420 b	1100 s	1410 s	620 s
La–D 1:1	3420 b	1120 s	1400 s	595 s
La–D 1:2	3400 b	1150 s	1400 s	595 s

[a] b, broad; s, strong.

TABLE 4

IR band assignment of the nitroso compounds under investigation (A–D) [a]

A	B	C	D	Band assignment
3500 vb	3540 vb	3500 vb	3300 s	νOH
–	–	1630 s	1660 s	νC=O (COOH)
1350 s	1370 s	1410 w	1400 w	νN=O (dimer *cis*)
1300 s	1325 s	1310 s	1290 s	νN=O (dimer *trans*)
1620 w	1590 w	1600 s	1600 s	νC=C
1510 w	1480 s	1510 s	1510 s	νC=C
1445 s	1450 s	1435 s	1445 s	δC–H
1310 s	1330 s	1340 s	1350 s	νC–N asymmetrical
1170 s	1160 s	1155 s	1150 s	νC–N symmetrical
1210 s	1200 s	1210 s	1220 w	νC–O asymmetrical
1040 s	1000 s	1020 w	1010 w	νC–O symmetrical
1110 s	1110 s	1110 s	1130 s	δOH
1060 s	1040 s	–	–	νSO_3^-
810 s	800 w	810 s	790 s	γOH

[a] vb, very broad; b, broad; s, strong; w, weak.

observed in the region 3400–3450 cm^{-1} may be assigned to νOH of water molecules coordinated to the central La(III) metal ion.

(b) The band at 1370–1350 cm^{-1}, assigned to νN=O in the free ligand (NNWA, NSA), disappears, indicating participation of the N=O group in chelation with these ligands. The bands at 1660–1630 cm^{-1}, assigned to C=O stretching of the carboxylic acid group, disappeared in the IR spectra of the La(III) complexes with N1HNA and N3HNA, indicating participation of the COOH group in chelate formation. N=O bands at 1410–1400 cm^{-1} in the IR spectra of N1HNA- and N3HNA–La(III) complexes do not show changes, which can be taken as evidence that in these cases the N=O group does not participate in chelation.

(c) All the lanthanum complexes show a band at 595–600 cm^{-1}, characteristic of the M ← O dative bond [19], which was not obviously present in the spectra of the free ligands. This can be attributed to interaction between the carboxylic and hydroxylic oxygen atoms and the La(III) metal ion.

Nuclear magnetic resonance spectra

Substantial support for the results obtained from the IR spectra is obtained by considering changes in the NMR spectra of some of the La(III) complexes under investigation compared to those of the ligands (Table 5).

The NMR spectra of the ligands under investigation exhibit multiplet signals at 6.4–8.2 ppm which are assigned to the aromatic C–H protons. The integration curves show 5 protons for A, B, C and D ligands. The signals at

TABLE 5

Proton NMR spectral data of some of the ligands under investigation and their lanthanum complexes

Compound	Chemical shift (ppm)	Assignment
A	8.1–8.7	OH
	7.5–8	Aromatic C–H
	2.6	CH_3 of solvent
B	8.8	OH
	6.4–8.2	Aromatic C–H
	3.6	Protons of H_2O
	2.6	CH_3 of solvent
C	8.3–8.5	OH, COOH
	7.1–8.0	Aromatic C–H
	2.5	CH_3 of solvent
D	8.6	OH, COOH
	7.3–8.1	Aromatic C–H
	2.5	CH_3 of solvent
La–A (1:1)	8.5–8.7	OH of neutralization
	7.5	Aromatic C–H
	3.0–4.0	H_2O of coordination
	2.5	CH_3 of solvent
La–C (1:1)	8.4	OH of neutralization
	7.4–8.0	Aromatic C–H
	3.3	H_2O of coordination
	2.5	CH_3 of solvent

8.1–8.8 ppm are assigned to the proton of the hydroxy naphthalenic OH in ligands A and B. For C and D, the signals due to OH and COOH are shifted downfield, as a result of intermolecular or intramolecular hydrogen bonding [20] and their signals are displayed at 8.3–8.6 ppm. Ligand B shows a signal at 3.6 ppm equivalent to 4 protons, which is assigned to the two molecules of water of crystallization [8] revealed by the integration curve and confirmed by C, H, N analysis.

