

Synthesis and Characterization of Lanthanide(III) Complexes of N,N'-Propylene-bis(3-carboxypropenamamide)

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Ten complexes of lanthanides with a polydentate ligand N,N'-propylene-bis(3-carboxypropenamamide) (PBCPH₂) have been synthesized and characterized by elemental analysis, conductance, magnetic measurements, infrared spectral and thermal analysis. The thermal analysis of the complexes proves the presence of three molecules of coordinated water molecules in all. The complexes have been assigned the formula [Ln·L·X·3H₂O] where Ln = lanthanide ions and L = [PBCP]²⁻ and X = NO₃⁻ or NCS⁻. In these complexes, the ligand acts as tetradentate.

Key Words: Lanthanide(III), Complexes, N,N'-propylene-bis(3-carboxy-propenamamide).

INTRODUCTION

In continuation to our interest on coordination characteristics of amide group containing ligands, a polydentate ligand using maleic anhydride and 1,3-diaminopropane have been synthesized. The complexes of Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) with this ligand, in the presence of anions nitrate and thiocyanate, were prepared and characterized by various physicochemical methods. It is well established that coordination numbers more than six are favoured in lanthanide complexes^{1,2}.

EXPERIMENTAL

All the chemicals used were of AR grade. The solvents were purified by standard methods. 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 on concentrating the aqueous solution and cooling the concentrate, crystals of lanthanide nitrate were obtained.

Preparation of N,N'-propylene-bis(3-carboxypropenamamide) (PBCPH₂)

Maleic anhydride (9.8 g, 0.1 mmol) was dissolved in glacial acetic acid and to this 1,3-diaminopropane (4.2 mL, 0.05 mmol) was added dropwise 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 reprecipitating by the addition of dilute hydrochloric acid in cold. The pure ligand has m.p. 163°C.

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 PBCPH₂ (0.1 mmol) was added slowly and refluxed for 2–3 h. The resulting solution was concentrated to half volume and the solid complexes formed were washed with ethanol, acetone and dried *in vacuo* over phosphorus pentoxide. The thiocyanate complexes of the lanthanides were prepared from the nitrate complexes by the substitution reaction. The nitrate complexes and ammonium thiocyanate were taken in the ratio of 1 : 1 in ethanol and refluxed to get the complexes³.

The TG, DTG and DTA curves of the complexes were recorded on a thermal analyzer in air at 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 Ln₂O₃ by the oxalate-oxide method⁴. In the case of praseodymium, the final product is Pr₆O₁₁. The nitrate was estimated gravimetrically using nitron reagent and thiocyanate was estimated as silver thiocyanate⁵.

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 FTIR spectrophotometer. The elemental analysis was carried out by micro-analytical 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.

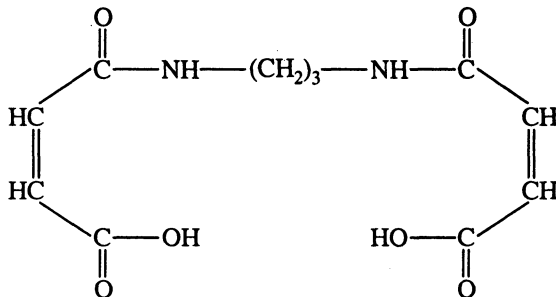
The IR spectrum of the ligand exhibits the stretching frequency of amide⁸ >NH at 3300 cm⁻¹, ν(OH) of COOH group, which is hydrogen bonded with carbonyl group of amide⁹ at 3100 cm⁻¹, another band at 1700 cm⁻¹ due to ν(CO) of COOH group, amide I ν(C=O) at 1600 cm⁻¹ and amide II [ν(CN) + δ(NH)] at 1500 cm⁻¹ and a band at 1590 cm⁻¹ due to ν(C=C) of olefinic linkage⁸.

The NMR spectrum of the ligand recorded in DMSO shows signals at 9.1 (2H, COOH), 3.6–4.3 (4H, CH₂) near to the secondary amide group. A quintet at 2.05 (2H, CH₂ in between the above protons), 8.2 (2H, amide NH) and 5.8–6.2 (doublet of doublet, [4H, CH=CH])⁹ ppm.

