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Synthesis and Characterization of Mixed Ligand Complexes of Some Lanthanide(III) with N,N′-Triethylenediamine-bis-(3-carboxypropenamide)

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A series of mixed ligand complexes of lanthanide ions with N,N′-triethylenediamine-bis-(3-carboxypropenamide) have been synthesized and characterized by chemical analysis, conductance, magnetic, thermal and infrared spectral studies. On the basis of the above studies, the following general formula is suggested with a coordination number seven for these complexes: [M(TEBCP)X], where M = Pr(III), Nd(III), Sm(III), Gd(III) or Dy(III) and X = NO_3^-, Cl^-, ClO_4^- or SCN^-.

Key Words: Synthesis, Mixed ligand complexes, Lanthanide(III) ions.

INTRODUCTION

Synthesis and characterization of complexes of ligands containing amide groups have been reported in literature[1]. The present communication reports the synthetic, structural and thermal aspects of the complexes of the polydentate ligand, triethylenediamine-bis-(3-carboxypropanamide) [$TEBCPH_2$] with praseodymium(III), neodymium(III), samarium(III), gadolinium(III) and dysprosium(III).

EXPERIMENTAL

All the chemicals used were of AR grade or pure quality. The solvents were double distilled.

Preparation of N,N′-triethylenediamine-bis-(3-carboxypropanamide) ($TEBCPH_2$): Maleic anhydride (0.1 mol) was dissolved in glacial acetic acid (50 mL) and to this triethylenetetramine (0.05 mol) was added dropwise with constant stirring under ice-cold conditions. The white solid formed was filtered, washed several times with acetone and then recrystallized from aqueous ethanol. The pure ligand has the melting point of 126°C.

Preparation of the nitrato, chloro and perchlorato complexes: 0.001 mol of the respective metal salt was dissolved in methanol. To this, a solution of 0.001 mol of $TEBCPH_2$ in methanol was added slowly and refluxed for 2–3 h.

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Immediate colour change was observed. The resulting solution was concentrated to half of its volume and allowed to cool. The solid complexes formed were filtered, washed with methanol and acetone and finally dried over calcium chloride in a desiccator.

Preparation of thiocyanato complexes: The nitrato complex of these metal ions with $TEBCPH_2$ were prepared first. These were dissolved in methanol and mixed with stoichiometric quantity of aqueous methanolic solution of ammonium thiocyanate. The reaction mixtures were refluxed for 2–3 h to replace the nitrate ions by thiocyanate ions. The resulting solutions were concentrated to half the volume and cooled. The solid complexes formed were filtered, washed with methanol and acetone and finally dried over calcium chloride in a desiccator.

The complexes were crystalline and stable at room temperature. All the complexes are moderately soluble in methanol, nitrobenzene, DMF and DMSO. The metal contents of the complexes were determined by gravimetric methods[2]. The anion contents were estimated wherever possible. The molar conductivities of the complexes in acetonitrile, methanol, nitrobenzene and DMF (*ca.* 10^{-3} M solutions) were determined at room temperature. Magnetic susceptibilities of the complexes were determined at room temperature by the Gouy method. The infrared spectra of the ligand and the complexes were recorded in the range 4000–400 cm^{-1}. In the case of chloro complexes, the infrared spectra were recorded in the far infrared region also. Molar masses of the complexes were determined by the Rast method using biphenyl as the solvent[3]. The TG and DTG curves of the complexes $[Gd(TEBCP)NO_3]$ and $[Dy(TEBCP)NO_3]$ were recorded on a thermal analyzer from ambient to 750°C.

RESULTS AND DISCUSSION

A total of twenty complexes of lanthanide metal ions with $TEBCPH_2$ have been isolated, all of which are solids with different colours. Analytical data, molar mass and μ_{eff} of the complexes are presented in Tables-1 (a) and (b). These show that the complexes have the general formula [M(TEBCP)X], where M = Pr, Nd, Gd, Sm or Dy; X = NO_3^-, Cl^-, ClO_4^- or SCN^-. The observed magnetic moments agree with the theoretical spin-orbit coupling values[4] (Hund rules) with the exception of Samarium(III) complexes. However, it is found that the experimental values for all the complexes including those of Samarium(III) agree with the theoretical values calculated from van Vleck formula[5]. This agreement between the observed values and the van Vleck values suggests the nonparticipation of 4*f* electrons in bond formation with the ligands.

