Thermochimica Acta, 156 (1989) 69–83
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

POTENTIOMETRIC, CONDUCTIMETRIC, SPECTROMETRIC, THERMOGRAVIMETRIC AND MAGNETIC STUDIES OF LANTHANUM COMPLEXES WITH SOME SYMMETRIC 1,5-DIARYL-3-CYANOFORMAZANS

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(Received 12 April 1989)

ABSTRACT

Many experimental techniques including potentiometric, conductimetric, IR, NMR, TG and magnetic susceptibility have been applied to obtain basic knowledge on the complexes of La(III) with some symmetric 1,5-diaryl-3-cyanoformazans. The ionization constants of the formazans as well as the formation constants of their lanthanum complexes were studied potentiometrically in solution by Sarin's method. The La(III) complexes formed were separated and their structures were elucidated by elemental analysis, IR, NMR spectroscopy, thermogravimetry (TG), molar conductance and magnetic susceptibility measurement.

INTRODUCTION

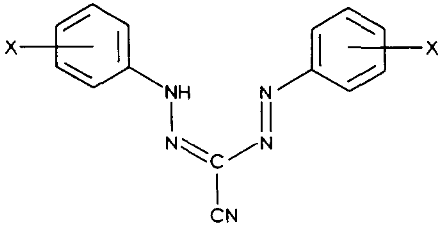
Formazans form a distinct class of organic compounds with characteristic properties. Such compounds have received great attention due to their uses in many fields, e.g. is analytical chemistry as complex ligands (with Ga, V, etc.) [1,2] and have also been studied with respect to their colouring power [3] and their biological activity [4]. Some derivatives of 3-cyanoformazans have been prepared and their metal complexes have been investigated [5–8]. The use of symmetric cyanoformazans as ligands with lanthanides has received little attention.

In the present work, the stability constants of trivalent lanthanum ion with some symmetric 3-cyanoformazans have been determined in dioxane–water and alcohol–water mixtures and ionic strength 0.1 M ($NaClO_4$) using Sarin and Munshi's technique [9]. Conductimetric titrations were carried out to obtain further information concerning the stoichiometry of the complexes in solutions. IR, NMR, TG, molar conductance and magnetic susceptibility measurements of La(III) complexes were performed to elucidate their structures.

0040-6031/89/$03.50

EXPERIMENTAL

All chemicals used in this investigation were of the highest available purity. Symmetrically substituted 1,5-diaryl-3-cyanoformazans were prepared as previously described [10]. The symmetric formazans used in this work can be represented by



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where X = H ($\mathbf{I}_a$), p-CH_3 ($\mathbf{I}_b$), p-OCH_3 ($\mathbf{I}_c$), p-Cl ($\mathbf{I}_d$), p-Br ($\mathbf{I}_e$), p-I ($\mathbf{I}_f$) and o-COOH ($\mathbf{I}_g$).

Stock 0.001 M solution of each formazan was prepared by dissolving the requisite weight in ethanol. 10^{-3} M lanthanum perchlorate solution was prepared [11] and standardized with EDTA using arsenaso I as indicator [12]. Three mixtures were prepared as previously described [13] and titrated potentiometrically against standard 0.125 M sodium hydroxide solution at 25°C using a digital pH-meter (Seibold G 103). This potentiometric study has been carried out in dioxane–water mixture (70% v/v) for all formazans under investigation and in 50% ethanol–water mixture for o-COOH $\mathbf{I}_g$, because permanent turbidity occurs in ethanol in the case of the other derivatives.

The average number of protons $\bar{n}_A$ associated with the ligand at various pH values, the average number of ligands attached per metal ion ($\bar{n}$) and the free ligand exponent pL were calculated using the equations given by Sarin and Munshi [9].

The stepwise formation constants of La(III) complexes were evaluated by four methods: a, interpolation at half $\bar{n}$ value; b, correction term; c, successive approximation; and d, mid-point methods [14]. Calculations were carried out using a Casio *fx*-700 programmable calculator.

Conductimetric titrations of 50 ml alcohol–water (different percentages) solutions containing 4×10^{-5} M of a given formazan against 10^{-3} M standard solution of lanthanum were carried out using a D812 conductivity meter model LBR at a frequency of 3 kHz s^{-1}.

The solid complexes were prepared by mixing alcoholic solutions of 0.001 M lanthanum perchlorate with the requisite amount of formazans under investigation, sufficient to form 1 : 1 and 1 : 2 (M : L). The separated solids were subjected to elemental analysis, IR, NMR spectroscopy, TG, molar conductance and magnetic susceptibility measurements. The IR of $\mathbf{I}_{a-g}$ and their lanthanum complexes were recorded as KBr pellets using a Pye UNICAM-SP 3-300 infrared spectrometer.