The NMR spectrum of SA (Schaffer's acid) displays signals at 7.2–8.2 and at 10 ppm, assigned to aromatic and OH protons. This indicates that introduction of the NO group into NSA led to an up-field shift of aromatic and hydroxy naphthalenic protons.

For La–A (1:1) and La–C (1:1) chelates, new signals appearing at 3.0–4.0 ppm in the spectra of the complexes indicate the presence of H_2O molecules in these complexes. The presence of water molecules is confirmed by the TG. On the other hand, the variation associated with the signals at 6.4–8.2 ppm, which are assigned to the aromatic protons, indicates that the chelation disturbs the charge distribution through the naphthyl moeity to some extent.

TABLE 6

Thermogravimetric analysis results of solid chelates of lanthanum complexes

Complex M : L	Hygroscopic water				Coordinated water				% of metallic residue
	Temperature up to (° C)	Weight loss %		No. of water molecules	Temperature range (° C)	Weight loss %		No. of water molecules	
		Calc.	Found			Calc.	Found		
La–A 1 : 1									
[La($C_{10}H_{11}NO_9SNa$)·2OH·$2H_2O$]$2H_2O$	120	6.93	6.53	2	120–250	7.45	7.83	2	29.23
La–A 1 : 2									
[La($C_{20}H_{13}N_2O_{12}S_2Na_2$)·OH·$H_2O$]$2H_2O$	120	4.74	4.26	2	120–200	3.74	3.95	1	19.97
La–C 1 : 1									
[La($C_{11}H_{12}NO_8$)·OH·$3H_2O$]H_2O	120	4.06	3.96	1	120–250	11.30	11.56	3	34.68
La–C 1 : 2									
[La($C_{22}H_{10}N_2O_{10}$)·$2H_2O$]H_2O	120	2.89	3.01	1	120–210	5.94	5.87	2	24.59
La–D 1 : 1									
[La($C_{11}H_{12}NO_8$)·OH·$3H_2O$]H_2O	110	4.06	4.19	1	110–300	11.30	11.45	3	34.35
La–D 1 : 2									
[La($C_{22}H_{16}N_2O_{10}$)·$2H_2O$]$2H_2O$	110	5.60	5.83	2	110–250	5.94	5.84	2	25.39

Thermogravimetric and differential thermal analysis

Some lanthanum chelates were subjected to TG. The weight loss was measured from the ambient temperature up to 800 °C at a rate of 10 °C min^{-1}. The weight loss for each chelate, obtained from the thermographs, was used to calculate the number of water molecules present (Table 6). The loss below 110 °C is attributed to moisture and hygroscopic water (see Figs. 1 and 2), since the chelates formed are hygroscopic in nature. For La(III)–NNWA (1 : 1) chelates, two water molecules are coordinated to the metal ion, giving a coordination number of six; these are expelled within the temperature range 120–250 °C. For La(III)–N1HNA and –N3HNA (1 : 1) chelates there are three water molecules coordinated to the metal ion, and these are expelled within the temperature range 110–300 °C. For 1 : 2 chelates, one water molecule is coordinated per each chelate molecule. In the case of NNWA, this is expelled within the temperature range 120–200 °C. However, for La(III)–N1HNA and –N3HNA chelates there are two coordinated water molecules and these are expelled within the temperature range 110–250 °C.

The results obtained are in good agreement with the calculated values, with the values obtained by determination of the metal ion content after decomposition of the chelate (according to the method described by Macdonald [21]), and with the results of elemental analysis. All the results indicate the formation of 1 : 1 and 1 : 2 lanthanum–ligand complexes (Table 7).

The DTA curves are characterized by the presence of one endothermic peak within the temperature range 50–200 °C. Within this range water molecules are expelled. This is followed by a sharp exothermic peak within the temperature range 270–325 °C. At these temperatures a phase change is

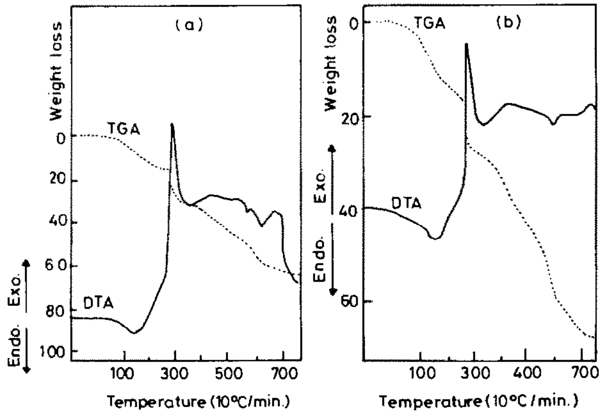


Fig. 1. Thermogravimetric and differential thermal analysis curves of La(III) complexes: (a) La–A (1 : 1), (b) La–A (1 : 2).