The molar conductance values of the complexes are presented in Table-2. The values show that the complexes behave like non-electrolytes in all the solvents used indicating that the anions present in all the complexes are coordinated to the respective metal ions. The comparatively higher values of the conductance for the complexes in methanol are probably due to partial displacement of the coordinated anions by polar methanol molecules[6].

TABLE-1 (a)
ANALYTICAL DATA, MOLAR MASS AND MAGNETIC MOMENTS OF THE COMPLEXES OF TEBCPH$_2$ WITH THE CHLORIDES, NITRATES AND THIOCYANATES OF Pr(III), Nd(III), Sm(III), Gd(III) AND Dy(III)

Complex	Molar mass Found (Calcd.)	% Analysis, Found (Calcd.)		μ_{eff} (BM)
		Metal	Anion	
[Pr(TEBCP)NO$_3$]	558.1	25.78	11.82	3.53
	(543.23)	(25.94)	(11.41)	
[Nd(TEBCP)NO$_3$]	561.4	26.18	10.88	3.58
	(546.50)	(26.39)	(11.34)	
[Sm(TEBCP)NO$_3$]	564.8	26.92	10.90	1.62
	(552.67)	(27.20)	(11.22)	
[Gd(TEBCP)NO$_3$]	548.1	28.74	10.78	7.84
	(559.57)	(28.10)	(11.05)	
[Dy(TEBCP)NO$_3$]	555.2	28.30	11.3	10.48
	(564.82)	(28.77)	(10.98)	
[Pr(TEBCP)Cl]	528.1	27.63	7.12	3.51
	(516.69)	(27.27)	(6.86)	
[Nd(TEBCP)Cl]	531.5	27.93	7.06	3.60
	(519.96)	(27.74)	(6.82)	
[Sm(TEBCP)Cl]	514.1	28.42	6.93	1.30
	(526.13)	(28.58)	(6.74)	
[Gd(TEBCP)Cl]	548.1	29.93	6.42	7.91
	(533.03)	(29.50)	(6.65)	
[Dy(TEBCP)Cl]	554.3	29.82	6.91	10.52
	(538.28)	(30.19)	(6.59)	
[Pr(TEBCP)(NCS)]	558.10	26.41	10.91	3.52
	(539.23)	(26.13)	(10.76)	
[Nd(TEBCP)(NCS)]	561.02	26.72	10.78	3.64
	(542.50)	(26.58)	(10.69)	
[Sm(TEBCP)(NCS)]	564.12	27.18	10.32	1.34
	(548.67)	(27.40)	(10.57)	
[Gd(TEBCP)(NCS)]	548.3	28.61	10.14	7.80
	(555.57)	(28.30)	(10.44)	
[Dy(TEBCP)(NCS)]	580.4	28.70	10.59	10.55
	(560.82)	(28.97)	(10.34)	

TABLE-1 (b)
ANALYTICAL DATA, MOLAR MASS AND MAGNETIC MOMENTS OF THE COMPLEXES OF TEBCPH$_2$ WITH PERCHLORATES OF LANTHANIDES

Complex	Molar mass Found (Calcd.)	% Analysis, Found (Calcd.)				μ_{eff} (BM)
		Metal	Carbon	Hydrogen	Nitrogen	
[Pr(TEBCP)ClO$_4$]	596.12	24.54	28.61	3.89	9.12	3.54
	(580.69)	(24.26)	(28.93)	(3.44)	(9.64)	
[Nd(TEBCP)ClO$_4$]	602.44	24.88	28.98	3.78	9.91	3.58
	(583.96)	(24.70)	(28.76)	(3.42)	(9.59)	
[Sm(TEBCP)ClO$_4$]	613.12	25.18	28.84	3.69	9.89	1.36
	(590.13)	(25.48)	(28.47)	(3.39)	(9.49)	
[Gd(TEBCP)ClO$_4$]	620.21	26.62	28.65	3.81	9.71	7.85
	(597.03)	(26.34)	(28.14)	(3.35)	(9.38)	
[Dy(TEBCP)ClO$_4$]	619.19	26.64	27.31	3.71	9.63	10.52
	(602.28)	(26.98)	(27.89)	(3.32)	(9.29)	

