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Synthesis and Characterization of Lanthanide(III) Complexes of N,N′-diethyleneamine-bis(3-carboxypropenamide)

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Ten complexes of lanthanides with a polydentate ligand N,N′-diethyleneamine-bis(3-carboxypropenamide) ($DBCPH_2$) have been synthesized and characterized by elemental analysis, conductance and magnetic measurements, infrared spectral and thermal analysis. The thermal analysis of the complexes proves the presence of two molecules of coordinated water molecules. The complexes have been assigned the formula $[LnL \cdot 2H_2O]$ where Ln = lanthanide ions and L = $[DBCP]^{2-}$. In these complexes the ligand acts as pentadentate.

Key Words: Synthesis, Lanthanide(III), Complexes, N,N′-Diethyleneamine-bis(3-carboxypropenamide).

INTRODUCTION

It is well established that coordination numbers more than six are favoured in lanthanide systems[1, 2]. As a part of our studies on coordination characteristics of amide group containing ligands, we have synthesized a polydentate ligand using maleic anhydride and diethylene-triamine. In the present work, the lanthanide complexes of Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) with this ligand in the presence of nitrate and thiocyanate anions were prepared and characterized by various physico-chemical methods.

EXPERIMENTAL

Lanthanide oxides (Indian Rare Earths Ltd., Kerala) were converted to the corresponding nitrates by dissolving in hot 50% (v/v) aqueous nitric acid. The undissolved metal oxide was filtered off and lanthanide nitrate was crystallized by concentrating the aqueous solution and cooling the concentrate.

Preparation of N,N′-diethyleneamine-bis(3-carboxypropenamide) ($DBCPH_2$)

Maleic anhydride (9.8 g, 0.1 mmol) was dissolved in glacial acetic acid and to this diethylenetriamine (5.4 mL, 0.05 mmol) was added drop wise with constant stirring while cooling in ice. The white solid formed was filtered, washed thoroughly with acetone and dried. It was purified by dissolving in sodium carbonate solution (5%) and reprecipitated by the addition of dilute hydrochloric acid in cold. m.p. 193°C and yield 85%.

Preparation of the complexes

The complexes with the ligand were prepared by the following general procedure. The respective lanthanide nitrate (0.1 mmol) was dissolved in methanol. To this a suspension of $DBCPH_2$ (0.1 mmol) in the same solvent was added slowly and refluxed for 2–3 h. The resulting solution was concentrated to half its volume and solid complexes formed were washed with ethanol, acetone and dried *in vacuo* over phosphorous pentoxide.

The thiocyanato complexes of the lanthanides were prepared from the nitrato complexes by the substitution reaction. The nitrato complexes and ammonium thiocyanate were taken in the ratio of 1 : 1 in ethanol and refluxed to get the desired complexes[3].

The TG, DTG and DTA curves of the complexes were recorded on a thermal analyzer in air over the temperature range 28–1200°C. Independent pyrolysis experiment in air was also carried out for each of the complexes studied and loss of mass determined in each case was compared with that obtained from TG.

The lanthanide contents of the complexes were determined gravimetrically as Ln_2O_3 by the oxalate-oxide method[4]. In the case of praseodymium the final product is Pr_6O_{11}.The nitrate was estimated gravimetrically using nitron reagent and thiocyanate was estimated as silver thiocyanate[5].

The molar conductivities of the complexes in methanol were measured at room temperature. The IR spectra of the ligand and complexes were recorded in potassium bromide pellets in the range 4000–400 cm^{-1} on a Perkin-Elmer FT-IR spectophotometer. The elemental analysis was carried out by microanalytical method. Magnetic susceptibility at room temperature was measured by Gouy method[6, 7].

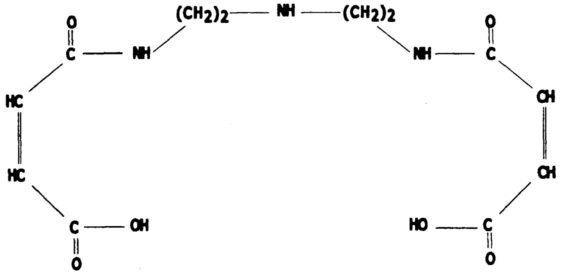
RESULTS AND DISCUSSION

All the complexes were non-hygroscopic crystalline solids, insoluble in benzene, petroleum ether and chloroform, but are sparingly soluble in acetonitrile, methanol and nitrobenzene. The analytical data are given in Table-1. The molar conductivity values of the complexes in methanol were in the range corresponding to those of non-electrolytes.

