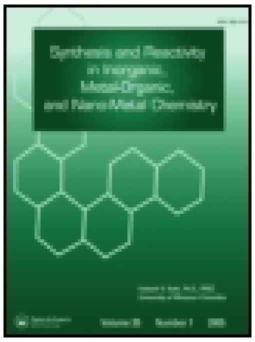

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Synthesis, Characterization and Antibacterial Activity of Complexes of Lanthanide(III) Nitrates with 2-Chloro-10-[3-(Diethylamino)Propyl]-Phenothiazine

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SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF COMPLEXES OF LANTHANIDE(III) NITRATES WITH 2-CHLORO-10-[3-(DIETHYLAMINO)PROPYL]-PHENOTHIAZINE

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ABSTRACT

Fourteen new complexes of lanthanide(III) nitrates with 2-chloro-10-[3-diethylaminopropyl]phenothiazine (chlorproethazine) of the type $[Ln(CPE)_2(NO_3)_2]NO_3$ (where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and CPE = chlorproethazine) have been synthesised and characterised on the basis of elemental analyses, magnetic moments, molar conductance measurements, IR, electronic spectra, TG and DTA. The analytical data suggest the Ln^{3+} ions are eight-coordinate. The nephelauxetic ratios (β), bonding parameters ($b^{1/2}$), Sinha's parameters ($\delta\%$) and covalency angular overlap parameters (η) have been calculated for the Pr(III), Nd(III) and Er(III) complexes. The complexes have been screened for their antibacterial activities against four bacteria.

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INTRODUCTION

N-alkylphenothiazines have been reported to be biologically versatile compounds possessing anticholinergic, antihistamine and antiamoebic activities[1,2]. They find extensive applications in industry[3] and chemical analysis[4,5]. Some of them are capable of causing a wide variety of adverse effects in patients including cardiovascular, hematologic and behavioural problems[6]. Biologically active complexes of copper(II)[7], titanium(IV)[8], zirconium(IV)[9] and yttrium(III)[10] with N-alkylphenothiazines have been synthesized and characterized. In view of the growing interest in lanthanides and their complexes, we report herein the synthesis, characterization and antibacterial activity of lanthanide(III) nitrate complexes with 2-chloro-10-[3-(diethylamino)propyl]phenothiazine (Fig. 1).

RESULTS AND DISCUSSION

The reaction between aqueous solutions of lanthanide(III) nitrates and chlorproethazine hydrochloride results in the formation of lanthanide(III) nitrate - CPE complexes. The following equation represents the 1:2 stoichiometry.

$$Ln(NO_3)_3 + 2\ CPE.HCl \longrightarrow [Ln(CPE)_2(NO_3)_2]NO_3 + 2HCl$$

The complexes are non-hygroscopic and are stable at room temperature for long periods. All complexes are soluble in DMF and DMSO, sparingly soluble in acetonitrile and chloroform and insoluble in water and other common organic solvents. They do not possess sharp melting points.

The analytical results are listed in Table 1, which are in accordance with a 1:2 metal-ligand stoichiometry. The molar conductances (Table I)

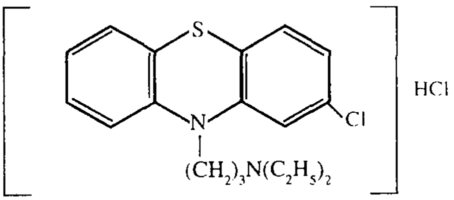

Fig. 1. Structure of Chlorproethazine Hydrochloride.

of the complexes in DMF (75-95 ohm^{-1} cm^{2} mol^{-1}) are in the range expected for 1:1 electrolytes[11]. Thus, the complexes may be formulated as $[Ln(CPE)_2(NO_3)_2]NO_3$.

