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Synthesis, characterisation and antimicrobial studies on La(III), Ce(III) and Pr(III) complexes with a tetraaza macrocyclic Ligand

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ABSTRACT

The Lanthanide(III) complexes of the chloro , hydroxo substituted 14-membered tetraaza macrocyclic solid complexes of La(III), Ce(III) and Pr(III) have been synthesized and characterized by elemental analysis, conductometry, magnetic susceptibility, UV–visible, FTIR, ^{1}H NMR spectra, X-ray diffraction, and thermal analysis and screened for antimicrobial activity. From the microanalytical data, the stoichiometry of the complexes has been found to be 1:1 (metal:ligand). The TGA-DSC data suggest all Lanthanide (III) complexes having one ionic nitrate, two coordinated nitrate ions, two water molecules for Ce(III) and four water molecules for La(III) and Pr(III). The X-ray diffraction data suggest orthorombic crystal system for La(III) and monoclinic crystal system for Ce(III) and Pr(III) complexes. The ligand and their metal complexes were screened for antibacterial activity against Staphylococcus aureus and Escherichia coli. Fungicidal activity against Aspergillus niger and Trichoderma viride.

Keywords: macrocyclic Ligand complexes, Lanthanide(III) complexes, Thermal analysis; Powder X-ray diffraction; Biological activity etc.

INTRODUCTION

The design and synthesis of complexes of lanthanide metal ions with macrocyclic ligands is fascinating area of research because of their importance in basic and applied chemistry [1-5], as well as useful in industrial and synthetic processes such as catalysis, photochemistry and biological systems [6]. Macrocyclic ligands are able to recognize the presence of lanthanide metal ions hence widely used in the selective extraction of metals [7-9], NMR shift reagents [10-11]. Lanthanide complexes have an increasingly important role in medicine, where they are employed as diagnostic as well as therapeutic agents [12].

Studies on complexes of Schiff-base macrocyclic ligands with different size, and number of donor atoms for coordination with a variety of metal centres have been published [13-15]. The stability of macrocyclic metal complexes depends upon a number of factors, including the number and types of donor atoms present in the ligand and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate ring formed on complexation [16-17]. Tetra dentate Schiff bases are well known for their coordination with various metal ions, forming stable compounds [18]. Schiff bases play an important role in the development of coordination chemistry related to catalysis, enzymatic reactions, magnetism, and molecular architectures [19]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [20].

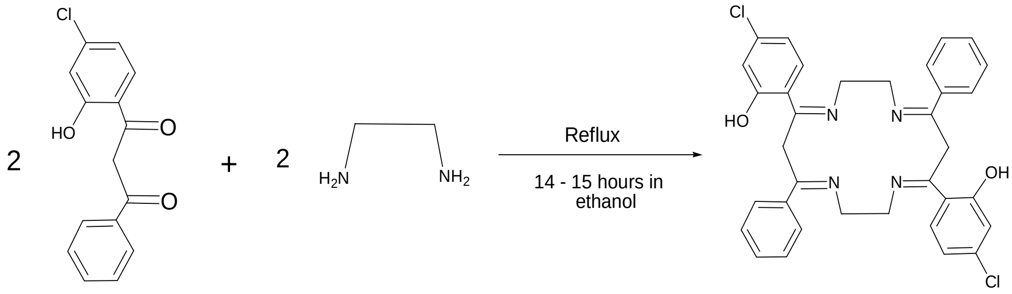
In view of these facts, reaction of the lanthanide nitrate hydrate and macrocyclic ligands has been carried out and structure of the resulting complex was investigated using spectroscopic techniques and X-ray diffraction. The results of this study are reported in this paper.