The NMR spectra were obtained using a Varian EM-390-90 M Hz NMR spectrometer. The TG was carried out using a STA 409 Netzsch thermal analyser. The molar conductances were determined using a CM-1K conductivity meter (cell constant 0.975). The magnetic measurements were carried out using Faraday's method.

RESULTS AND DISCUSSION

The $\bar{n}_A$ values were calculated at different pH values utilizing the two titration curves of $HClO_4$ and of formazan. The formation curves for the proton–ligand systems were obtained by plotting the relation between $\bar{n}_A$ and pH, from which the protonation constants pK_a were obtained (i.e. at $\bar{n}_A = 1.5$ and 0.5) as well as by plotting pH as abscissa versus log $\bar{n}_A/1 - \bar{n}_A$ and $\log(\bar{n}_A - 1)/2 - \bar{n}_A$ for the first and second ionization constants respectively. The values of pK_a obtained by both methods are given in Table 1, indicating the presence of one pK_a for the unsubstituted formazan ($\mathbf{I}_a$) and the symmetric formazans substituted in the *p*-positions of the phenyl nucleus, corresponding to the ionization of N–H. For the *o*-carboxy derivative $\mathbf{I}_g$, there are three pK_a values, being assigned to the two *o*-COOH groups and the N–H group.

In our study, the ionization of the N–H group is influenced by varying substituent X as well as the presence of the –C≡N– group making the imino N–H group titrable. It is of interest to note that the NH group in many other 1,5-diphenyl and 1,3,5-triphenylformazans was reported to be non-ionizable or the ionization is said to be very difficult, the expected pK values being higher than 15 [15]. The release of the proton of the NH group in the formazans under investigation ($\mathbf{I}_{a-g}$) may be attributed to the high electron-withdrawing effect of the –C≡N– group ($\sigma = +1.00$) which will of course decrease the strength of the hydrogen bond between the NH group and the N_5 atom. This was confirmed by calculation of the electron density distribution using SCF CI PPP [10].

From Table 1, it can be seen that the pK_{NH} values of *p*-Cl, *p*-Br and *p*-I derivatives are smaller than that of the unsubstituted compound. This may be explained by the electronegativities of the halogen atoms which exert a strong inductive effect ($-$I effect), thereby facilitating the release of the proton from the imino group. In the case of *p*-OCH_3 and *p*-CH_3 formazan derivatives, the methoxy and methyl have a +I effect, and so the net result is to increase the value of pK_{NH}. For the *o*-carboxy derivative $\mathbf{I}_g$, the low pK values are due to the ionization of the carboxylic groups. The high pK_{NH} value in the case of the *o*-carboxy derivative may be attributed to the electron-repelling characteristics of the carboxylate ion formed at moderate

TABLE 1

Evaluation of the ionization constants of formazans $\mathbf{I}_{a-g}$

Formazan No.	Substituent X	1st method			2nd method			Mean value ± S [b]		
		pK_{COOH}	pK_{COOH}	pK_{NH}	pK_{COOH}	pK_{COOH}	pK_{NH}	pK_{COOH}	pK_{COOH}	pK_{NH}
$\mathbf{I}_a$ [a]	H	–	–	9.35	–	–	9.30	–	–	9.33 ± 0.02
$\mathbf{I}_b$	p-CH_3	–	–	9.88	–	–	9.85	–	–	9.87 ± 0.04
$\mathbf{I}_c$	p-OCH_3	–	–	9.80	–	–	9.65	–	–	9.73 ± 0.03
$\mathbf{I}_d$	p-Cl	–	–	8.35	–	–	8.35	–	–	8.35 ± 0.02
$\mathbf{I}_e$	p-Br	–	–	8.40	–	–	8.35	–	–	8.38 ± 0.02
$\mathbf{I}_f$	p-I	–	–	8.50	–	–	8.50	–	–	8.5 ± 0.04
$\mathbf{I}_g$	o-COOH	4.70	6.95	12.40	4.70	6.90	12.40	4.70 ± 0.03	6.93 ± 0.01	12.40 ± 0.06
$\mathbf{I}_g$ [c]	o-COOH	3.90	5.55	11.76	3.90	5.57	11.75	3.9 ± 0.03	5.56 ± 0.02	11.76 ± 0.05

[a] $[\mathbf{I}_{a-g}]$ in 70% dioxane–water mixture.

