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Synthesis and Characterization of Open-ring Polycomponent Complexes Formed in the Reaction of Lanthanides with *m*-Phenylenediamine and Dibenzoyl Methane

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Six new polycomponent complexes of lanthanides have been prepared by template reaction of *m*-phenylenediamine with dibenzoyl methane in the presence of lanthanide chlorides and conc. HCl in methanol solution. They have been characterized by elemental analysis, molar conductivity data, IR, UV, ^{1}H NMR and TG-DTA. The measured results show that *m*-phenylenediamine is mono-condensed with dibenzoyl methane, forming a mono-condensate *m*-phenylenediaminediphenylpropane-1,3-dioneimine (L). The L is coordinated with lanthanide by carbonyl oxygen and azomethine nitrogen to form the complexes. The formula of the complexes is $LnL_2Cl_3 \cdot 2H_2O$, where Ln is Nd, Sm, Eu, Gd, Dy and Er, respectively.

Key Words: Lanthanide, Complexes, *m*-Phenylenediamine, Dibenzoyl methane.

INTRODUCTION

There is a continued interest in synthesizing complexes of lanthanides because of variable coordination numbers of rare earth elements[1] and their potential applications in fundamental and applied sciences. For example, they can serve as NMR shift reagents[2–4], as luminescent chemosensors[5], as luminescent probes[6], in biomedical analyses[7–9], cancer phototherapy[10], fluoroimmunoassay[6], etc. The authors earlier reported preparation and characterization of several multidentate and mono-and di-nuclear rare earth complexes containing aza (N) and oxa (O) ligating atoms[11–13]. This paper studies the template reaction of lanthanide chlorides with *m*-phenylenediamine and dibenzoyl methane in the presence of conc. HCl, and synthesizes six new lanthanide complexes. Their compositions and structures are corroborated by elemental analysis and various spectrum measurements.

EXPERIMENTAL

All chemicals and solvents used were purchased as AR grade and without further purification before use. The hydrated lanthanide chlorides were prepared by the reported method[13].

The IR spectra in the 4000–400 cm^{-1} range in KBr pellets were recorded on a Shimadzu FTIR 3000 instrument. The UV-Vis spectra in 200–700 nm range were recorded on a Shimadzu UV-160 A spectrophotometer in DMF solution. 1D ^{1}H NMR spectra were acquired on Variant Mercury-UX 300 MHZ spectrophotometer for DMSO-d_6 solution, using TMS as internal standard. Molar conductivities were obtained on a DDSJ-308 type instrument for DMF as solvent at

14 ± 1°C. DTA-TG measurements were performed using Shimadzu DT-40 type instrument.

Metal contents of the complexes were determined by EDTA titration using xylenol orange as an indicator, while halides were measured by Volhard's method.

Preparation of complexes

All the six lanthanide complexes were prepared by the following general method: To a solution of metal salt (0.5 mmol) in 15 mL methanol, 15 mL methanolic solution of dibenzoyl methane (1 mmol) was added with stirring and refluxed for 15 min. Then *m*-phenylenediamine (1 mmol) dissolved in 15 mL methanol was added and the mixture solution refluxed again for 0.5 h. After dropping in 0.2 mL conc. HCl the reaction mixture turned to red and continued refluxing for 24 h till no colour-changing; the reaction mixture was concentrated to *ca.* 5 mL and cooled. To it *ca.* 8 mL anhydrous ether was added. A powder precipitate was formed immediately. The product was filtered off, repeatedly washed with ether and dried *in vacuo*.

RESULTS AND DISCUSSION

The elemental analysis data of the complexes are presented in Table-1 which correspond to the formula $Ln(C_{21}H_{19}N_2OCl)_2Cl_3 \cdot 2H_2O$, where Ln = Nd, Sm, Eu, Gd, Dy and Er. All complexes are coloured crystals and soluble in H_2O, methanol, ethanol, DMF; insoluble in acetone, ether. All the metal complexes are stable to air and light.