MATERIALS AND METHODS

4-Chloro 2-Hydroxy acetophenone was prepared from p-chloro phenol by fries rearrangement. 1-(4-chloro-2-hydroxyphenyl)-3-phenylpropane-1,3-dione was prepared from 4-chloro 2-Hydroxy acetophenone and benzoic acid by Bekar Vankataraman rearrangement. p-chlorophenol, acetic anhydride, anhydrous aluminum tri chloride, Benzoic acid, phosphorus oxychloride, pyridine, Potasium hydroxide, Ethylene diamine of AR grade were used for synthesis of ligand. AR grade metal nitrate was used for the complex preparation. The carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CNS analyzer. FTIR spectra were recorded on Jasco FTIR-4100 spectrometer using KBr pellets. ^{1}H NMR spectra of ligand were measured in $CDCl_3$ +DMSO using TMS as internal standard. The TGA-DSC and XRD were recorded on Perkin Elmer TA/SDT-2960 and Philips 3701, respectively. The UV–visible spectra of the complex were recorded on JascoUV-530 spectrometer. Magnetic susceptibility measurements of the metal chelates were determined on a Guoy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10^{-3} M solution in DMF.

2.1 Synthesis of ligand

A hot ethanolic solution (30 ml) of 1-(4-chloro-2-hydroxyphenyl)-3-phenylpropane-1,3-dione. (5.48g, 0.02 mol) and a hot ethanolic solution (30 ml) of ethylene diamine (1.20 g, 0.02 mol) were mixed slowly with constant stirring. This reaction mixture was refluxed at 80-90°c for 14–15 h in the presence of few drops of concentrated HCl (pH 3–4). On cooling, a solid yellow precipitate was formed, which was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10} [21-23]. (Yield: 71%) (scheme 1)



Scheme 1 Synthesis of ligand

2.2 Synthesis of complexes

A hot ethanolic (20 ml) solution of the ligand (0.001 mol) and a hot ethanolic (20 ml) solution of the corresponding metal salt (0.001 mol) were mixed together with constant stirring. The pH of the reaction mixture was adjusted in the range 7-8 by adding 10% alcoholic ammonia solution. The reaction mixture was refluxed for 5–6 h at 80-90°C.On cooling, a colored precipitate was formed. It was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10} [21-23] . (Yield 52-55%).

RESULTS AND DISCUSSION

Physical characteristics, micro analytical, molar conductance data of ligand and metal complexes are given in Table 1. The analytical data of complexes reveal 1:1 molar ratio (metal:ligand) and correspond well with the general formula $[La\ L(NO_3)_2\ H_2O]\ NO_3.nH_2O$ (where M = La(III), Ce(III) and Pr(III) and n=1 for Ce(III), n=3 for La(III) and Pr(III). The presence of water molecules and nitrate ions was confirmed by TGA-DSC analysis as well as by FTIR spectroscopy. The X-ray diffraction data suggest orthorhombic crystal system for La(III), monoclinic crystal system for Ce(III) and Pr(III). The metal chelate solutions in DMF shows low conductance which supports non-electrolyte nature of metal chelates.

3.1 ^{1}H NMR spectra of ligand

^{1}H NMR ($CDCl_3$-DMSO): δ=1.2 (s, 4H, $–CH_2$), 3.8 (s, 8H, $N=C–CH_2$), 5.7 (s, 2H, Ar-OH), 6.60–7.80 (m, 16H, Ar–H).

3.2 FTIR spectra

The IR spectrum of the ligand (L) shows a ν(C=N) peak at 1671 cm^{-1}, and the absence of a ν(C=O) peak at around 1700 cm^{-1} is indicative of Schiff's base condensation. The IR spectra of all complexes show ν(C=N) bands at 1618-1639 cm^{-1} [24-25] and it is found that the ν(C=N)bands in the complexes are shifted by about 70–29 cm^{-1} to lower energy regions compared to that in the free ligand (L). This phenomenon appears to be due to the coordination of