Magnetic Data

The magnetic data (Table I) indicate that the lanthanum and lutetium complexes are diamagnetic and the remaining complexes are paramagnetic. The observed magnetic moments show little deviation from the Van Vleck values[12] which suggest that the 4f electrons play only a small role in bonding and also the values are found to be close to the theoretical values calculated using the formula[13] $\mu = g\sqrt{J(J+1)}$, indicating the non-participation of f-electrons in bonding.

Electronic Spectral Studies

The electronic spectrum of chlorproethazine hydrochloride shows $n \to \pi^*$ and $\pi \to \pi^*$ transitions at 31,796 and 37,383 cm^{-1}, respectively. In the spectra of corresponding complexes of the lanthanides the $n \to \pi^*$ bands are blue-shifted to 32,051-31,847 cm^{-1} and the $\pi \to \pi^*$ bands are red-shifted to 37,313 to 36,968 cm^{-1}. The f-f bands for the Pr(III), Nd(III) and Er(III) complexes in the visible region with various calculated parameters (β, $b^{1/2}$, $\delta\%$, η)[14] in 10^{-3} M DMF solutions and their tentative

Table I. Analytical, Molar Conductance and Magnetic Data of Lanthanide(III)-CPE Complexes

Complex	F.W. (Decomp. Temp.)°C	Found (Calcd), %				NO_3^- (ionic)[a]	Λ^b_M (%,yield)	μ_{eff} B.M.
		Ln	C	H	N			
$[La(CPE)_2(NO_3)_2]NO_3$ $LaC_{38}H_{46}N_7S_2Cl_2)_9$	1018.74 (125-136)	13.58 (13.63)	44.70 (44.80)	4.53 (4.55)	9.58 (9.62)	0.0602 (0.0608)	88.89 (74.8)	Dia
$[Ce(CPE)_2(NO_3)_2]NO_3$ $CeC_{38}H_{46}N_7S_2Cl_2O_9$	1019.95 (135-146)	13.67 (13.73)	44.65 (44.74)	(4.52) (4.54)	9.59 (9.61)	0.0605 (0.0607)	87.08 (74.5)	2.60
$[Pr(CPE)_2(NO_3)_2]NO_3$ $PrC_{38}H_{46}N_7S_2Cl_2O_9$	1020.74 (130-138)	13.70 (13.80)	44.60 (44.71)	4.53 (4.54)	9.60 (9.60)	0.0604 (0.0607)	93.78 (74.8)	3.58
$[Nd(CPE)_2(NO_3)_2]NO_3$ $NdC_{38}H_{46}N_7S_2Cl_2O_9$	1024.74 (132-140)	14.03 (14.08)	44.44 (44.56)	4.52 (4.52)	9.54 (9.57)	0.0601 (0.0605)	94.88 (74.8)	3.62
$[Sm(CPE)_2(NO_3)_2]NO_3$ $SmC_{38}H_{46}N_7S_2Cl_2O_9$	1030.18 (138-146)	14.50 (14.59)	44.20 (44.30)	4.48 (4.50)	9.49 (9.51)	0.0600 (0.0601)	90.78 (74.6)	1.65
$Eu(CPE)_2(NO_3)_2]NO_3$ $EuC_{38}H_{46}N_7S_2Cl_2O_9$	1031.79 (132-142)	14.68 (14.08)	44.18 (44.23)	4.47 (4.49)	9.47 (9.50)	0.0594 (0.0600)	91.76 (75.0)	3.22
$[Gd(CPE)_2(NO_3)_2]NO_3$ $GdC_{38}H_{46}N_7S_2Cl_2O_9$	1037.08 (129-139)	15.10 (15.16)	43.92 (44.00)	4.44 (4.47)	9.42 (9.45)	0.0595 (0.0597)	92.76 (74.7)	7.83

