

## Studies on N,N'-bis(8-acetyl-7-hydroxy-4-methylcoumarin)ethylenediamine complexes of trivalent lanthanides

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Complexes having the composition  $\text{LnL}(\text{H}_2\text{O})\text{Cl}$  (where Ln = trivalent lanthanides and  $\text{H}_2\text{L}$  = schiff base derived from the condensation of 8-acetyl-7-hydroxy-4-methylcoumarin with ethylenediamine) have been prepared and characterized by elemental analysis, conductance, magnetic moment, TG and DT, electronic and infrared spectral measurements. The conductivity measurements show non-electrolytic nature of the complexes. The schiff base behaves as a dibasic tetradentate ligand with O:N:N:O donor sequence.

The present work is in continuation of the author's earlier work<sup>1</sup> on complexes of some bivalent metal ions with the schiff base derived from 8-acetyl-7-hydroxy-4-methylcoumarin and ethylenediamine.

### Experimental

The lanthanide(III) chlorides were obtained from M/s Rare-Earth Products (India). The synthesis of the ligand has been reported earlier<sup>1</sup>. Further characterization data of the ligand are as follows: m.p. 151°; IR: 3500 ( $\nu\text{OH}$ ), 1700 ( $\nu\text{C}=\text{O}$ , lactone), 1625 ( $\nu\text{C}=\text{N}$ , azomethine), 1490 ( $\nu\text{C}-\text{O}$ , phenolic); PMR:  $\delta$  2.9 (3H, s,  $(\text{CH}_3)-\text{C}=\text{N}-$ ), 9.4 (1H, s, ArOH), 2.3 (3H, s, a- $\text{CH}_3$ ), 3.8 (3H, s, b- $\text{CH}_3$ ), 6.5 (1H, s,  $\text{C}_3-\text{H}$ ), 6.9 (1H, d,  $\text{C}_5-\text{H}$ ) and 7.6 (1H, d,  $\text{C}_6-\text{H}$ ).

The metal complexes were prepared by mixing the solution of the ligand (0.01 mol) in nitromethane with lanthanide chlorides (0.01 mol). On heating and vigorous stirring, the whole mixture turned red (except for La complex) and a precipitate separated. The precipitate was isolated by centrifugation, washed several times with chloroform, dissolved in methanol, the solution concentrated and the complex reprecipitated by adding chloroform. The product so obtained was dried by keeping it for several days *in vacuo* over phosphorus pentoxide.

The methods used for analysis and physical measurements were as reported earlier<sup>1-3</sup>.

Table 1 - Characterization data of the complexes

Complex	Colour (m.p., °C)	Found (Calc.) %					$\mu_{\text{eff}}$ (B.M.)
		Metal	C	H	N	Cl	
[LaL(H <sub>2</sub> O)Cl]	White (283)	21.17 (21.35)	47.65 (47.97)	3.63 (3.69)	4.18 (4.30)	5.30 (5.45)	Diamag.
[PrL(H <sub>2</sub> O)Cl]	Red (292)	21.53 (21.59)	47.63 (47.82)	3.62 (3.67)	4.25 (4.29)	5.40 (5.44)	3.46
[NdL(H <sub>2</sub> O)Cl]	Red (299)	21.91 (21.99)	47.40 (47.52)	3.62 (3.66)	4.25 (4.27)	5.39 (5.41)	3.55
[SmL(H <sub>2</sub> O)Cl]	Brown (285)	22.63 (22.70)	47.02 (47.14)	3.60 (3.62)	4.20 (4.23)	5.33 (5.36)	1.62
[GdL(H <sub>2</sub> O)Cl]	Dark-red (288)	23.42 (23.50)	46.48 (46.65)	3.53 (3.58)	4.11 (4.18)	5.26 (5.30)	7.71
[DyL(H <sub>2</sub> O)Cl]	Brick-red (301)	24.00 (24.10)	46.10 (46.29)	3.53 (3.56)	4.10 (4.15)	5.24 (5.25)	10.55
[HoL(H <sub>2</sub> O)Cl]	Dark-red (287)	24.14 (24.38)	46.00 (46.12)	3.50 (3.54)	4.11 (4.13)	5.22 (5.24)	10.50
[ErL(H <sub>2</sub> O)Cl]	Dark-red (300)	24.52 (24.64)	45.84 (45.96)	3.47 (3.53)	4.10 (4.12)	5.20 (5.23)	9.51
[YbL(H <sub>2</sub> O)Cl]	Red (286)	25.20 (25.27)	45.47 (45.57)	3.46 (3.50)	4.02 (4.09)	5.13 (5.18)	4.36