Azo-methine nitrogen to the metal ion [26-28]. The absorption bands appearing in the 1540 - 1560 cm^{-1} region in the complexes are attributed to the ν (C=C) vibration. The absorption bands appearing in the 2935-2920 cm^{-1} region in the complexes is due to ν(C-H) vibrations. The ν(OH) vibration of the phenolic proton appears as a broad band in the region 3200-3600 cm^{-1} probably due to the overlapping of the symmetric and antisymmetric OH stretching vibrations of lattice water [29]. The presence of coordinated water is also established and supported by TGA-DSC analysis of these complexes . The band in the 310–370 cm^{-1} regions may be assigned to ν(M–N) vibration. The IR spectra of the complexes are characterized by the appearance of a broad band in the region at 3400–3450 cm^{-1} due to OH groups [30-32]. All nitrato complexes exhibit absorption bands at ~ 1500 & 1320cm^{-1} due to the ν(N=O) (ν_1) and ν_a (NO_2) (ν_5) vibrations, respectively of the coordinated nitrate ion. The ν_s (NO_2) vibration (ν_2) appearing at ~1030 cm^{-1} is characteristic of a bidentate chelating nitrate. The separation ($\Delta\nu$) of the nitrate stretching fundamental (ν_1-ν_5) has been used as a criterion to distinguish between monodentate and bidentate chelating nitrates. $\Delta\nu$ increases as the coordination of the nitrate group varies from monodentate to bidentate. The magnitude of this separation ($\Delta\nu$ =129,206,184 for the La(III), Ce(III) and Pr(III) complexes respectively) is indicative of bidentate coordination of the nitrate ion. Nitrate ion has a strong preference for bidentate chelation with the lanthanide (III) ions [33-34]. The strong and sharp band at 1384 cm^{-1} is characteristic of ionic nitrate [25]. On the basis of above discussion, a four coordinated structure is proposed for all the complexes in which the ligands coordinate *via* four azomethine nitrogens. (Table 2).

3.3 Electronic spectra

The electron absorption spectra of the ligand and complexes are recorded after preparing the solution and after standing the solution for 3 weeks in DMF. No appreciable change in the spectrum with time is observed[42]. The bands at 324- 374 nm are indicative of benzene and other chromophore moieties present in the ligand .The absorption bands of the complexes shifted to longer wave numbers compared to that of ligand. A moderately intensive band observed in the range 320-380 nm is due to existence of ligand to metal charge transfer [25]. A broad and intense absorption band at 370-380 nm which can be assigned $\pi - \pi^*$ and n-n* transition of the imines group [35]. The Pr(III)complexes display the characteristic bands due to f-f transition[36].

3.4 Magnetic measurements

The magnetic measurements were carried out at room temperature with a Gouy's balance using [$HgCo(SCN)_4$] as a calibrant. Results are as shown in Table.1

Table 1. Physical characterization, analytical and molar conductance data of ligand and its metal complexes

Ligand/complexes	F.W.	M.P. (^0C)	Magnetic moment (B.M.)	Molar conduc. Mho (cm^2 mol^{-1})	% Found (Calcd.)			
					C	H	**N**	**M**
(L)	597	189	---	2.38	68.92 (68.34)	4.87 (5.02)	9.10 (9.38)	-----
[La $L(NO_3)_2$ H_2O] $NO_3.3H_2O$	994	>300	Dia.	102.30	40.52 (41.04)	3.46 (3.82)	9.96 (9.85)	13.46 (13.98)
[Ce $L(NO_3)_2$ H_2O] $NO_3.H_2O$	959	>300	2.521	88.22	42.50 (42.54)	3.23 (3.54)	9.81 (10.21)	14.91 (14.59)
[Pr $L(NO_3)_2$ H_2O] $NO_3.3H_2O$	996	>300	3.456	104.57	40.25 (40.96)	3.53 (3.81)	9.24 (9.83)	14.60 (14.15)

Table 2. FTIR spectra of the ligand (L) and its Metal complexes (cm^{-1}).