$[Tb(CPE)_2(NO_3)_2]NO_3$ $TbC_{38}H_{46}N_7S_2Cl_2O_9$	1038.75 (132-141)	15.22 (15.29)	43.85 (43.93)	4.42 (4.46)	9.45 (9.40)	0.0592 (0.0596)	90.78 (74.9)	9.75
$[Dy(CPE)_2(NO_3)_2]NO_3$ $DyC_{38}H_{46}N_7S_2Cl_2O_9$	1042.33 (133-142)	15.51 (15.58)	43.68 (43.78)	4.43 (4.44)	9.36 (9.40)	0.0590 (0.0594)	92.76 (75.0)	10.52
$[Ho(CPE)_2(NO_3)_2]NO_3$ $HoC_{38}H_{46}N_7S_2Cl_2O_9$	1044.76 (126-134)	15.73 (15.78)	43.57 (43.68)	4.41 (4.43)	9.34 (9.38)	0.0585 (0.0593)	77.58 (74.6)	10.44
$[Er(CPE)_2(NO_3)_2]NO_3$ $ErC_{38}H_{46}N_7S_2Cl_2O_9$	1047.09 (138-145)	15.90 (15.97)	43.49 (43.58)	4.42 (4.42)	9.35 (9.36)	0.0586 (0.0592)	93.78 (74.7)	9.32
$[Tm(CPE)_2(NO_3)_2]NO_3$ $TmC_{38}H_{46}N_7S_2Cl_2O_9$	1048.76 (132-141)	16.05 (16.10)	43.45 (43.51)	4.40 (4.42)	9.33 (9.34)	0.0587 (0.0591)	87.08 (74.5)	7.64
$[Yb(CPE)_2(NO_3)_2]NO_3$ $YbC_{38}H_{46}N_7S_2Cl_2O_9$	1052.87 (130-140)	16.34 (16.43)	43.28 (43.34)	4.38 (4.40)	9.28 (9.31)	0.0584 (0.0588)	91.76 (74.3)	4.61
$[Lu(CPE)_2(NO_3)_2]NO_3$ $LuC_{38}H_{46}N_7S_2Cl_2O_9$	1054.80 (136 140)	16.55 (16.58)	43.20 (43.27)	4.36 (4.39)	9.30 (9.29)	0.0586 (0.0587)	75.15 (74.9)	Dia

[a]Sample taken for determination of ionic nitrate = 1.0 g and the results are given in gram.

[b](Ohm^{-1} cm^2 $mole^{-1}$) in DMF as solvent.

assignments are given in Table II. It is found that the values of the nephelauxetic ratio (β) are smaller than unity and the values of the bonding parameters ($b^{1/2}$) and Sinha's parameter (δ%) are both positive, suggesting the occurence of a covalent character in metal ligand bonding. The shapes of the hypersensitive transitions closely resembles those of the eight-coordinate complexes reported by Karraker[15]. The electronic spectral parameters also suggest the weak covalent nature[16] of the metal-ligand bonds.

Infrared Spectra

Selected IR absorption frequencies of the lanthanide(III) nitrate chlorproethazine complexes are listed in Table III. The band observed in 2842 cm^{-1} region in the IR spectra of the chlorproethazine hydrochloride may be due to the heterocyclic nitrogen atom attached to an alkyl group[1]. This band has been shifted to the 2830-2815 cm^{-1} region in the spectra of the corresponding lanthanide(III) complexes, suggesting the coordination of the heterocyclic nitrogen atom. A broad band at 2580-2500 cm^{-1} observed in the IR spectrum of chlorproethazine hydrochloride corresponds to the interaction of $CH_2NR_2H^+$ with X^- anion (where R=ethyl and X^-=chloride). In the IR spectra of the lanthanide(III) complexes this band has been shifted to the 2657-2630 cm^{-1} region, indicating the participation of the tertiary nitrogen atom of the side chain in coordination. Thus, chlorproethazine acts as a bidentate ligand. The strong band at 760 cm^{-1} observed in the spectrum of the ligand assignable to the ν(CSC)[17] stretching frequency remains unaffected in the spectra of the complexes, supporting the non-coordination of the heterocyclic sulphur atom.