The IR spectrum of the ligand exhibits a stretching frequency of amide[8] >NH at 3300 cm^{-1}, ν(OH) of COOH group which is hydrogen bonded with carbonyl group of amide[9] at 3100 cm^{-1}, another band at 1700 cm^{-1} due to ν(CO) of COOH group, amide-I [ν(C=O)] at 1626 cm^{-1} and amide-II [ν(CN) + δ(NH)] at 1500 cm^{-1} and a band at 3320 cm^{-1} due to secondary amino group[8].

The NMR spectrum of the ligand recorded in DMSO shows signals at 4.5 (8H, CH_2), 8.4 (2H, amide NH), 5.8–6.1 (doublet of doublet, (CH=CH), 5.1 (singlet 1H, sec. amino group) and a sharp singlet at 9.1 (2H, COOH) ppm[9].

The mass spectrum of the ligand exhibits molecular ion peak at 299 and the base peak at m/z = 183 due to $[C_8N_3O_2H_{13}]^+$ ion. The peak observed at m/z 116 is due to $[C_4H_4O_4]^+$ which is maleic acid and a peak at m/z 72 is due to $[CH_2{=}CH{\cdot}COOH]$ and one at m/z 45 is due to $[COOH]^+$. From these data the following structure has been assigned to the ligand.



Structure of N,N′-diethyleneamine-bis(3-carboxypropenamide) ($DBCPH_2$)

TABLE-1
CHARACTERISATION OF THE LIGAND AND COMPLEXES

Compound	Analysis: Found (Calcd.) (%)					μ_{eff} (B.M.)	λ_m*
	C	H	N	M	H_2O		
$DBCPH_2$	46.12	5.46	13.82	—	—	—	—
	(48.16)	(5.68)	(14.04)				
$[Pr(DBCP)NO_3{\cdot}2H_2O]$	25.91	3.48	10.22	25.84	6.66	3.54	22.1
	(26.86)	(3.54)	(10.44)	(26.30)	(6.76)		
$[Nd(DBCP)NO_3{\cdot}2H_2O]$	25.87	3.43	10.16	25.12	6.63	3.61	18.4
	(26.70)	(3.52)	(10.30)	(25.72)	(6.67)		
$[Sm(DBCP)NO_3{\cdot}2H_2O]$	25.10	3.22	10.03	26.36	6.43	1.62	17.5
	(26.44)	(3.40)	(10.26)	(27.57)	(6.67)		
$[Gd(DBCP)NO_3{\cdot}2H_2O]$	25.80	3.39	10.01	26.12	6.42	7.97	13.8
	(26.07)	(3.44)	(10.14)	(28.47)	(6.51)		
$[Dy(DBCP)NO_3{\cdot}2H_2O]$	25.02	3.28	9.78	27.02	6.32	10.64	18.6
	(25.82)	(3.41)	(10.01)	(29.14)	(6.45)		
$[Pr(DBCP)NCS{\cdot}2H_2O]$	28.03	3.36	9.86	25.14	6.62	3.58	16.7
	(29.32)	(3.57)	(10.52)	(26.50)	(6.76)		
$[Nd(DBCP)NCS{\cdot}2H_2O]$	27.16	3.28	9.96	25.36	6.59	3.62	18.2
	(29.14)	(3.54)	(10.46)	(26.93)	(6.72)		
$[Sm(DBCP)NCS{\cdot}2H_2O]$	27.54	3.39	9.93	25.93	6.61	1.63	20.1
	(28.61)	(3.51)	(10.34)	(27.68)	(6.64)		
$[Gd(DBCP)NCS{\cdot}2H_2O]$	26.32	3.26	9.82	26.62	6.50	7.96	28.2
	(28.40)	(3.46)	(10.21)	(28.68)	(6.56)		
$[Dy(DBCP)NCS{\cdot}2H_2O]$	27.56	3.33	9.77	28.12	6.42	10.65	16.3
	(27.18)	(3.43)	(10.11)	(29.35)	(6.50)		

* λ_m in $ohm^{-1}\ cm^2\ mol^{-1}$.