Ligand/complexes	(OH)	(C=N)	(C–O)	(C–Cl)	(M–N)	Ionic nitrate	Coordinated nitrate			
						NO_3	(N=O) (ν_1)	(NO_2) (ν_5)	(NO_2) (ν_3)	$\Delta\nu$= ν_1-ν_5
(L)	3465	1671	1230	658	---	---	---	---	--	---
[La $L(NO_3)_2$ H_2O] $NO_3.3H_2O$	3435	1639	1211	656	366	1384	1447	1318	1032	129
[Ce $L(NO_3)_2$ H_2O] $NO_3.H_2O$	3436	1618	1215	656	359	1384	1524	1318	1027	206
[Pr $L(NO_3)_2$ H_2O] $NO_3.3H_2O$	3439	1627	1217	655	321	1384	1505	1321	1029	184

3.5 Powder X-ray diffraction

The X-ray diffraction of representative metal complexes was scanned in the range 20-80° at wave length 1.540Å. The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). The diffractogram of La(III) complex had 23 reflections with maxima at 2θ= 27.190° and its intensity 120.25 a.u. corresponding to d value 3.277 Å. The diffractogram of Ce(III) complex shows 21 reflection with maxima at 2θ = 28.444° and its intensity 421.77 a.u. corresponding to d value 3.135Å. The diffractogram of Pr(III) complex had 21 reflections with maxima at 2θ = 27.174° and its intensity 323.23 a.u. corresponding to d value 3.278Å. The X-ray diffraction pattern of these complexes with respect to major peaks having relative intensity greater than 10% has been indexed by using computer programme. The above indexing method also yields Miller indices (hkl), unit cell parameters and unit cell volume. The unit cell of La(III) complex yielded values of lattice constants, a=16.49 Å, b = 5.37 Å, c = 5.08 Å and unit cell volume V= 451.85Å^3. In concurrence with these cell parameters, the conditions such as a ≠b ≠ c and α = β = γ = 90 required for sample to be orthorhombic were tested and found to be satisfactory. Hence, it can be concluded that La(III) complex have orthorhombic crystal system. The unit cell of Ce(III) complex yielded values of lattice constants, a= 7.41 Å, b = 5.69Å, c=6.10 Å, and unit cell volume V =223.24 Å^3. The unit cell of Pr(III) complex yielded values of lattice constants, a = 9.65 Å, b= 6.65 Å, c = 6.04 Å and unit cell volume V= 338.01 Å^3. In concurrence with these cell parameters, the conditions such as a ≠b ≠ c and α = γ =90^0 ≠ β required for sample to be monoclinic were tested and found to be satisfactory Hence, it can be concluded that Ce(III) and Pr(III) complexes have monoclinic crystal system (fig 1).

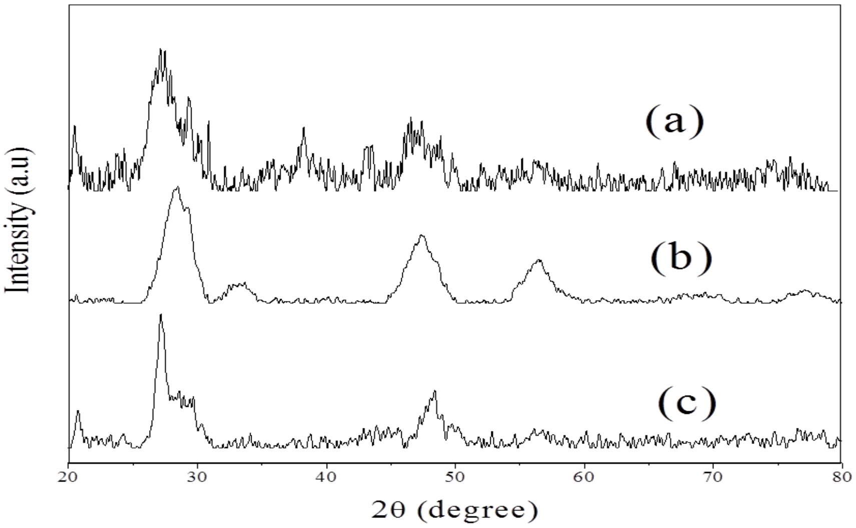


Fig. 1. X-ray diffractograms of (a)- La(III); (b)- Ce(III); (c)- Pr(III) complexes.

