Asian Journal of Chemistry Vol. 15, No. 1 (2003), 411–417

Macrocyclic Lanthanide(III) Complexes with a 14-Membered Tetraaza Ambivalent Ligand

H.C. RAI*, I. CHAKRABORTI and ASHWINI KUMAR
Department of Chemistry, L.S. College, Muzaffarpur-842 001, India

A series of complexes of the type $[Ln(mac)Cl_2(H_2O)_2]Cl$ {Ln = La, Pr, Nd, Sm, Eu, Gd, Tb and Dy; mac = 1,4,8,11-tetraazacyclotetradeca-2,3-dione] have been prepared by template reaction of the lanthanide ion. The ligand has been obtained by the reaction of 1,10-diamino-4,7-diazadecane with diethyloxalate. The complex $[La(mac)Cl_2(H_2O)_2]Cl$ reacts with lanthanide chlorides to yield the complexes of the type $[\{La(mac)Cl_2(H_2O)\}_2LnCl_3(H_2O)_2]Cl$. The chemical composition of both the mononuclear and trinuclear complexes have been established from analytical, molar conductance and FAB mass data. It is observed that the macrocycle is bonded in a tetrakis manner in the mononuclear complexes and in a hexakis manner in the trinuclear complexes. The coordination number eight around the encapsulated metal ions and nine around the exocyclic oxygen bonded metal ion are established from infrared and electronic spectral studies. The symmetry of the ligand field around the metal ion is indicated from the emission spectra.

Key Words: Lanthanide, Coordination compound, Macrocyclic ligand.

INTRODUCTION

A series of papers on the use of transition metal ions as templating agents in the synthesis of 14-, 16-, 18-, 20-, 22-, 24-, 32-, 34- and 36-membered mono, bi and trinuclear macrocyclic complexes[1–5] as well as a number of lanthanide(III) complexes with 4[N-(benzylidene) amino] antipyrine semicarbazone have been reported recently from our laboratory[6]. Macrocyclic ligands containing the oxalato groups (free >C═O groups) are scarce[7–9]. Therefore, it appeared worth while to study the possibility of formation of macrocycles comprising such groups and explore their coordination behaviour towards transition metal ions and lanthanide ions. Consequently, in continuation of our work in this field we, in the present paper, report the synthesis and characterization of mono and trinuclear complexes of a 14-membered dioxotetraaza macrocyclic ligand **(mac)** with lanthanide ions.

EXPERIMENTAL

1,10-Diamino-4,7-diazadecane was prepared as reported in the literature[10]. Diethyloxalate was an Aldrich reagent. Hydrated lanthanide chlorides (Indian

Rare Earths Ltd., Kerala, India) were used as obtained. The other chemicals used were of reagent grade.

Synthesis of the ligand 1,4,8,11-tetraazacyclotetradeca-2,3-dione, mac

1,10-Diamino-4,7-diazadecane (0.5 mmol) was diluted by dry methanol (50 mL) and diethyloxalate (0.68 mL, 5 mmol) in methanol (10 mL was added dropwise with stirring at room temperature. After stirring for more than 4 h, the solvent was removed by rotary evaporation to give an oily solid. Cold ethanol was then added and a colourless solid was obtained by slow evaporation. It was filtered and washed with cold ethanol and dried under reduced pressure. Yield *ca.* 15% (m.p. = 112 ± 1°C).

[Found: C, 52.72; H, 8.78; N, 24.58%; required for $C_{10}H_{20}N_4O_2$: C, 52.63; N, 8.77; N, 24.56%]

Synthesis of mononuclear complexes $[Ln(mac)Cl_2(H_2O)_2]Cl$

1,10-Diamino-4,7-diazadecane (0.5 mL, 1 mmol) was added to methanolic solution (7.5 mL) of diethyloxalate (0.14 mL, 1 mmol) and refluxed for 3 h; when the solution turned yellow, a solution of an equimolar amount of metal chlorides (1 mmol) in dry methanol (30 mL) was added slowly to the above solution with refluxing with continuous stirring over a period of 2 h. A gummy solid was obtained after concentrating the reaction solution. The crystallization of the complex was induced by adding acetonitrile. The compound obtained was filtered and washed with acetonitrile-ethanol mixture (3 : 1) and dried under reduced pressure; yield 80–85%.