TABLE-1
COLOUR, YIELDS AND ELEMENTAL ANALYSIS DATA OF THE LANTHANIDE(III) COMPLEXES

Complex	Colour	Yield (%)	Cl (%)		Ln (%)	
			Found	Calcd.	Found	Calcd.
$NdL_2Cl_3 \cdot 2H_2O$	Grey blue	43	17.85	17.90	14.31	14.60
$SmL_2Cl_3 \cdot 2H_2O$	Blue	46	17.43	17.85	15.56	15.13
$EuL_2Cl_3 \cdot 2H_2O$	Grey	37	17.66	17.82	15.45	15.25
$GdL_2Cl_3 \cdot 2H_2O$	Grey blue	41	17.47	17.73	15.32	15.69
$DyL_2Cl_3 \cdot 2H_2O$	Blue	27	18.09	17.70	16.35	16.13
$ErL_2Cl_3 \cdot 2H_2O$	Grey	38	17.83	17.55	16.70	16.54

Various important bands and their assignments are given in Table-2. The IR spectra of the six complexes are similar indicating the presence of the same ligand throughout the series. Compared with dibenzoyl methane and *m*-phenylenediamine, the appearance of a new strong band at *ca.* 1622 cm^{-1} suggests the condensation of the diamine with the diketone, forming the —C=N— bond.[14] But the presence of the —C=O and the —NH_2 stretching frequencies indicates that only one —NH_2 and one >C=O are condensed in the reaction. A wide and strong band at *ca.* 2860–2600 cm^{-1} substantiates the presence of —$NH_2 \cdot HCl$,[15] showing that another —NH_2 in *m*-phenylenediamine exists as ammonium salt in the ligand. The medium bands at *ca.* 450 cm^{-1} and *ca.* 519 cm^{-1}, attributed to

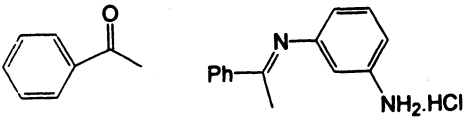
ν(Ln—N) and ν(Ln—O), respectively[16, 17], imply that carbonyl oxygen and azomethine nitrogen coordinate to metal atom. The presence of water molecules in the complexes is corroborated by the wide and strong band at *ca.* 3400 cm^{-1} assigned to —OH of H_2O[15] and two weak bands at *ca.* 740 cm^{-1} and *ca.* 665 cm^{-1} due to $\rho_r(H_2O)$ and $\rho_w(H_2O)$ modes[18], respectively.

TABLE-2
IMPORTANT INFRARED SPECTRA DATA OF THE COMPLEXES (cm^{-1})

Complex	ν(—OH)	ν(—NH_3)	ν(—C=O)	ν(—C=N—)	ν(Ln—N)	ν(Ln—O)
$Nd_2Cl_3 \cdot 2H_2O$	3398	2870	1556	1623	451	519
$SmL_2Cl_3 \cdot 2H_2O$	3399	2864	1558	1622	451	517
$EuL_2Cl_3 \cdot 2H_2O$	3382	2869	1552	1619	450	518
$GdL_2Cl_3 \cdot 2H_2O$	3389	2832	1553	1620	451	519
$DyL_2Cl_3 \cdot 2H_2O$	3401	2868	1552	1617	451	519
$ErL_2Cl_3 \cdot 2H_2O$	3386	2834	1554	1622	431	519

In the IR spectra of the complexes, there are some other important bands: *ca.* 1500 cm^{-1}: ν(phenyl ring); *ca.* 1450 cm^{-1}: ν(—CH_2–); *ca.* 1200 cm^{-1}: ν(—C—N).