3.6 **Thermal analysis**

The simultaneous TGA-DSC analysis of metal complexes was studied from ambient temperature to 1000 $^{\circ}$C in nitrogen atmosphere using α-Al_2O_3 as reference. The La(III), Ce(III) and Pr(III) complexes of ligand were chosen for thermal study. Themogravimetric analysis shows that the lanthanide (III) complexes of ligand exhibit high thermal stability. The lattice water is removed in the temperature range of 55–110 $^{\circ}$C and the ionic nitrates are removed in the 178–360 $^{\circ}$C range. The macrocycle is lost in the temperature range of 361– 825 $^{\circ}$C along with the coordinated nitrate [37].

Lanthanum (III) complexes in which three lattice water and one coordinated water molecules are removed with mass lose of 7.9% (calcd.7.24%) between 50-210 $^{\circ}$C and one ionic nitrate ion is removed with loss of 7.20% (calcd.6.79%) between 200-323°C. An endothermic peak in the range 200-220 $^{\circ}$C (δ_{max} 210 $^{\circ}$C) on the DSC curve corresponds to the dehydration step and second endothermic peak in the range 320-330 $^{\circ}$C (δ_{max}323 $^{\circ}$C) corresponds to the denitration step. The macrocycle is lost in the temperature range of 323– 820 $^{\circ}$C along with the coordinated nitrate. The mass of final residue corresponds to stable La_2O_3, 60.47% (calcd. 58.62%).

Cerium (III) complexes in which one lattice water, one ionic nitrate are removed with mass lose of 8.2% (calcd.7.92%) between 50-2130 $^{\circ}$C. An endothermic peak in the range 210-230 $^{\circ}$C (δ_{max} 213 $^{\circ}$C) on the DSC curve corresponds to the dehydration and denitration step. The macrocycle is lost in the temperature range of 213– 820 $^{\circ}$C along with the coordinated water and coordinated nitrate. The mass of final residue corresponds to stable Ce_2O_3, 72.24% (calcd. 68.31%).

Praseodymium(III) complexes in which three lattice water and one coordinated water molecules are removed with mass lose of 7.30% (calcd.7.22%) between 50-200 $^{\circ}$C .and one ionic nitrate ion is removed with loss of 7.3% (calcd.6.81%) between 200-310°C. An endothermic peak in the range 190-210 $^{\circ}$C (δ_{max} 200 $^{\circ}$C) on the DSC curve corresponds to the dehydration step and second endothermic peak in the range 300-320 $^{\circ}$C (δ_{max} 310 $^{\circ}$C) corresponds to the denitration step. The macrocycle is lost in the temperature range of 310–820 $^{\circ}$C along with the coordinated nitrate. The mass of final residue corresponds to stable Pr_2O_3, 55.77% (calcd. 54.15%).

3.7 Antimicrobial activity

The antibacterial activity of ligand and its metal complexes were evaluated in vitro against bacteria such as gram +ve bacteria *(Staphylococcus aureus)*and gram –ve bacteria (*Escherichia coli)* by paper disc plate method [38]. Sterile (10 mm) diameter Whatmann No. 42 paper discs were soaked in different concentrations of the ligand/complexes (500 ppm and 1000 ppm) in DMF dried and then placed on the lawn culture of nutrient agar plates. The plates were then incubated for 24 h at 37 °C and the inhibition zone around each disc was measured. The results obtained were compared with known antibiotics, Ciprofloxin. Three replicates were taken and average values are given in (Table 3).