λ_m in ohm^{-1} cm^2 mol^{-1} The infrared spectra of the complexes exhibit characteristic absorptions of all the fundamental groups of the ligand but at shifted positions in the case of coordinated groups. The absorption band due to ν(OH) of COOH observed at 3100 cm^{-1} (H-bonded) is absent in the spectra of the complexes and a new band around 3400 cm^{-1} appears, due to the ν(OH) of the coordinated water[8]. The absorption bands at 850 and 640 cm^{-1} support the presence of coordinated water molecules. These bands are due to the rocking $\rho_r(H_2O)$ and wagging $\rho_w(H_2O)$ of coordinated water molecule. In complexes the new bands observed at 1620–1570 and 1400–1320 cm^{-1} could be assigned to asymmetric and symmetric stretching frequencies of coordinated carboxyl group[8]. The large separation between these bands (*ca.* 200 cm^{-1}) confirms the unidentate nature of the carboxyl group[8]. The amide carbonyl group stretching frequency remains unaltered indicating its non-participation in bonding to metal ion. The >NH stretching frequency of amide observed at 3300 cm^{-1} in the spectrum of the ligand is shifted to lower frequency around 3260 cm^{-1} and the band at 3320 cm^{-1} due to ν(NH) of secondary amino group is shifted to 3290 cm^{-1} in all complexes showing the coordination through nitrogen atoms of the amide and secondary amino groups. The combined band due to amide-II [ν(CN) + δ(NH)] observed at 1500 cm^{-1} in the ligand undergoes a negative shift of 20 cm^{-1}. This also confirms that amide nitrogen is coordinated to metal ion.

In the case of nitrato complexes three additional bands due to coordinated NO_3 group are also observed. They appear at 1440, 1320 and 1028 cm^{-1} which are assigned respectively to ν_4, ν_1 and ν_2 modes of coordinated nitrate ion. The magnitude of separation between ν_4 and ν_1 is found to be in the order of 120 cm^{-1} suggesting the unidentate nature of nitrate ion[8].

The infrared spectra of thiocyanato complexes exhibit three additional bands at 2050, 824 and 490 cm^{-1} which are assigned respectively to ν(CN), ν(CS) and δ(NCS) modes of the coordinated thiocyanate ion[10]. Since ν(CN) mode is lower than 2100 cm^{-1} and ν(CS) vibration greater than 720 cm^{-1}, the thiocyanate ion is coordinated to the metal ion through nitrogen atom in unidentate fashion[11, 12].

In addition to these, new absorption bands appear at 540, 440 and 410 cm^{-1}, which are not present in the spectrum of the ligand. These are due to ν(Ln—N), ν(Ln—O) (ligand) and ν(Ln—O)(H_2O) modes respectively[8].

The molar conductance values of the complexes in methanol are given in Table-1, which suggest that the complexes are non-electrolytes.

The magnetic moment studies of the complexes show very little deviation from Van Vleck values[13] indicating little participation of $4f$ electrons in bonding, as these electrons are well shielded by $5s^2 5p^6$ octet. The slightly higher magnetic moment values of Sm(III) complexes than the theoretical spin orbit coupling value are due to the fact that the energy difference between the ground state and next higher J level is of the order of kT which causes thermal population of the next higher J level of the metal ion arising from the first order Zeeman effect[14].

The thermal stability of the lanthanide complexes of $DBCPH_2$ was studied in the temperature range 28–1200°C. All the complexes are stable in air at room temperature and do not change their mass after storage. When heated they decompose in various steps. According to Nikolaev *et al.*[15] and Singh *et al.*[16], water eliminated below 413–423 K can be considered as water of crystallization and above 423 K may be due to coordinated water. In the present case lanthanide(III) complexes with $DBCPH_2$, water is eliminated above 423 K as revealed from the TG analysis. The first break in TG curves (430–483) of these complexes shows a mass loss corresponding to two molecules of water. The percentage of mass loss due to two molecules of water by thermal method and calculated values for different complexes are presented in Table-1. The DTA curves of lanthanide complexes also showed one sharp endothermic peak around 453 K. There are corresponding peaks in DTG, but at slightly lower temperature. It is thus inferred from thermal and IR studies that two molecules of water are coordinated to the metal ion.

TG curves of the complexes showed three-stage decomposition. The first stage corresponds to the removal of water molecule followed by the breaking up of organic moiety of the complexes (553–900 K). Decomposition continues with gradual decrease in weight and a constant weight due to the formation of stable lanthanide oxides at about 875 K is observed. The independent pyrolysis also shows that the final decomposition product is lanthanide oxide, which is in conformity with the mass loss data obtained from TG. On the basis of the above observations it is concluded that the ligand $DBCPH_2$ is pentadentate, the coordination sites being three nitrogen and two oxygen atoms. Incorporating the anion and water molecules a coordination number of eight is assigned to the lanthanides in all the nitrato and thiocyanato complexes.

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