TABLE-1
CHARACTERIZATION OF THE LIGANDS AND COMPLEXES

Compound	Found (Calcd.)%, λ_m in $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$					μ_{eff} (BM)	λ_m
	C	H	N	M	H ₂ O		
PBCPH ₂	47.48 (48.88)	4.96 (5.18)	10.16 (10.37)	—	—	—	—
[Pr(PBCP)NO ₃ ·3H ₂ O]	24.12 (25.14)	3.12 (3.42)	7.62 (7.99)	26.02 (26.85)	9.86 (10.20)	3.54	21.4
[Nd(PBCP)NO ₃ ·3H ₂ O]	23.82 (24.98)	3.24 (3.40)	7.82 (7.95)	25.82 (25.30)	10.11 (10.22)	3.61	20.4
[Sm(PBCP)NO ₃ ·3H ₂ O]	24.02 (24.70)	3.13 (3.30)	7.52 (7.85)	27.72 (28.31)	9.92 (10.10)	1.64	18.5
[Gd(PBCP)NO ₃ ·3H ₂ O]	23.98 (24.38)	3.21 (3.32)	7.48 (7.75)	28.12 (29.05)	9.82 (9.97)	7.92	16.8
[Dy(PBCP)NO ₃ ·3H ₂ O]	23.15 (24.15)	3.08 (3.29)	7.56 (7.68)	27.92 (27.93)	9.64 (9.88)	10.64	19.6
[Pr(PBCP)NCS·3H ₂ O]	27.96 (27.63)	3.22 (3.45)	7.91 (8.06)	26.12 (27.07)	10.12 (10.36)	3.52	18.7
[Nd(PBCP)NCS·3H ₂ O]	25.22 (27.46)	3.31 (3.42)	7.82 (8.01)	26.12 (27.51)	10.18 (10.30)	3.62	28.2
[Sm(PBCP)NCS·3H ₂ O]	26.31 (27.15)	3.21 (3.39)	7.43 (7.91)	27.02 (28.38)	9.86 (10.18)	1.64	20.6
[Gd(PBCP)NCS·3H ₂ O]	24.90 (26.80)	3.11 (3.35)	7.56 (7.81)	27.12 (29.26)	9.67 (10.05)	7.91	18.2
[Dy(PBCP)NCS·3H ₂ O]	25.12 (26.54)	3.16 (3.31)	7.32 (7.74)	27.10 (29.09)	9.32 (9.95)	10.63	26.3

The mass spectrum of the ligand exhibits molecular ion peak at m/z 270 and a base peak at $m/z = 116$ due to $[\text{C}_4\text{H}_4\text{O}_4]^+$ ion and the peak at m/z 72 is due to $[\text{CH}_2=\text{CHCOOH}]^+$ and one at m/z 45 is due to $[\text{COOH}]^+$. From these data the following structure has been assigned to the ligand.



N,N'-Propylene-bis(3-carboxypropenamide) (PBCPH₂)

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 $\nu(\text{OH})$ 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 $\nu(\text{OH})$ of the coordinated water⁸. The absorption bands at 850 and 640 cm^{-1} support the presence of coordinated water molecules. These bands are due to the rocking $\rho_1(\text{H}_2\text{O})$ and wagging $\rho_w(\text{H}_2\text{O})$ of coordinated water molecule. In the complexes bands observed at 1620–1570 and 1400–1320 cm^{-1} could be assigned to asymmetric and symmetric stretching frequencies of coordinated carboxyl group⁸. The large separation between these bands (*ca.* 200 cm^{-1}) confirms the unidentate nature of the carboxy group⁸. The amide carbonyl group stretching frequency remains unaltered indicating its non-participation in bonding to metal ion. The $>\text{NH}$ stretching frequency of the ligand observed at 3300 cm^{-1} in the spectrum of the ligand is shifted to lower frequency around 3260 cm^{-1} . The combined band due to amide II [$\nu(\text{CN}) + \delta(\text{NH})$] observed at 1500 cm^{-1} in the ligand undergoes negative shift of 20 cm^{-1} . This also confirms that amide nitrogen is coordinated to metal ion in the complexes.

In the case of nitrate 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 ion⁸.

The infrared spectra of thiocyanato complexes exhibit three additional bands at 2050, 824 and 490 cm^{-1} which are assigned respectively to $\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$ modes of the coordinated thiocyanate ion¹⁰. Since $\nu(\text{CN})$ mode is lower than 2100 cm^{-1} and $\nu(\text{CS})$ 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 $\nu(\text{Ln—N})$, $\nu(\text{Ln—O})$ (ligand) and $\nu(\text{Ln—O})(\text{H}_2\text{O})$ modes respectively⁸.

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 values¹³ 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 effect¹⁴.

The thermal stability of the lanthanide complexes of PBCPH₂ 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 water eliminated above 423 K may be due to coordinated water. In the present case, lanthanide(III) complexes with PBCPH₂, water is eliminated above 423 K as revealed from the TG analysis. The first arrest in TG curves (430–483 K) of these complexes shows a mass loss corresponding to three molecules of water.

The percentage of mass loss due to three molecules of water by thermal method and calculated values for different complexes are presented in Table-1. The DTA curves of lanthanide complexes also show 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 three molecules of water are coordinated to the metal ion.

TG curves of the complexes show 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 is observed at about 825 K. 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 PBCPH₂ is tetradentate, the coordination sites being two 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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