[b] S = standard deviation.

[c] $\mathbf{I}_g$ in 50% ethanol–water mixture.

TABLE 2

Collective data of log β_1 and log β_2 values for chelates of the investigated ligands ($\mathbf{I}_a$, $\mathbf{I}_b$, $\mathbf{I}_d$ and $\mathbf{I}_g$) with lanthanum metal ion at 25 °C and $\mu = 0.1$ M

La(III) complex	log β_1				log β_2				
	a	b	c	Mean	a	b	c	d	Mean
In 70% dioxane–water mixture									
La(III)–$\mathbf{I}_a$	7.14	7.14	7.00	7.09	14.14	14.16	14.10	14.08	14.12
La(III)–$\mathbf{I}_b$	8.94	8.94	8.92	8.93	16.85	16.86	16.86	16.20	16.69
La(III)–$\mathbf{I}_d$	9.11	9.10	8.86	9.02	18.05	18.04	17.88	17.90	17.97
La(III)–$\mathbf{I}_g$	11.08	11.02	11.09	11.06	20.00	19.94	20.01	-	19.98
In 50% ethanol–water mixture.									
La(III)–$\mathbf{I}_g$	9.83	9.82	9.85	9.83	18.87	18.90	18.95	18.78	18.88

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

pH values as a result of ionization of the COOH groups. From the titration curves, $\bar{n}$ and pL values were also calculated. For formation curves for the metal complexes were obtained by plotting the relation between $\bar{n}$ and pL. These plots indicate that the values of $\bar{n}$ obtained are of the order of 2.0 for the La(III)–formazan complexes, indicating the formation of 1 : 1 and 1 : 2 complexes. The successive stability constants log β_n were calculated using the methods described earlier. The values of log β_n are given in Table 2. Regarding the results given in Table 2, it is clear that the formazan derivative $\mathbf{I}_g$ is characterized by a higher ability for chelation with lanthanum than the other formazans. This can be explained on the basis that the *o*-substituted formazan $\mathbf{I}_g$ has more coordination sites than the other ones. In addition, from the values of pK_{COOH} and pK_{NH} of the formazans under investigation, as previously discussed, the weaker the acid, the stronger its conjugate base, L^{3-}, with a higher chelating affinity and higher stability of its complexes; this is the case with $\mathbf{I}_g$.

IR SPECTRA

The IR spectra of the formazans $\mathbf{I}_{a-g}$ have been discussed in a previous paper [10]. The band assignment of the IR spectra of the La(III)–$\mathbf{I}_{a-g}$ complexes is listed in Table 3. It is apparent that the NH group is still observed in the spectra of some chelates but it is shifted to higher or lower frequency values, whereas it disappears in the case of the La(III)–$\mathbf{I}_g$ complex. This provides proof that the NH proton is not removed in chelate formation for some La(III) complexes, whereas the shift in the ν_{NH} in these complexes of ~ 20 cm^{-1} indicates the involvement of the imino nitrogen in coordination. The absence of an NH band in the spectra of La(III)–$\mathbf{I}_g$

TABLE 3

Band assignment of IR spectra of La(III) complexes of $\mathbf{I}_{a-g}$

Complex	M:L	ν_{OH} alcohol (cm^{-1})	ν_{OH} water (cm^{-1})	ν_{NH} (cm^{-1})	δ_{OH} (C_2H_5OH) (cm^{-1})	δ_{OH} (H_2O) (cm^{-1})	$\nu_{N=N}$ (cm^{-1})	$\nu_{asym.}$ (cm^{-1})	
								ClO_4^-	OH
La(III)–$\mathbf{I}_a$	1:1	3300–3600(b)		3245(m)	1600(s)			–	850(w)
	1:2	–	3400–3600(w)	3225(s)	–	1600(m)	1415(s)	–	830(w)
La(III)–$\mathbf{I}_b$	1:1	–	3300–3640(b)	3230(s)	–	1600(s)	1395(m)	–	820(s)
	1:2	3300–3600(b)	–	3230(s)	–	1600(s)	1395(s)	–	820(s)
La(III)–$\mathbf{I}_c$	1:1	3300–3600(b)	–	3230(s)	1600(s)	–	1420(w)	1090(w), 630(s)	825(s)
	1:2	3300–3600(b)	–	3230(m)	1600(s)	–	1430(w)	1100(w), 630(s)	825(s)
La(III)–$\mathbf{I}_d$	1:1	3300–3660(b)	–	3250(m)	1595(w)	–	1420(w)	1090(s), 630(s)	820(s)
	1:2	3300–3600(b)		3245(m)	1590(m)		1425(w)	–	820(s)
La(III)–$\mathbf{I}_e$	1:1	3300–3660(b)	–	3245(m)	1595(m)	–	1430(w)	1090(w), 630(m)	820(s)
	1:2	3300–3660(b)	–	3240(s)	1590(m)	–	1430(m)	1090(w), 630(m)	820(s)
La(III)–$\mathbf{I}_f$	1:1	3300–3660(b)	–	3250(m)	1590(m)	–	1400(s)	1090(m), 630(s)	820(s)
	1:2	3300–3660(b)	–	3220(m)	1590(m)	–	1390(m)	1090(w), 630(m)	820(s)
La(III)–$\mathbf{I}_g$	1:1	3100–3660(b)		–	1590(m)		–	–	820(m)
	1:2	3200–3640(b)		–	1590(m)		–	–	820(m)