TABLE-2
MOLAR CONDUCTANCE DATA OF THE COMPLEXES OF TEBCPH$_2$ WITH LANTHANIDES(III)

Complex	Molar conductance (ohm^{-1} cm^2 mol^{-1})			
	Methanol	Acetonitrile	Nitrobenzene	DMF
[Pr(TEBCP)NO$_3$]	28.51	12.1	5.31	2.80
[Nd(TEBCP)NO$_3$]	27.21	9.8	2.82	2.50
[Sm(TEBCP)NO$_3$]	32.12	4.9	3.94	2.20
[Gd(TEBCP)NO$_3$]	26.19	3.5	2.60	1.90
[Dy(TEBCP)NO$_3$]	34.10	4.4	4.48	3.10
[Pr(TEBCP)Cl]	32.18	11.8	4.68	2.42
[Nd(TEBCP)Cl]	29.16	10.20	2.14	3.20
[Sm(TEBCP)Cl]	24.24	4.50	3.08	2.61
[Gd(TEBCP)Cl]	33.10	3.20	2.86	2.81
[Dy(TEBCP)Cl]	25.26	2.80	1.98	1.68
[Pr(TEBCP)ClO$_4$]	34.18	12.22	6.12	2.81
[Nd(TEBCP)ClO$_4$]	26.46	8.61	2.74	2.42
[Sm(TEBCP)ClO$_4$]	32.14	3.72	3.66	1.84
[Gd(TEBCP)ClO$_4$]	22.84	4.12	2.48	2.63
[Dy(TEBCP)ClO$_4$]	27.21	4.20	4.18	3.26
[Pr(TEBCP)NCS]	29.35	11.20	2.68	1.98
[Nd(TEBCP)NCS]	32.84	12.24	4.12	2.41
[Sm(TEBCP)NCS]	28.36	6.25	3.08	2.62
[Gd(TEBCP)NCS]	34.12	2.84	2.44	1.84
[Dy(TEBCP)NCS]	24.62	4.12	2.12	2.48

*Concentration *ca.* 10^{-3} M

The infrared spectra of the complexes of lanthanide salts were compared with that of the ligand. Infrared spectra of the ligand showed a medium band at 3100 cm^{-1} and it is assigned to ν(O—H) of carboxylic acid group[7]. This group is hydrogen bonded (intramolecular) with the carbonyl group of the amide. The disappearance of this band in the spectra of the complexes indicates deprotonation of the acid and coordination through the hydroxyl oxygen. The disappearance of the band at 1700 cm^{-1} which is due to ν(C═O) of COOH group and the appearance of two new bands at 1570–1550 cm^{-1} and 1390–1360 cm^{-1} indicated the presence of coordinated carboxylate group. The shifting of the band at 1400 cm^{-1} which is due to ν(C—O) of carboxyl group to 1360–1320 cm^{-1} also supports the above conclusion. Here, Δν(OCO) is about 200 cm^{-1} which indicates the monodentate nature of the carboxylate ion. The medium band around 3320 cm^{-1} in the spectrum of the ligand which is due to ν(N—H) of secondary amino group is shifted to a lower frequency, 3290–3280 cm^{-1}, on complex formation. This shows the participation of the secondary amino group in complex formation. The amide carbonyl stretching frequency of the ligand at 1620 cm^{-1} is shifted to lower frequency, 1590–1580 cm^{-1}, on complex formation. Therefore, it may be concluded that amide carbonyl group is coordinated to the metal ion. The medium intensity bands observed around 600–515 cm^{-1} are assigned to ν(M—N). The medium bands observed in the spectra of the complexes around

490–430 cm^{-1} and 420–410 cm^{-1} are assigned to ν(M—O) (covalent) and ν(M—O) (coordinated) respectively. The neutral nature of the complexes shown by the nonelectrolytic conductance values of the complexes indicates the presence of a uninegative anionic group (nitrate, chloride, perchlorate or thiocyanate group) inside the coordination sphere.