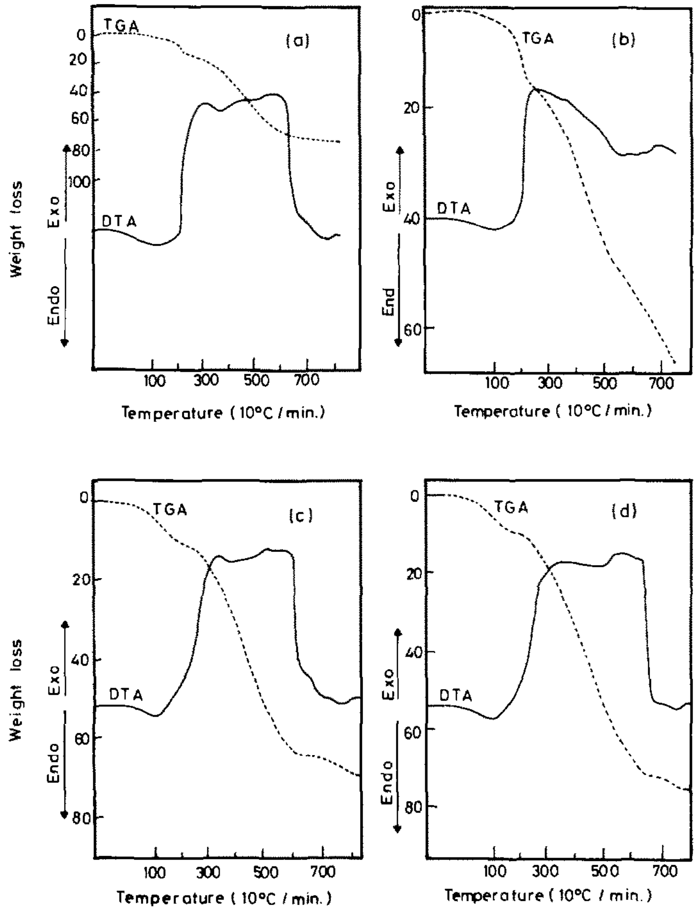


Fig. 2. Thermogravimetric and differential thermal analysis curves of La(III) complexes: (a) La–C (1 : 1), (b) La–C (1 : 2), (c) La–D (1 : 1), (d) La–D (1 : 2).

liable to occur, owing to a change in the crystal structure of the complex, i.e. crystallographic phase transition. Above these temperatures decomposition and combustion begin, followed by decarbonization of the organic material in the presence of oxygen, leaving a final residue of metallic oxide contaminated with sodium carbonate.

Molar conductance

The molar conductivities of the solid complexes were measured in DMF solution within the limits of their solubilities. The conductance values (Λ_m) were found to be in the range 24–56 Ω^{-1} cm^2 mol^{-1}. For La(III)–NNWA 1 : 1 and 1 : 2 the values are 40 and 56, while for La(III)–N1HNA 1 : 2 the value is 24 Ω^{-1} cm^2 mol^{-1}. These molar conductance values reveal that there are no anions present outside the coordination sphere, and particularly