$\text{L} = \text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_7$

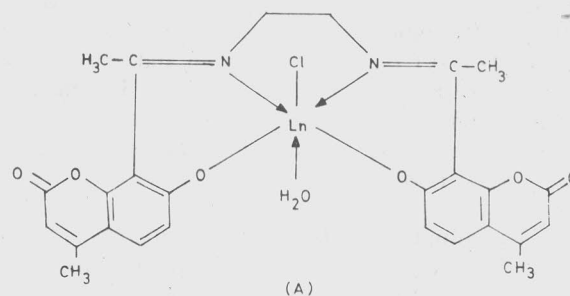
### Results and discussion

The analytical data of the complexes (Table 1) are in agreement with the composition  $[\text{LnL}(\text{H}_2\text{O})\text{Cl}]$ . The complexes are high melting solids, soluble in methanol, ethanol, dimethyl sulphoxide and dimethylformamide. The molar conductances of  $10^{-3} M$  solutions of the complexes in methanol indicate these to be non-electrolytes. The observed room temperature magnetic moments of all the complexes agree closely with the values given by Van Vleck<sup>4</sup>.

The IR spectra of complexes exhibit a broad band in the region  $3300\text{--}3000\text{ cm}^{-1}$  due to  $\nu\text{OH}$  of coordinated water; this assignment is corroborated by the occurrence of the corresponding rocking mode in the region  $850\text{--}840\text{ cm}^{-1}$  (ref. 5). The TG analysis of the complexes shows an endothermic peak between  $110$  and  $140^\circ\text{C}$  corresponding to a mass loss of  $2.5\text{--}2.7\%$  supporting the presence of coordinated water. The absence of  $\nu\text{OH}$  (phenolic) (occurring at  $\sim 3500\text{ cm}^{-1}$  in the ligand) in the spectra of all the complexes suggests coordination of phenolic oxygen to the metal ion after deprotonation. The  $\nu\text{C}=\text{N}$  (azomethine) band is shifted to lower frequency by  $\sim 50\text{ cm}^{-1}$  in the complexes indicating that the azomethine nitrogen is coordinated in all these complexes<sup>6</sup>. New bands observed in the region ( $600\text{--}450\text{ cm}^{-1}$ ) are assigned to  $\nu\text{M}-\text{O}$  and  $\nu\text{M}-\text{N}$  modes<sup>5</sup>. The  $\nu\text{M}-\text{Cl}$  mode in the complexes appears in the region  $365\text{--}335\text{ cm}^{-1}$ .

The electronic spectra of the complexes of Pr(III), Nd(III), Sm(III), Dy(III), Ho(III) and Er(III) have been recorded in DMF. Pr(III) complex shows bands around  $20200$ ,  $21250$  and  $22500\text{ cm}^{-1}$  corresponding to the energy levels  $^3P_0$ ,  $^3P_1$  and  $^3P_2$  respectively. Nd(III) complex shows bands around  $12450$ ,  $13330$ ,  $16680$  and  $19474\text{ cm}^{-1}$  corresponding to the levels ( $^4F_{5/2}$ ,  $^2H_{9/2}$ ), ( $^4F_{7/2}$ ,  $S_{3/2}$ ), ( $^4G_{5/2}$ ,  $^2G_{7/2}$ ) and  $^4G_{9/2}$  respectively. Sm(III) complex shows bands around  $21000$  and  $23500\text{ cm}^{-1}$

corresponding to the energy levels  $^4I_{9/2}$  and  $^6P_{5/2}$  while Dy(III) complex shows bands at  $9100$  and  $10700$  corresponding to the energy levels  $^6H_{5/2}$  and  $^6F_{7/2}$  respectively. Ho(III) complex shows bands around  $15500$  ( $^5F_6$ ),  $18450$  ( $^5S_2$ ,  $^5F_3$ ,  $^5F_4$ ) and  $28735\text{ cm}^{-1}$  ( $^5G_3$ ) whereas Er(III) complex exhibits bands at  $19000$  ( $^2H_{11/2}$ ) and  $27670\text{ cm}^{-1}$  ( $^2G_{7/2}$ ). The bands around  $32200\text{ cm}^{-1}$  observed in all the complexes may be assigned to intra-ligand transition of azomethine group<sup>6</sup>. The electronic spectra of the present complexes exhibit two bands (split components of one allowed transition) which indicate that these complexes may have  $D_{4h}$  symmetry<sup>7</sup>. The separation of the bands in  $\Delta\text{HCEN}$  and aquo complexes is of the order of  $\sim 500\text{ cm}^{-1}$  showing that these complexes are distorted octahedral. Tentative structures of the complexes can be represented by structure (A).



### References

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