(s) strong, (b) broad, (m) medium, (w) weak.

complexes indicates that the complex formation for this ligand takes place through the displacement of a hydrogen from the NH group by the metal ion, particularly in the 1 : 1 complex. However, for the 1 : 2 complex, the disappearance of the NH band may be attributed to its being overlapped by the broad water band (3320–3600 cm^{-1}). In the IR spectra of La(III)–$\mathrm{I_g}$ chelates, bands at 1250 and 790 cm^{-1}, characteristic for the COOH group, and the band at 1730 cm^{-1}, arising from C=O, disappeared. This observation indicates the participation of the COOH group in chelation. Some new broad bands appeared on chelation at 1595, 1550, 1490, 1400 and 870 cm^{-1} [16] due to asymmetric $\mathrm{COO^-}$, asymmetric $\mathrm{C}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\lessgtr}}\mathrm{La}$, symmetric $\mathrm{COO^-}$, symmetric $\mathrm{C}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\lessgtr}}\mathrm{La}$ and C–O, respectively.

The C≡N band is still present in all complexes (2210–2230 cm^{-1}); the N=N band is shifted to lower values in the investigated chelates as a result of coordination with the central metal ion (Fig. 1).

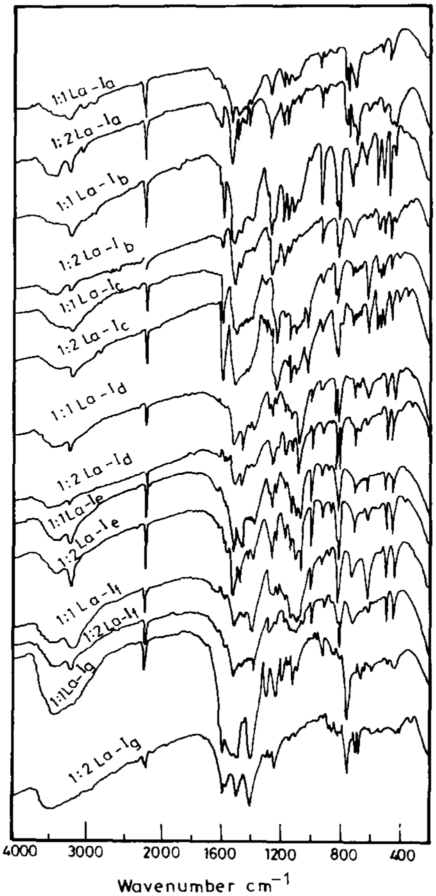

Fig. 1. IR spectra of La(III)–($\mathrm{I_{a-g}}$) complexes.

TABLE 4

Proton NMR spectral data of formazans and some of their La(III) complexes

Compound	Chemical shift (δ) (ppm)	Assignment
I_a	12.6	(s, 1H, NH)
	7.3–7.9	(m, 10H, ArH)
	2.6	CH_3 of solvent
I_b	12.5	(s, 1H, NH)
	7.3–7.8	(m, 8H, ArH)
	2.4	(s, 6H, $2ArCH_3$)
	2.6	CH_3 of solvent
I_c	12.4	(s, 1H, NH)
	6.9–7.8	(m, 8H, ArH)
	3.8	(s, 6H, 2 $ArOCH_3$)
	2.6	CH_3 of solvent
I_d	9.2	(d, 2H*, ArH)
	8.95	(b, 1H, NH)
	7.9–8.2	(m, 6H, ArH)
	2.6	CH_3 of solvent
I_e	9.2	(d, 2H*, ArH)
	8.8	(b, 1H, NH)
	7.4–7.9	(m, 6H, ArH)
	2.6	CH_3 of solvent
I_f	9.15	(d, 2H *, ArH)
	8.85	(b, 1H, NH)
	7.4–8.0	(m, 6H, ArH)
	2.6	CH_3 of solvent
I_g	7.3–8.0	(m, 8H, ArH + 1H, NH)
	3.6	(s, 2H, COOH)
	2.6	CH_3 of solvent
La(III)–I_e (1 : 1)	8.0	(s, –NH)
	7.5	(s, ArH)
	2.5	CH_3 of solvent
La(III)–I_e (1 : 2)	7.5	(s, ArH)
	3.6	(s, –NH)
	2.6	CH_3 of solvent
La(III)–I_g (1 : 1)	7.2–7.8	(m, ArH)
	2.5	CH_3 of solvent