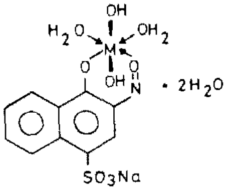
TABLE 7

Elemental analysis of La(III): (A–D) chelates

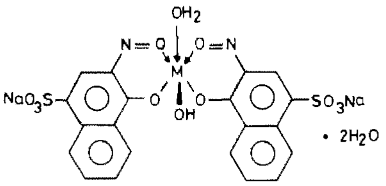
Ligand	(M : L)	Formula	C (%)		H (%)		N (%)		S (%)		M (%)	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
A	(1 : 1)	$[La(C_{10}H_5NO_5S)\cdot Na\cdot 2OH\cdot 2H_2O]2H_2O$	23.13	23.41	2.89	3.10	2.69	2.52	6.17	6.21	26.77	26.90
A	(1 : 2)	$[La(C_{10}H_5NO_5S)_2\cdot 2Na\cdot OH\cdot H_2O]2H_2O$	31.67	31.82	2.24	2.33	3.69	3.50	8.44	8.52	18.33	18.10
B	(1 : 1)	$[La(C_{10}H_5NO_5S)\cdot Na\cdot 2OH\cdot 2H_2O]H_2O$	23.96	23.62	2.60	2.55	2.79	2.70	6.39	6.34	27.73	27.20
B	(1 : 2)	$[La(C_{10}H_5NO_5S)_2\cdot 2Na\cdot OH\cdot H_2O]H_2O$	32.44	32.40	2.03	2.12	3.78	3.70	8.65	8.61	18.77	18.30
C	(1 : 1)	$[La(C_{11}H_5NO_4)\cdot OH\cdot 3H_2O]H_2O$	29.80	29.61	3.16	3.32	3.16	3.10	–	–	31.36	31.10
C	(1 : 2)	$[La(C_{11}H_5NO_4)_2\cdot 2H_2O]H_2O$	42.31	42.50	2.72	2.94	4.49	4.61	–	–	22.26	22.60
D	(1 : 1)	$[La(C_{11}H_5NO_4)\cdot OH\cdot 3H_2O]H_2O$	29.80	30.00	3.16	3.20	3.16	3.24	–	–	31.36	31.50
D	(1 : 2)	$[La(C_{11}H_5NO_4)_2\cdot 2H_2O]2H_2O$	41.13	41.10	2.65	2.57	4.36	4.40	–	–	21.64	21.70

no ClO_4^- although the metals are perchlorates. This was confirmed by elemental analysis, which did not show any Cl content. The low molar conductance values obtained can therefore be attributed to the ionized SO_3Na groups and to the partially ionic characters of the lanthanum–ligand bonds. In the light of the above findings, the structure of the 1 : 1 and 1 : 2 chelates may be represented by the following formulae.

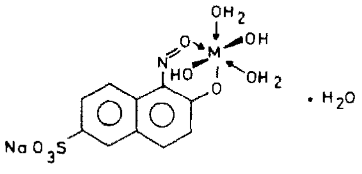
M - A (1:1)



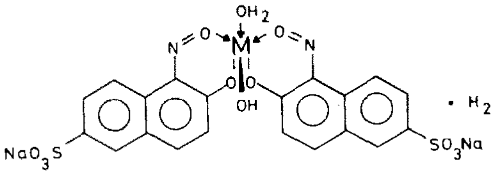
M - A (1:2)



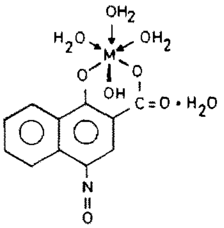
M - B (1:1)



M - B (1:2)



M - C (1:1)



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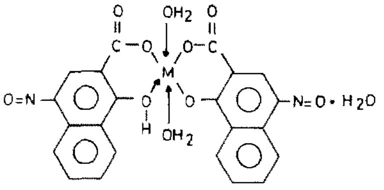
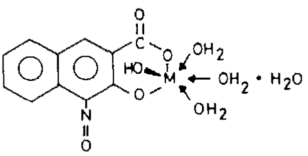
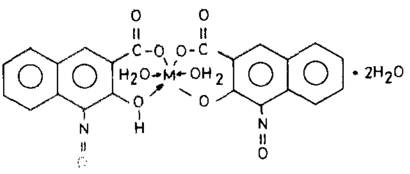


M - D (1:1)



M - D (1:2)



Magnetic susceptibility measurements

Magnetic moment measurements of the ligands and their lanthanum complexes were carried out at room temperature (300 °K), according to

Faraday's method. All the complexes were found to be diamagnetic, which confirms the electronic structure of the lanthanum ion, i.e. the absence of unpaired electrons. The diamagnetic behaviour of both the ligands and their complexes reflects the fact that the electronic structure of La(III) is not affected by the external field, nor by the surrounding matrices.

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