In the infrared spectra of the nitrato complexes, three additional bands are observed at 1430, 1300 and 1020 cm^{-1}. These three bands are attributed correspondingly to ν_4, ν_1 and ν_2 modes of the coordinated nitrate ions[8–10]. Since the difference between ν_4 and ν_1 is *ca.* 130 cm^{-1}, it can be concluded that the nitrate ions are coordinated unidentately to the lanthanide ions in the present complexes.

In the infrared spectra of the perchlorato complexes, there are three additional bands at 1100, 1080 and 630 cm^{-1}. These are assigned to the stretching vibrations of the perchlorate ion, *i.e.*, ν_4, ν_1 and ν_3 respectively. The strong bands at 1100 and 1080 cm^{-1} are assigned to ν_4 and ν_1 modes which are the split bands of the coordinated perchlorate ions. This kind of splitting indicates that the perchlorate ions are coordinated unidentately[11].

There is an additional band at 275–270 cm^{-1}, in the spectra of the chloro complexes of lanthanide ions, which is assigned to ν(M—Cl)[12].

In the infrared spectra of the thiocyanato complexes, some additional bands are observed at 2050–2040, 860 and 460 cm^{-1} which are assigned to ν(CN), ν(CS) and δ(NCS) modes of the coordinated thiocyanate ion. It has been well established that ν(CN) occurs at a lower wavenumber around 2050 cm^{-1} in N-bonded complexes as compared to the position in the case of S-bonded complexes[13] appearing around 2100 cm^{-1}. Moreover, ν(CS) mode appears in the range 860–780 cm^{-1} for N bonded complexes while it appears in the range 720–690 cm^{-1} for S-bonded complexes. N-bonded complexes[14, 15] also exhibit a single sharp band corresponding to δ(NCS) mode around 460 cm^{-1}. From these, it is evident that in the present complexes, the thiocyanate ions are coordinated unidentately to the lanthanide metal ions through the N-atom. Coordination of the thiocyanate ion agrees with the non-electrolytic conductance values of the complex. The infrared spectral studies show that the primary ligand is hexadentate coordinating through the carboxylate groups, carbonyl groups of the secondary amide and —NH of the secondary amino groups. The monovalent anions are coordinated to the lanthanide ions in a unidentate fashion[16].

Thermal studies were conducted on [Gd(TEBCP)NO_3] and [Dy(TEBCP)NO_3]. Independent pyrolysis experiment in air was also carried out for these complexes. For this, a known amount of the complex was heated in a procelain crucible up to 700°C for about 1 h. From the mass of the residue, the loss of mass was calculated in each case, which was compared with the percentage loss of mass obtained from the experiment. For the complex, [Gd(TEBCP)NO_3], the TG plateau shows that the complex is stable up to 230°C. The DTG curve shows two peaks at 245.1°C and 590.2°C which indicates that there are two decomposition stages. The TG curve shows a second plateau after 620°C indicating the completion of decomposition. The complex decomposes rapidly at 245.1°C due to the breaking up of the organic moiety and shows a weight loss of 32.1%. Decomposition continues with a gradual decrease in weight and a constant weight due to the formation of Gd_2O_3 is obtained at about 620°C with a weight loss of 72%. For the complex [Dy(TEBCP)NO_3], the TG plateau shows that the complex is stable up to 220°C. The DTG curve has two peaks at 205.7°C and 610.4°C showing the decomposition of the complex in two stages. The complex shows a weight loss of 38.4% at 205.7°C due to the decomposition of the organic moiety in the complex. The TG curve shows the second plateau at about 642°C indicating the completion in decomposition. The residual mass is about 32.5% (theoretical value is 33.01%) which corresponds to the product Dy_2O_3. Independent pyrolysis also confirms that Dy_2O_3 is the decomposition product.

On the basis of the experimental evidence gathered and the discussion therefrom, the following general formula is suggested with a coordination number seven for these complexes. [M(TEBCP)X], M = Pr(III), Nd(III), Sm(III), Gd(III) or Dy(III) and X = NO_3^-, Cl^-, ClO_4^-, or SCN^-.

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