Ar, aromatic; s, singlet, d, doublet; m, multiplet; b, broad.

The coordination of perchlorate ion in some cases manifests itself by the presence of two bands at 1080 and 625 cm^{-1} [17].

The peaks found at around 570 and 450 cm^{-1} may be attributed to

(Ln ← N) and (Ln ← O) [18], respectively. La(III)–I_g complexes show a band at 590 cm^{-1} which is characteristic of M–O bonds. For 1 : 1 and 1 : 2 La(III)–I_g complexes, another band is observed at 450 and 430 cm^{-1}, respectively, which may be attributed to the M–N stretching frequency. Thus, it can be concluded that the NH and COOH groups are linked with La(III) after their deprotonation.

NUCLEAR MAGNETIC RESONANCE SPECTRA

Further support for the conclusions obtained from the IR spectra is provided by the changes in the proton NMR (PMR) spectra of some of the La(III) complexes under investigation in comparison with those of the ligands.

The PMR spectra of the formazans I_{a-g} were taken in dimethylsulphoxide solutions using tetramethylsilane (TMS) as internal standard. In addition, the PMR spectra of I_b and I_g were measured in deuterium oxide. The chemical shifts of the different types of protons are recorded in Table 4.

The PMR spectra of all ligands exhibit a multiplet signal at 6.9–8.2 ppm which is assigned to the aromatic C–H protons. The PMR spectra of I_{d-f} show a signal near 9.2 ppm (doublet, 2H, aromatic protons); the large deshielding of these protons is mainly attributed to the anisotropy of the double bond of the azo group [19].

It is also clear that complexes I_{a-c} exhibit sharp NH signals at 12.4–12.6 ppm [20], whereas I_{d-f} show a broad NH peak at 8.8–8.9 ppm [19,21]. In the case of the *o*-COOH derivative I_g, the NH proton signal is obscured by the aromatic protons signals and the carboxylic protons exchange quite rapidly with protons of water or alcohol, traces of which may contaminate the solvent; the position of this signal depends on concentration [21]. Accordingly the signal at 3.6 ppm is assigned to the two carboxylic protons as revealed from the integration curve. The PMR spectra of I_b and I_c exhibit a singlet at 2.4 and 3.8 ppm corresponding to the 6-CH protons of the two methyl and two methoxy groups, respectively, which occur more or less at the known general positions [19]. Deuteration of I_b and I_g derivatives leads to the disappearance of the imino proton N–H signals which in turn leads to some variation in the multiplet signals in the case of I_g. These results can be taken as evidence for the ionizing nature of the –NH group and are in agreement with the earlier results obtained potentiometrically. In the case of I_g, the exchange proton absorption was also removed, simply by obtaining a spectrum in deuterium oxide.

In the PMR spectra of La–I_e complexes, the –NH proton of the formazan appears at 8.0 ppm in the (1 : 1) complex but shifts to higher field with the 1 : 2 species. This may be attributed to the steric hindrance arising from attaching two ligand molecules to one central metal ion.

In the PMR spectra of the La(III)–I_g (1 : 1) complex, the sharp signal at

3.6 ppm disappeared and the multiplet at 7.3–8.0 ppm is shifted to higher field. This is an indication that COOH and –NH groups are involved in the chelation.

A new proton signal is observed at 3.2–3.5 ppm in the case of the La(III)–$\mathbf{I}_g$ (1 : 1) and La(III)–$\mathbf{I}_e$ complexes and is assigned to the water molecules in these complexes. The existence of water molecules is confirmed by TG.

The previous calculations of the electron density distribution [10] predict higher electron density on the formazan ring which in turn leads to less shielding of the attached protons. Hence the upper limit of the multiplet signal, in the case of $\mathbf{I}_g$, can be assigned to the NH proton.