The nitrate complexes exhibit four bands at 1470-1460, 1270-1260, 1035-1030 and 835-830 cm^{-1} which can be assigned to the

Table II. Electronic Spectral Data of Praseodymium(III), Neodymium(III) and Erbium(III) Complexes

Λ(cm^{-1})		Assignment	Calculated parameters				
$Ln(NO_3)_3$	Complex		ε	β	$b^{1/2}$	δ%	η
$Pr(NO_3)_3$	$[Pr(CPE)_2(NO_3)_2]NO_3$						
16849	16806	$^3H_4$—>$^1D_2$	341.9	0.9974	0.0360	0.2606	0.0013
20646	20618	—>$^3P_0$	414.5	0.9986	0.0265	0.1402	0.0007
21418	21367	—>$^3P_1$	707.7	0.9976	0.0346	0.2406	0.0012
22539	22472	—>$^3P_2$	1031.5	0.9970	0.0387	0.3009	0.0015
$Nd(NO_3)_3$	$[Nd(CPE)_2(NO_3)_2NO_3$						
11569	11494	$^4I_{9/2}$—>$^4F_{3/2}$	777.2	0.9935	0.0570	0.6542	0.0032
12565	12500	—>$^4F_{5/2}$	1585.0	0.9948	0.0509	0.5227	0.0026
13428	13422	—>$^2S_{3/4}$,$^4F_{7/2}$	1602.0	0.9995	0.0159	0.0500	0.0002
14644	14598	—>$^4F_{9/2}$	435.3	0.9968	0.0324	0.3210	0.0016
17317	17182	—>$^4G_{5/2}$,$^2G_{7/2}$	1920.8	0.9922	0.0625	0.7861	0.0039
19338	19230	—>$^4G_{7/2}$	1086.1	0.9944	0.0529	0.5631	0.0028
$Er(NO_3)_3$	$[Er(CPE)_2(NO_3)_2]NO_3$						
15414	15337	$^4I_{15/2}$—>$^4F_{9/2}$	369.5	0.9950	0.0500	0.5025	0.0025
18488	18348	—>$^4S_{3/2}$	578.3	0.9924	0.0430	0.7658	0.0038
19087	19047	—>$^2H_{11/2}$	671.6	0.9979	0.0324	0.2104	0.0010
20585	20491	—>$^4F_{7/2}$	375.7	0.9954	0.0200	0.4621	0.0023

Table III. Main IR Spectral Bands (cm^{-1}) of Lanthanide(III) Nitrate CPE Complexes

Complex	(NO_3) coordinated				NO_3^- ionic	υ(Ln-N)
$[La(CPE)_2(NO_3)_2]NO_3$	1465 s	1263 m	1035 s	832 s	1384 s	441 s
$[Ce(CPE)_2(NO_3)_2]NO_3$	1466 s	1265 w	1030 m	834 s	1380 s	450 s
$[Pr(CPE)_2(NO_3)_2]NO_3$	1470 m	1268 m	1032 w	835 m	1385 b	448 s
$[Nd(CPE)_2(NO_3)_2]NO_3$	1460 s	1263 b	1034 m	830 m	1383 w	455 m
$[Sm(CPE)_2(NO_3)_2]NO_3$	1465 s	1260 s	1030 s	833 s	1380 s	450 s
$[Eu(CPE)_2(NO_3)_2]NO_3$	1466 w	1268 b	1032 w	830 s	1383 m	452 s
$[Gd(CPE)_2(NO_3)_2]NO_3$	1460 m	1263 s	1034 s	835 m	1378 s	450 m
$[Tb(CPE)_2(NO_3)_2]NO_3$	1470 w	1270 m	1031 m	834 s	1384 b	452 m
$[Dy(CPE)_2(NO_3)_2]NO_3$	1465 b	1262 m	1035 s	832 w	1382 s	450 s
$[Ho(CPE)_2(NO_3)_2]NO_3$	1466 s	1263 s	1034 s	835 s	1378 m	445 s
$[Er(CPE)_2(NO_3)_2]NO_3$	1470 b	1265 w	1030 m	830 b	1380 s	448 s
$[Tm(CPE)_2(NO_3)_2]NO_3$	1468 s	1260 m	1032 w	835 s	1382 s	446 s
$[Yb(CPE)_2(NO_3)_2]NO_3$	1465 s	1262 m	1035 s	831 s	1384 s	440 s
$[Lu(CPE)_2(NO_3)_2]NO_3$	1470 m	1268 s	1033 m	830 m	1380 s	450 s