The Antifungal activity of ligand and its metal complexes were screened in vitro against *Aspergillus niger*, *Trichoderma viride* by mycelia dry weight method [38-39]. The compounds were tested at the concentrations 250 and 500 ppm in DMF and compared with control. The culture of fungi was purified by single spore isolation technique. The glucose nitrate (GN) medium was used for the growth of fungi. The mycelial biomass was then dried along with filter paper in an oven at 655 °C to constant weight, cooled and finally weighed. The mycelial dry weight (MDW) was obtained by subtracting the weight of mycelium free filter paper from final dry weight. Three replicates of each treatment were repeated in all experiments. The yields of MDW in mg are presented in (Table 4).

From Tables 3 and 4, it is clear that the inhibition by metal chelates is higher than that of ligand and the results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes [39-40]. Such enhanced activity of metal chelates is due to the lipophilic nature of the metal ions in complexes [41]. The increase in activity with concentration is due to the effect of metal ions on the normal process. The action of compounds may involve the formation of hydrogen bond with the active center of cell constituents, resulting in interference with the normal cell process [52].

Table 3. Antibacterial activity of ligand and its metal complexes

Ligand/complexes	Inhibition zone diameter (mm)			
	E. coli		*Staphylococcus aureus*	
	500ppm	1000ppm	500ppm	1000ppm
Ciprofloxin	16	20	15	19
(L)	06	08	06	07
$[La\,L(NO_3)_2\,H_2O]\,NO_3.3H_2O$	08	10	07	10
$[Ce\,L(NO_3)_2\,H_2O]\,NO_3$.H2O	08	11	08	10
$[Pr\,L(NO_3)_2\,H_2O]\,NO_3.3H_2O$	09	11	07	11

Table 4. Antifungal activity of ligand and its metal complexes of mycelial dry weight in mg (% inhibition)

Ligand/complexes	*Aspergillus niger*		*Trichoderma viride*	
	250ppm	500ppm	250ppm	500ppm
Control	89	89	83	83
(L)	70 (21)	68(24)	63 (24)	60(28)
$[La\,L(NO_3)_2\,H_2O]\,NO_3.3H_2O$	62 (30)	61(31)	57 (31)	52(37)
$[Ce\,L(NO_3)_2\,H_2O]\,NO_3$.H2O	59 (33)	58(35)	51 (39)	49(41)
$[Pr\,L(NO_3)_2\,H_2O]\,NO_3.3H_2O$	57 (35)	54(39)	49 (41)	46(45)

CONCLUSION

Based on analytical, conductance, magnetic, infrared, electronic spectral data, TGA and X-ray powder pattern, all these complexes exhibit cordination number nine. A tentative, general structure of La(III), Ce(III) and Pr(III) macrocyclic ligand complexes is given in Fig. 2. Biological studies of these complexes reveal that these complexes show better activity compared to their respective ligands. The FTIR spectral data suggest that the ligand behaves as a tetradentate ligand with N_4 donor atoms towards central metal ion. The X-ray diffraction data suggest orthorhombic crystal system for La(III) and monoclinic crystal system for Ce(III) and Nd(III). Thermal study reveals thermal stability of complexes.

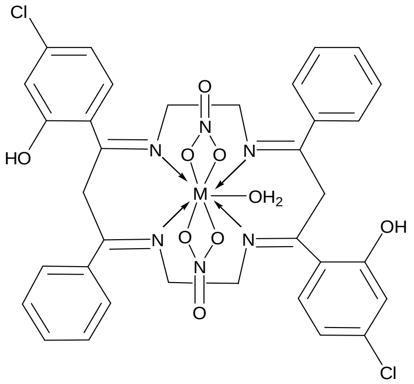


Fig. 2. Structure of metal complexes. Where M = La(III), Ce(III) and Pr(III).

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