THERMOGRAVIMETRY

In the present investigation, heating rates were maintained at 10 ° C min^{-1} and the weight loss was measured from ambient temperature up to 800 ° C. The initial weight loss occurring in the temperature range 50–120 ° C is interpreted as a loss of moisture and hygroscopic water during the drying of the complexes, whereas that at 120–200 ° C is due to the coordinated water in the chelate.

Some complexes show an inflection in the temperature range 325–500 ° C. Such an inflection may be attributed to the formation of an unstable intermediate product (e.g. 1 : 1 complex, aryl-carboxylate, carbonate).

Accordingly, the final state at 460–700 ° C includes the conversion of such an intermediate to the stoichiometric oxide La_2O_3 end product. In the case of La(III)–$\mathbf{I}_g$ chelates, the small inflection observed near 550 ° C is attributed to the formation of La_2CO_5 (oxycarbonate) before the oxide formation. The found and the calculated mass losses are listed in Table 5. For the 1 : 1 La(III) complex of $\mathbf{I}_a$, the first stage of decomposition in the 170–235 ° C range indicates loss of three molecules of ethanol which are coordinated to the metal ion to fulfil the coordination centres, while for 1 : 2 La(III)–$\mathbf{I}_a$ species, the initial loss of 2.43% at 135–165 ° C is due to the loss of one coordinated water molecule. The inflection observed near 400 ° C in both complexes is attributed to the conversion of the complexes to an intermediate. However in the case of (1 : 1) La(III)–$\mathbf{I}_d$ complex, the mass loss in the temperature range 120–140 ° C is attributed to the loss of one coordinated ethanol molecule, see Figs. 2 and 3.

For the 1 : 1 La(III)–$\mathbf{I}_g$ complex, the first decomposition stage indicates a loss of 6.24% at 40–135 ° C which is due to the loss of two molecules of water of hydration. In the second decomposition stage (135–235 ° C) a loss of 3.42% is mainly attributed to the loss of one coordinated water molecule. This complex shows an inflexion in the range 235–275 ° C which corresponds to the loss of one coordinated ethanol molecule.

TABLE 5

TG results of some solid chelates with formazans $\mathbf{I}_a$, $\mathbf{I}_d$ and $\mathbf{I}_g$

Suggested formula	M:L	Dehydration stage			Decoordination stage			Metallic residue (% oxide)		
		Temp. range (°C)	% Weight loss		Temp. range (°C)	% Weight loss		Temp. (°C)	Calc.	Found
			Calc.	Found		Calc.	Found			
La(III)–$\mathbf{I}_a$ $[La(HL)\cdot 3OH^-\cdot(C_2H_5OH)_3]$	1:1				170–235	23.94	23.73	600	28.21	28.21
La(III)–$\mathbf{I}_a$ $[La(2HL)\cdot 3OH^-\cdot H_2O]$	1:2				135–165	2.55	2.43	650	23.10	23.23
La(III)–$\mathbf{I}_d$ $[La(HL)\cdot OH^-\cdot(C_2H_5OH)_2](ClO_4^-)_2$	1:1				120–240	12.04	12.18	570	21.29	21.31
La(III)–$\mathbf{I}_g$ $[LaL\cdot H_2O\cdot C_2H_5OH]2H_2O$	1:1	40–135	6.28	6.24	135–235 235–275	3.14 8.04	3.42 7.97	650	28.42	28.10
La(III)–$\mathbf{I}_g$ $[La(HL)(H_2L)\cdot 2H_2O\cdot C_2H_5OH]H_2O$	1:2	60–125	3.95	4.04	125–185 185–265	1.98 5.06	1.86 4.97	550	17.89	18.00

For 1 : 2 La(III)–I_g, one molecule of water of hydration and two coordinated water molecules are expelled in the temperature ranges 60–125 and 125–185° C, respectively, as well as one ethanol molecule coordinated to the metal ion which is expelled in the range 185–265° C. In all the complexes under investigation, La_2O_3 is formed as a final product.

The results of the mass losses obtained by TG are in good agreement with the values calculated using the results of microchemical analysis for these complexes and with those obtained by determination of the metal ion content after decomposition of the chelates, applying the method described by Macdonald and Sirichanya [22] and with the results of the elemental analysis, see Table 6.