The UV spectral data are shown in Table-3. All the complexes show four strong absorption bands which may be attributed to π-π^* charge transfer. λ_1 (206 nm) can be assigned to K band of phenyl ring; λ_2 (224 nm), K band of *m*-phenylenediamine; λ_3 (242 nm), λ_4 (267 nm) may be due to the K bands of two conjugated systems, respectively:



The absence of a strong band due to a much larger conjugated system of enol form suggests that the ligand exists as keto form[19]. This is also confirmed by the presence of smooth and symmetrical weak band (293 nm) assignable to the *n*-π^*-characteristic band of >C=O[15].

The ^1H NMR of Sm complex has been recorded to confirm the structure and bonding of the complex. The wide signal at δ 8.0–8.8 ppm is assigned to the H of —NH_3^+.[20] The signals at δ 7.1 ppm and δ 7.6 ppm are attributed to and  respectively. The latter appears at lower field than the former for the inductive effect of N atoms[15]. The signal of —CH_2— protons is observed at δ 2.9 ppm. The ratio of integral values for the four kinds of protons is 3 : 10 : 4 : 2 and supports the proposed formulation of the complex. The signal of H_2O is overlapped by the solvent signal.

The molar conductivity data of the complexes are given in Table-3. For a comparative study, the conductivities of $NdCl_3$ and anhydrous $NiCl_2$ have been

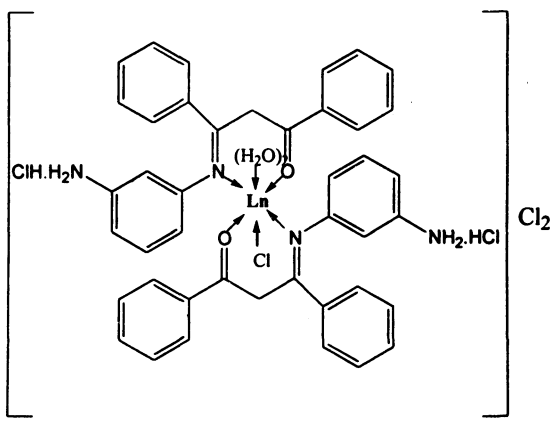
recorded at the same condition, whose molar conductance values are 106 s cm^2 mol^{-1} and 172 s cm^2 mol^{-1}, respectively. The molar conductance values for the complexes in DMF are near to that of anhydrous $NiCl_2$ and in the range reported for 1 : 2 electrolyte in the solvent[21]. This suggests that one chloride ion is coordinated to metal atom, at least in DMF[21]. The molar conductivities are higher than that of $NdCl_3$. This may be due to the ionization of —NH_2·HCl in the solvent and steric barrier of the ligand to block the coordination of chloride ions.

TABLE-3
UV SPECTRAL DATA (nm) AND MOLAR CONDUCTIVITY DATA FOR THE COMPLEXES

Complex	λ_1	λ_2	λ_3	λ_4	Λ (m/s cm^2 mol^{-1})
$NdL_2Cl_3·2H_2O$	206	219	243	267	181
$SmL_2Cl_3·2H_2O$	205	223	243	268	174
$EuL_2Cl_3·2H_2O$	207	221	243	267	170
$GdL_2Cl_3·2H_2O$	207	219	244	268	199
$DyL_2Cl_3·2H_2O$	206	224	242	267	176
$ErL_2Cl_3·2H_2O$	206	222	244	268	183

The thermal behaviur of the Er complex in N_2 surroundings has been studied by TG-DTA. The absence of transformation endothermic peak indicates that the complex hasn't been melted on heating[22]. The complex begins to lose water at 145°C and suggests that the waters in the complex are coordination waters. The presence of only one exothermic peak shows that the complex is immediately decomposed after losing water and then loses its ligand. The decomposition temperature is 270°C. The TG curve shows that the whole weight-losing rate is 80.0% and indicates that the complex transforms to oxide after being completely decomposed.

Thus, based on the result of elemental analysis, molar conductance measurements, UV, IR, ^1H NMR and TG-DTA study, the following structure is suggested for the complexes:



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