Synthesis of trinuclear complexes $[\{La(mac)Cl_2(H_2O)_2\}_2LnCl_3(H_2O)_2]Cl_2$

The compound $[Ln(mac)Cl_2(H_2O)_2]Cl$ (0.5 g, 1 mmol) was dissolved in dry methanol (50 mL). To this, a solution of lanthanide chlorides (0.5 mmol) in dry methanol (10 mL) was added slowly. The solution mixture was refluxed for 2 h and concentrated resulting in a gummy solid. Adding actonitrile (15 mL) induced crystallization. The compound obtained was filtered and washed with acetonitrile-ethanol mixture (3 : 1) and dried under reduced pressure. The compounds are obtained in almost quantitative yield.

The metal contents were determined volumetrically[11] and chloride was determined gravimetrically[12]. Electronic spectra were recorded on a Shimadzu 160A spectrophotometer in nujol mull and 0.1% methanol solution. The analytical, magnetic moment and conductivity data have been presented in Table-1.

RESULTS AND DISCUSSION

In the infrared spectra of **mac** the amide ν(N—H) and amine ν(N—H) appear as sharp distinct bands at 3345 and 3285 cm^{-1} respectively. In the spectra of both mono and trinuclear complexes, a broad multiplet spreading over 3500–3200 cm^{-1} is observed which can be attributed to ν(N—H) of bonded NH and ν(O--H) of coordinated water molecules. Presence of strong hydrogen bonding is indicated by broadness of the ν(O—H) bond.

TABLE-1
ANALYTICAL, CONDUCTIVITY AND MAGNETIC MOMENT DATA OF LANTHANIDE(III) COORDINATION COMPOUNDS OF **mac**

Complex	% Analysis, Found (Calculated)			Λ_{max} (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)
	Ln	N	Cl		
$[La(mac)Cl_2(H_2O)_2]Cl$	27.29 (27.27)	11.03 (10.99)	20.95 (20.90)	94.6	Diamag
$[Pr(mac)Cl_2(H_2O)_2]Cl$	27.50 (27.55)	11.00 (10.95)	20.90 (20.82)	91.3	3.68
$[Nd(mac)Cl_2(H_2O)_2]Cl$	28.05 (28.02)	10.95 (10.87)	20.75 (20.69)	86.15	3.36
$[Sm(mac)Cl_2(H_2O)_2]Cl$	28.95 (28.86)	10.80 (10.75)	20.50 (20.44)	97.28	2.59
$[Eu(mac)Cl_2(H_2O)_2]Cl$	29.15 (29.08)	10.76 (10.71)	20.44 (20.38)	83.17	2.72
$[Gd(mac)Cl_2(H_2O)_2]Cl$	29.85 (29.79)	10.65 (10.61)	20.25 (20.18)	95.68	7.85
$[Tb(mac)Cl_2(H_2O)_2]Cl$	30.26 (30.20)	10.65 (10.61)	20.20 (20.11)	92.51	8.91
$[Dy(mac)Cl_2(H_2O)_2]Cl$	30.53 (30.48)	10.64 (10.57)	20.00 (19.98)	91.13	9.65
$[\{La(mac)Cl_2(H_2O)_2\}_2LaCl_3(H_2O)_2]Cl_2$	32.11 (32.05)	10.57 (10.50)	24.65 (24.57)	215.12	Diamag
$[\{La(mac)Cl_2(H_2O)_2\}_2PrCl_3(H_2O)_2]Cl_2$	32.21 (32.15)	8.67 (8.60)	24.70 (24.53)	217.21	3.08
$[\{La(mac)Cl_2(H_2O)_2\}_2NdCl_3(H_2O)_2]Cl_2$	32.40 (32.32)	8.63 (8.57)	24.55 (24.47)	198.10	3.71
$[\{La(mac)Cl_2(H_2O)_2\}_2SmCl_3(H_2O)_2]Cl_2$	32.69 (32.64)	8.60 (8.54)	24.41 (24.35)	200.12	2.58
$[\{La(mac)Cl_2(H_2O)_2\}_2EuCl_3(H_2O)_2]Cl_2$	32.78 (32.72)	8.60 (8.52)	24.39 (24.34)	213.42	3.42
$[\{La(mac)Cl_2(H_2O)_2\}_2GdCl_3(H_2O)_2]Cl_2$	32.66 (32.59)	8.55 (8.49)	24.30 (24.23)	210.12	7.61
$[\{La(mac)Cl_2(H_2O)_2\}_2TbCl_3(H_2O)_2]Cl_2$	33.15 (33.08)	8.55 (8.48)	24.25 (24.19)	205.15	9.68
$[\{La(mac)Cl_2(H_2O)_2\}_2DyCl_3(H_2O)_2]Cl_2$	33.32 (3.26)	8.51 (8.46)	24.17 (24.13)	210.12	9.95