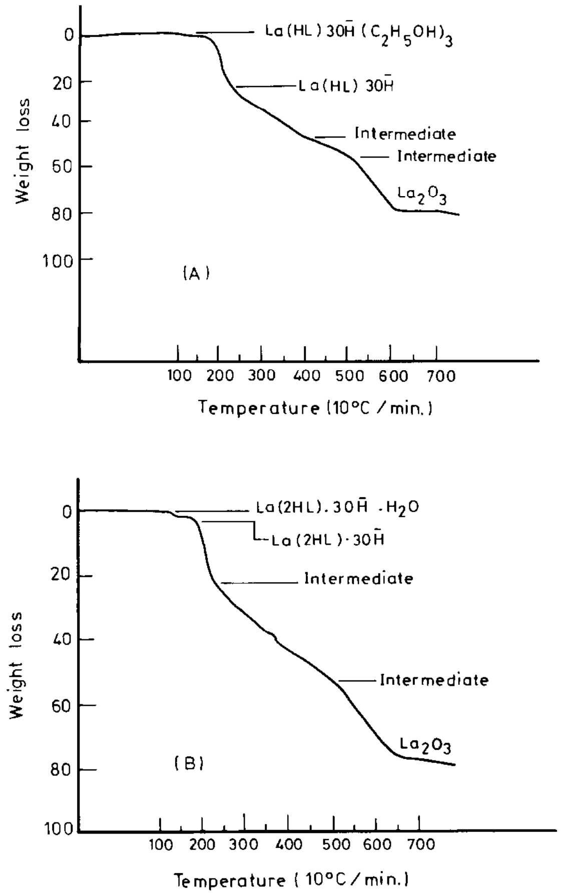

Fig. 2. TG curves of La(III)–I_a (1 : 1) (A) and La(III)–I_a (1 : 2) (B).

MOLAR CONDUCTIVITY

The molar conductivities of 1 mM solutions of the La(III) complexes were measured in DMF. The molar conductivities (Δ_m) of the solid complexes measured for the solutions of 1 : 1 La(III) complexes with formazans $\mathbf{I}_{a-c}$, and 1 : 1 and 1 : 2 (M : L) La with $\mathbf{I}_{f-g}$ are in the range 19.5–23.4 Ω^{-1} cm^2 mol^{-1}, while those of 1 : 2 complexes of La(III) with $\mathbf{I}_{a-d}$, and 1 : 1 complex species of La–$\mathbf{I}_e$ are in the range 31.2–35 Ω^{-1} cm^2 mol^{-1}. These values were measurably less than those reported [23] for the ionic complexes of trivalent transition metal ions in the same solvent. Hence, these low values may be attributed to the coordination of perchlorate ions in the above complexes rather than ionic association to the lanthanum(III) cation during complex formation. This directly supports the fact that all perchlorate ions in these complexes are non-ionized in nature, i.e. the non-conducting character of the above complexes in DMF indicates the direct bonding of the perchlorate ion to the metal ion.

The values 117 and 66.3 Ω^{-1} cm^2 mol^{-1} for 1 : 1 La(III)–$\mathbf{I}_d$ and 1 : 2 La(III)–$\mathbf{I}_e$, respectively, indicate the ionic nature of these chelates and that the perchlorate ions are present outside the cation coordination sphere.

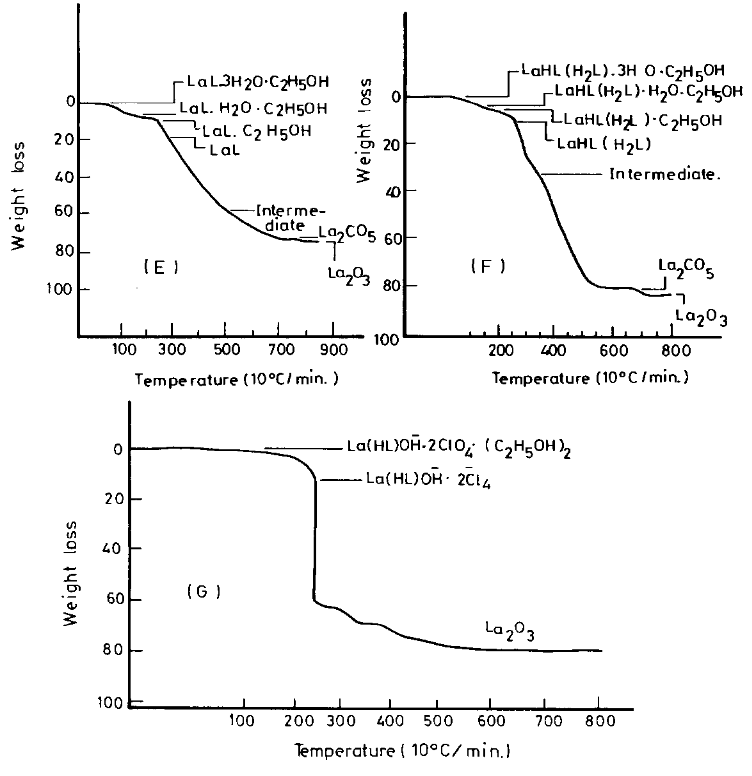

Fig. 3. TG curves of La(III)–$\mathbf{I}_g$ (1 : 1) (E), La(III)–$\mathbf{I}_g$ (1 : 2) (F) and La(II)–$\mathbf{I}_d$ (1 : 1) (G).