vibrational modes of coordinated (C_{2v}) nitrate groups[18]. The magnitude of splitting of the bands at higher energies is about 200 cm^{-1} suggesting that the nitrate groups are attached bidentately to the metal atom. The absorption band observed at 1385-1378 cm^{-1} is due to the ionic nitrate in the complexes. This indicates that these complexes have both ionic and coordinated nitrate groups. The new bands observed in the region 452-440 cm^{-1} may be assigned to a ν(Ln-N)[19] mode. This mode suggests the participation of the nitrogen atoms of chlorproethazine in coordination.

Thermogravimetric Studies

Thermogravimetric analyses with a linear heating rate of 10° min^{-1} in static air show that the complexes are stable up to 230° C indicating the absence of water and other coordinated solvent molecules. The complexes undergo a two-stage decomposition in the range 310-410° C with a weight loss of 67.75 to 70.25% due to loss of the organic moiety and at 430-740° C with a weight loss of 15.36 to 19.15% due to loss of nitrate followed by the formation of lanthanide(III) oxide. The residue reached constant mass at 755-765° C. The experimental results are in good agreement with the calculated values on the basis of the stoichiometry proposed for the complexes. DTA studies indicate that both the decomposition of the organic moiety and the formation of lanthanide(III) oxides are exothermic processes.

Antibacterial Activity

The results of the antibacterial activity against three bacteria are given in Table IV. These results indicate that chlorproethazine hydrochloride and lanthanide nitrate solutions do not show any antimicrobial activity. The complexes are found to be inactive against *Escherichia coli* but they inhibited the growth of *Bacillus subtilis* sp,

Table IV. Antibacterial Activity of Lanthanide Nitrates, the Ligand and its Complexes with Lanthanum(III), Samarium(III) and Gadolinium(III)

Complex	Average Inhibition Zone (in mm)								
	Bacillus subtilis			*S.coccus sp*			*salmonella sp*		
	a	b	c	a	b	c	a	b	c
$[La(CPE)_2(NO_3)_2]NO_3$	1.5	3.5	5.5	1.0	4.0	6.0	1.5	4.0	6.0
$[Sm(CPE)_2(NO_3)_2]NO_3$	1.5	4.0	6.5	1.5	3.5	5.5	1.5	4.5	6.0
$[Gd(CPE)_2(NO_3)_2]NO_3$	1.0	4.0	6.0	1.0	4.0	6.5	1.5	4.0	5.0
$La(NO_3)_3$	-	-	0.5	-	-	0.5	-	-	0.5
$Sm(NO_3)_3$	-	-	0.5	-	-	0.5	-	-	0.5
$Gd(NO_3)_3$	-	-	0.5	-	-	0.5	-	-	0.5
CPE.HCl	-	-	0.5	-	-	0.5	-	-	0.5

Concentration of the Complex in DMF : $^{a}1000$ μg mL^{-1}; $^{b}3000$ μg mL^{-1} and $^{c}5000$ μg mL^{-1}.

Staphylococcus aures and *Salmonella sp.* This is due to complexation which reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with donor groups and possible π-electron delocalization over the whole complex molecule.

In the light of the foregoing discussion, the structure in Fig. 2 has been proposed for the lanthanide(III) nitrate-chlorproethazine complexes.