The ν(C=O) observed at 1670 cm^{-1} in the spectrum of **mac** shifts to lower frequency by 10–20 cm^{-1} in the spectra of $[Ln(mac)Cl_2(H_2O)_2]Cl$. The lowering is possibly due to shifting of electron density towards nitrogen which is bonded to the metal ion. In the trinuclear complexes ν(C=O) band remains in the same position as in the mononuclear complex. This may be due to the fact that >C=O is in the *trans* position with respect to the amide nitrogen. Coordination through both the carbonyl oxygen and amide nitrogen will have opposite effects on ν(C═O) shift. Since the ν(C═O) band in the complexes is almost unchanged, it may be concluded that the magnitudes of these two opposing shifts are comparable.

The coordinated nature of water is indicated by the presence of bands in the regions 720–700 and 610–590 cm^{-1} due to rocking and wagging modes of water molecule respectively.

The magnetic moments of mono and trinuclear complexes are presented in Table-1. The mononuclear complexes exhibit a slight deviation from Van Vleck values and indicate[13] participation of 4f-electrons in bonding. The higher values of magnetic moments in case of the Sm(III) complex is due to T.I.P. because of low J-J separation[14].

In trinuclear complexes, the magnetic moments are near to the mononuclear complexes. The paramagnetism is only due to the presence of one of the metal ions like Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+}. There is no exchange interaction as La^{3+} has no unpaired electron.

The bands in the electronic spectra of the complexes are observed at lower wavenumbers as compared to the corresponding absorption in aqua metal ion[15]. This has been attributed to the effect of crystal field upon inter-electronic repulsion parameter in the complexes.

The hypersensitive absorption, $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ in the Nd(III) complexes has been used to probe the lanthanide ligand interaction and coordination environment around the lanthanide ions. The spectral profile of the hypersensitive band in $[Nd(mac)Cl_2(H_2O)_2]Cl$ in methanol solution is similar to that of the solid state (nujol mull). This indicates that the complexes retain their identity in solution as well[16]. The shape of the hypersensitive transition of Nd(III) complex suggests coordination number eight around the metal ion[17]. The various spectral parameters such as β, $b^{1/2}$, $\delta\%$ and η (Table-2) have been calculated from the spectra of the Nd(III) and Pr(III) complexes. The β values are less than unity and $b^{1/2}$ and $\delta\%$ values are small and positive. These suggest weak covalent bonding between Ln(III) and ligand[18, 19]. The emission spectra of mono and trinuclear Eu(III), Tb(III) and Sm(III) complexes show emission bands when excited with 350 nm radiation at liquid nitrogen temperature[20].

The mononuclear Eu(III) complex exhibits two doublets in its emission spectrum in the regions 595–590 and 620–610 nm which can be assigned to the transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ respectively. A weak band at 695 nm may be assigned to the transition, $^5D_0 \rightarrow {}^7F_4$. The emission lines due to $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_3$ transitions are not observed. The high intensity of electronic dipole allowed transition ($^5D_0 \rightarrow {}^7F_2$) compared to the magnetic dipole allowed transition ($^5D_0 \rightarrow {}^7F_1$) suggests low symmetry of complex and absence of inversion centre[21, 22]. Two peaks due to each of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions suggest D_{2d} site symmetry around the Eu(III) ion[23].