TABLE 6

Elemental analysis of lanthanum(III) complexes with formazans $\mathbf{I}_{a-g}$

Complex	Formula	M : L	C%		H%		Cl%		M%	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
La(III)–$\mathbf{I}_a$	$[La(C_{14}H_{11}N_5)\cdot 3OH^-(C_2H_5OH)_3]$	1 : 1	41.60	41.10	5.59	5.70	–	–	24.06	24.50
	$[La(C_{14}H_{11}N_5)_2\cdot 3OH^-\cdot H_2O]$	1 : 2	47.60	47.50	3.85	3.90	–	–	19.66	20.00
La(III)–$\mathbf{I}_b$	$[La(C_{16}H_{15}N_5)\cdot 3OH^-\cdot H_2O]$	1 : 1	39.60	40.00	4.15	4.00	–	–	28.63	27.70
	$[La(C_{16}H_{15}N_5)_2\cdot 3OH^-\cdot C_2H_5OH]$	1 : 2	51.63	51.40	4.97	4.80	–	–	17.57	17.20
La(III)–$\mathbf{I}_c$	$[La(C_{16}H_{15}N_5O_2)\cdot 2OH^-\cdot ClO_4^-\cdot(C_2H_5OH)_4]$	1 : 1	37.63	37.80	5.39	4.90	4.63	4.50	18.13	18.50
	$[La(C_{16}H_{15}N_5O_2)_2 2OH^-\cdot ClO_4^-\cdot C_2H_5OH]$	1 : 2	43.58	43.60	4.09	4.20	3.78	3.90	14.82	14.30
La(III)–$\mathbf{I}_d$	$[La(C_{14}H_9N_5Cl_2)\cdot OH^-\cdot(C_2H_5OH)_2](ClO_4)_2^-$	1 : 1	28.26	28.50	2.89	3.00	18.54	18.80	18.16	18.40
	$[La(C_{14}H_9N_5Cl_2)_2\cdot 3OH^-\cdot H_2O(C_2H_5OH)_2]$	1 : 2	41.03	41.10	3.77	3.70	15.16	15.30	14.83	15.10
La(III)–$\mathbf{I}_e$	$[La(C_{14}H_9N_5Br_2)\cdot OH^-\cdot 2ClO_4^-\cdot(C_2H_5OH)_5]$	1 : 1	29.03	29.20	4.06	3.80	7.14	7.70	13.99	14.30
	$[La(C_{14}H_9N_5Br_2)_2\cdot OH^-\cdot H_2O\cdot(C_2H_5OH)_4](ClO_4^-)_2$	1 : 2	31.53	31.50	3.39	3.30	5.18	5.30	10.13	10.30
La(III)–$\mathbf{I}_f$	$[La(C_{14}H_9N_5I_2)\cdot 3ClO_4^-\cdot(C_2H_5OH)_3]$	1 : 1	22.31	22.10	2.53	2.50	9.89	10.00	12.90	13.30
	$[La(C_{14}H_9N_5I_2)_2\cdot 3ClO_4^-\cdot(C_2H_5OH)_5]$	1 : 2	27.33	27.50	2.89	3.10	6.38	6.50	8.32	8.10
La(III)–$\mathbf{I}_g$	$[La(C_{16}H_8N_5O_4)\cdot 3H_2O\cdot C_2H_5OH]$	1 : 1	37.70	37.80	3.52	3.50	–	–	24.23	23.40
	$[La(C_{32}H_{19}N_{10}O_8)\cdot 3H_2O\cdot C_2H_5OH]$	1 : 2	44.02	44.10	3.37	3.80	–	–	14.97	15.20

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

The magnetic moment measurements of the ligands and their lanthanum complexes were measured at room temperature (300 K) using Faraday's method. All complexes were found to be diamagnetic which confirms the electronic structure of lanthanum ion, i.e. the absence of unpaired electrons. The diamagnetic behaviour of both the ligands and their complexes indicates that the electronic structure of La(III) has not been affected by the external field or by the surrounding matrices.

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