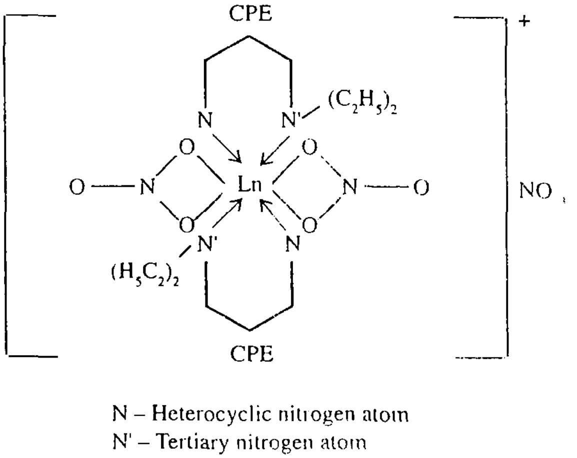

Fig. 2. Proposed Structure of Lanthanide(III) Nitrate-CPE Complexes

EXPERIMENTAL

Materials

The nitrates of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy were procured from Indian Rare Earths Ltd., Trivandrum, India and the nitrates of Ho, Er, Tm, Yb and Lu from Aldrich Chemical Company, Inc., Milwaukee, WI, U.S.A. Chlorproethazine hydrochloride was obtained from Rhone Poulenc, Paris, France. All other chemicals and solvents were of AR grade.

Analysis of the Complexes

The contents of carbon, hydrogen and nitrogen were determined with a Carlo Erba 1106 elemental analyser. The metal content of the complexes was determined by complexometric EDTA titration using xylenol orange as indicator[20] and the ionic nitrate content was determined gravimetrically using nitron as nitron nitrate.[21]

Physical Measurements

Molar conductances were measured in 10^{-3} M DMF solutions using a digital ELICO conductivity bridge. The IR spectra of samples in KBr pellets were recorded on a Shimadzu FTIR Model 470 spectrometer. The electronic spectra in DMF were measured on a JASCO-UVIDEC-610 double-beam spectrophotometer. Magnetic susceptibilities were determined by the Gouy method at room temperature using $Hg[Co(SCN)_4]$ as calibrant. Thermal analyses were carried out on a RIGAKU-TGA instrument with a linear heating rate of 10° min^{-1} in static air.

Preparation of the Complexes

An aqueous solution (50 mL) of lanthanide(III) nitrate (0.40-0.45g, 0.92-1.24 mmol) was added to an aqueous solution (50 mL) of chlorproethazine hydrochloride (1.20g, 3.11 mmol) with continuous stirring. The reaction mixture was kept aside for 1 h and the solid complex in each case was filtered, washed with water followed by ether and dried *in vacuo* over fused $CaCl_2$. Yield, 0.955-1.022g, (75%).

Antibacterial Activity

The antibacterial activity of the ligand (CPE.HCl), lanthanide nitrates (La(III), Sm(III) and Gd(III)) and their corresponding complexes with chlorproethazine were tested against *Escherichia coli, Bacillus subtilis sp, Staphylococcus aures* and *Salmonella sp* by using the paper disc method[22]. The cultures of the used microorganisms were obtained from the characterized stock culture of Department of Studies in Applied Botany and Bio-technology, University of Mysore, Mysore.

All the bacteria were cultured for 24 h on a Mueller-Hinton medium in glass petri plates. Sterilized medium was cooled to 40° C, poured into petri plates seeded with 0.5 mL of 24 h bacterial culture (10^3 colony forming units/mL) and the medium was allowed to solidify. Sterile Whatman No. 1 paper discs (4 mm diameter) were dipped in the filtered complexes, chlorproethazine hydrochloride and lanthanide nitrate solutions of concentrations 1000-5000 $\mu g\ mL^{-1}$ individually and placed at equidistance on the medium. Filter paper discs dipped in sterile distilled water and DMF solvent separately were used as controls. Replicates of two plates were maintained for each of the concentrations tested. The plates were incubated at 37° C for 24 h and observed for inhibition zones. A compound is regarded as active at a particular concentration if a minimum of 1 mm circle around a disc showed no growth of the bacteria.

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