TABLE-2

ELECTRONIC SPECTRAL BANDS AND BONDING PARAMETERS OF MONO AND TRINUCLEAR LANTHANIDE(III) COMPLEXES

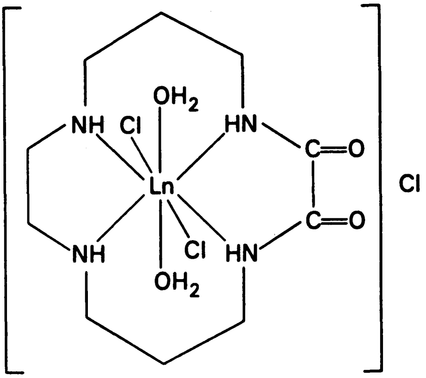
Complex	Band (cm^{-1})		J-Levels	β	$b^{1/2}$	δ%	η
	Nujol	CH_3OH					
$[Pr(mac)Cl_2(H_2O)_2]Cl$	20580	20620	$^3P_0$	0.9968	0.040	0.3210	0.0016
	21325	21284	$^3P_1$				
	22490	22471	$^3P_2$				
$[Nd(mac)Cl_2(H_2O)_2]Cl$	11510	11495	$^4F_{3/2}$	0.9958	0.0458	0.4218	0.0021
	12470	12470	$^4F_{5/2}$				
	13490	13420	$^4S_{3/2}$				
	17270	17250	$^4G_{5/2}$	$^2G_{7/2}$			
	19050	19160	$^4G_{9/2}$				
	26200	25980	$^2P_{3/2}$	$^2D_{3/2}$			
	16800		$^1D_{5/2}$				
$[\{La(mac)Cl_2(H_2O)_2\}_2PrCl_3(H_2O)_2]Cl_2$	20660		$^3P_0$	0.9964	0.0425	0.3615	0.4018
	21275		$^3P_1$				
	22370		$^3P_2$				
$[\{La(mac)Cl_2(H_2O)_2\}_2NdCl_3(H_2O)_2]Cl_2$	11490		$^4F_{3/2}$	0.9980	0.0744	0.1122	0.0055
	12400		$^4F_{5/2}$				
	13370		$^4F_{7/2}$				
	17240		$^4G_{5/2}$	$^2G_{7/2}$			
	19125		$^4G_{9/2}$				
	25840		$^2P_{3/2}$	$^2D_{3/2}$			

In the trinuclear complex, $[\{La(mac)Cl_2(H_2O)_2\}_2EuCl_3(H_2O)_2]Cl_2$, the emission lines due to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions appear at 590 and 612 nm respectively without any splitting. The emission lines due to $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_3$ transitions are not observed. The high intensity of $^5D_0 \rightarrow {}^7F_2$ compared to $^5D_0 \rightarrow {}^7F_1$ suggest low symmetry of complex and absence of inversion centre[21, 22].

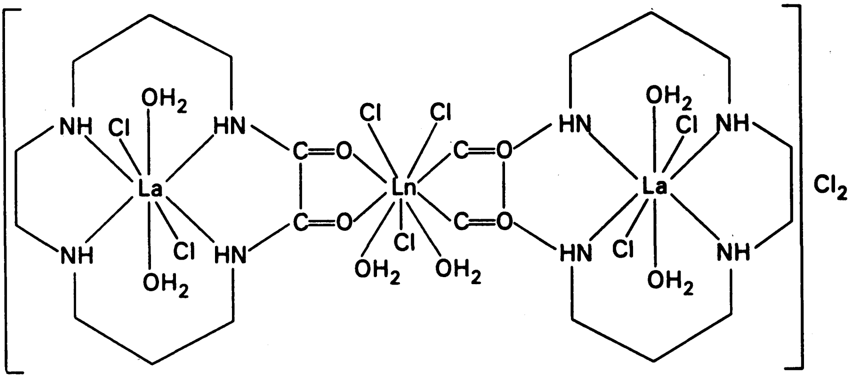
Mononuclear Tb(III) complex shows three bands in its emission spectrum at 550, 586 and 624 nm which can be assigned to the transitions $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ respectively. Trinuclear complex exhibits two bands at 538 and 590 nm due to transitions $^5D_4 \rightarrow {}^7F_5$ and $^5D_4 \rightarrow {}^7F_4$ respectively. Absence of splitting suggests high symmetry around Tb(III) ion[24].

The mononuclear Sm(III) complex does not fluoresce even at LNT. It is attributed to internal quenching through strong coupling of metal ion with crystal forces. The trinuclear Sm(III) complex exhibits intense lines at 588 nm and 612 nm which can be assigned to the transitionss $^4G_{5/2} \rightarrow {}^6H_{5/2}$ and $^4G_{5/2} \rightarrow {}^6H_{7/2}$ respectively. The number of lines associated with these transitions are rather small which are in tune with a high symmetry around Sm(III) ion[25].

On the basis of above studies, structures as shown in Figs. 1 and 2 can be proposed respectively for mononuclear and trinuclear complexes.



(Ln = La, Pr, Nd, Sm, Eu, Gd, Tb or Dy)
Fig. 1.



(Ln = La, Pr, Nd, Sm, Eu, Gd, Tb or Dy)
Fig. 2.

REFERENCES

1. H.C. Rai, *Asian J. Phys.*, **9**, 370 (2000).
2. ———, *Asian J. Chem.*, **12**, 771 (2000).
3. ———, Ashwini Kumar and Anuradha Kumari, *Asian J. Chem.*, **12**, 557 (2000).
4. H.C. Rai, A Kumar and Veena Kumari, *Asian J. Chem.*, **12**, 625 (2000).
5. H.C. Rai, A. Kumar and A. Kumari, *Asian J. Chem.*, **12**, 1189 (2000).
6. I. Chakrabarti, H.C. Rai, Neetu Goel and N.M. Hashmi, *Asian J. Chem.*, **14**, 1035 (2002).
7. M.B. Inoue, C.A. Villegas, K. Asano, M. Nakamura, M. Inoue and Q. Fernando, *Inorg. Chem.*, **31**, 2480 (1992).
8. H.C. Rai, M. Kumar, M.K. Roy and K.K. Sharma, *Asian J. Phys.*, **6**, 499 (1997).
9. B. Singh and V.L. Singh, *Indian J. Chem.*, **38A**, 802 (1999).
10. M. Micheloni and P. Paoletti, *Inorg. Chim. Acta*. **43**, 109 (1980).
11. S.J. Lyle and M.M. Rahman, *Talanta*, **10**, 1177 (1963).
12. A.I. Vogel, Textbook of Quantitative Inorganic Analysis, 4th Edn., revised by J. Bessett,

13. J.H. Van Vleck and A. Frank, *Phys. Rev.*, **34**, 1494 (1929).
14. B.N. Figgis and J. Lewis, Techniques of Inorganic Chemistry, Interscience, New York, **4**, 137 (1965).
15. W.T. Carnall, P.R. Fields and K.J. Rajnak, *J. Chem. Phys.*, **49**, 4422 (1968).
16. D.G. Karraker, *Inorg. Chem.*, **7**, 473 (1968).
17. ———, *Inorg. Chem.*, **6**, 1863 (1967).
18. S.P. Tandon and P.C. Mehta, *J. Chem. Phys.*, **52**, 4896 (1970).
19. K. Iftikhar, *Inorg. Chim. Acta*, **129**, 261 (1987).
20. C.E. Schaffer and C.K. Jorgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958).
21. G. Blasse, in: K.H.G. Schneider (Jr.) and L. Eyring (Eds.), Handbook on Physics and Chemistry of Rare Earths, Vol. 4, North Holland, Amsterdam, Chap. 34 (1979).
22. G. Blasse, A. Bril and W.C. Niewpoort, *J. Phys. Chem. Solids*, **27**, 1587 (1966).
23. G. Vicentini and V.B. De-Belis, *J. Less Common Metals*, **94**, 285 (1983).
24. A. Musumeci, R.P. Bonomo and A. Seminara, *Inorg. Chim. Acta*, **45**, 169 (1980).
25. A. Musumeci and A. Seminara, *Inorg. Chim. Acta*, **54**, L81 (1981).

(*Received*: 29 July 2002; *Accepted:* 16 September 2002) AJC-2853