

Synthesis and Characterization of Some Lanthanide(III) Complexes with N-(Pyrrolidinobenzyl)benzamide

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A new series of complexes of the lanthanide metal ions, viz., Pr(III), Sm(III), Nd(III), Gd(III) and Dy(III) with a Mannich base derived from benzamide, pyrrolidine and benzaldehyde have been synthesized and characterized. The analytical data include elemental analysis, determination of molar mass, conductivity, magnetic, spectral, thermal, X-ray powder diffraction and antimicrobial studies. The complexes exhibit the following general formula $[Ln(PBB)_3]$ where $Ln = Nd^{3+}$, Pr^{3+} , Gd^{3+} , Sm^{3+} and Dy^{3+} . PBB = N-(pyrrolidinobenzyl)benzamide. All the complexes exhibit octahedral geometry.

Key Words: Pr(III), Nd(III), Gd(III), Sm(III), Dy(III), Complexes, N-(Pyrrolidinobenzyl) benzamide.

INTRODUCTION

Literature survey shows that the compounds containing amide moiety have a strong ability to form metal complexes and show a wide range of biological activities¹⁻⁴. An amide group has two potential binding sites, i.e., oxygen and nitrogen for complexation. It is a generally accepted fact that for neutral amide groups both protonation and metal ion binding will be at the amide oxygen⁵. On deprotonation the binding shifts to the amide nitrogen⁶. But the coordination may also take place at amide nitrogen due to factors such as steric hindrance. The present work reports the synthesis of the Mannich base, N-(pyrrolidinobenzyl) benzamide (PBB) which also contains an amide moiety. The synthesis of PBB (Fig. 1), its complexation characteristics with Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) salts and the antibacterial activity of the ligand and the complexes are described in this communication.

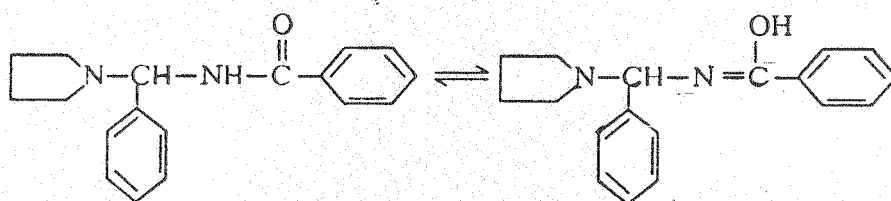


Fig. 1

EXPERIMENTAL

All the chemicals used were of AnalaR or GR (Merck) grade. Organic solvents were purified by standard methods.

Synthesis of N-(pyrrolidinobenzyl)benzamide (PBB)

Benzamide (1.21 g, 10 mmol) in 20 mL of ethanol was mixed with pyrrolidine (0.7 mL, 10 mmol) with stirring to get a clear solution at a temperature of 10°C. To this, benzaldehyde (1 mL, 10 mmol) was added in drops with stirring for about 15–20 min. The reaction mixture was kept at room temperature for 2 days. The colourless crystals were filtered and recrystallized from ethanol (yield 69.5%; m.p. 89°C).

Synthesis of metal complexes

A solution of PBB and metal salt (3 : 1 mole ratio) in ethanol-chloroform mixture (1 : 6 v/v) was boiled under reflux at 58°C (b.p. of azeotropic mixture) for about 3–4 h. The resulting solution was concentrated and then cooled. The precipitated complexes were filtered, washed with ethanol and dried *in vacuo*.

The carbon, hydrogen and nitrogen contents in each complex were determined by microanalytical method at RRL, Pappanamcode, Trivandrum. The metal contents of the complexes were determined by gravimetric methods⁷. The molar conductance of the complexes in ethanol (*ca.* 10⁻³ M solutions) were measured at room temperature by using an ELICO conductivity bridge type CM82T with a dip type conductivity cell having platinum electrodes (cell constant = 0.94 cm⁻¹). Magnetic susceptibilities were measured at room temperature using EG and G Parc model 155 vibrating sample magnetometer at RSIC, IIT, Madras. The IR spectra of the ligand and the complexes were recorded in KBr pellets using a Bruker IPS 66V FT-IR spectrophotometer at RSIC, IIT Madras. The X-ray powder patterns of the complexes were recorded on a Rigaku (Japan) PW 1710 X-ray powder diffractometer on a chart recorded at RRL, Pappanamcode, Trivandrum. The mass spectra were recorded on a Finnigan MAT 8230 mass spectrometer at RSIC, Madras. The TG-DTG curves were recorded on a thermal analyzer from ambient to 800°C at Sree Chithra Thirunal Institute for Medical Sciences and Technology. The mass percentage vs. temperature curves obtained were redrawn on appropriate scales. Independent pyrolysis experiment in air was also carried out for each of the complexes studied and the loss of mass determined in each case was compared with that obtained from TG. The antimicrobial studies of the complexes at various concentrations were also done using four different bacteria, viz., *S. aureus*, *K. pneumoniae*, *P. aeruginosa* and *E. coli* by well diffusion method⁸ at Sree Chithra Thirunal Institute for Medical Sciences and Technology, Trivandrum.

RESULTS AND DISCUSSION

The five complexes of the lanthanide metal ions with PBB have been isolated which are nonhygroscopic crystalline solids. The analytical data, molar masses, magnetic moments and molar conductance data are given Table-1.

TABLE-1
ANALYTICAL DATA, MOLAR MASS, MOLAR CONDUCTANCE AND
MAGNETIC MOMENTS (μ_{eff}) OF THE COMPLEXES OF PBU
WITH LANTHANIDE IONS AT ROOM TEMPERATURE

Complex/ Compound	Molar mass Found (Calcd.)	μ_{eff} (BM)	% Analysis, Found (Calcd.)				λ_m ($\text{ohm}^{-1} \text{cm}^2$ mol^{-1})
			Ln	C	H	N	
[C ₁₈ H ₂₀ N ₂ O]	280	—	—	77.30 (77.14)	6.89 (7.14)	9.88 (10.00)	—
Pr(PBB) ₃ [C ₅₄ H ₅₇ N ₆ O ₃ Pr]	984.1 (977.91)	3.52	14.35 (14.42)	66.70 (66.10)	5.75 (5.82)	8.49 (8.61)	19.1
Nd(PBB) ₃ [C ₅₄ H ₅₇ N ₆ O ₃ Nd]	989.6 (981.24)	3.61	14.50 (14.70)	66.30 (66.00)	5.84 (5.80)	8.39 (8.56)	18.2
Sm(PBB) ₃ [C ₅₄ H ₅₇ N ₆ O ₃ Sm]	975.8 (987.35)	1.36	15.45 (15.20)	64.90 (65.60)	5.71 (5.77)	8.41 (8.50)	17.3
Gd(PBB) ₃ [C ₅₄ H ₄₇ N ₆ O ₃ Gd]	986.2 (994.25)	7.92	15.71 (15.80)	65.80 (65.20)	5.86 (5.73)	8.32 (8.44)	13.6
Dy(PBB) ₃ [C ₅₄ H ₄₇ N ₆ O ₃ Dy]	989.8 (999.5)	10.56	16.41 (16.30)	63.90 (64.80)	5.79 (5.70)	8.29 (8.40)	16.4

The complexes are soluble in DMSO, nitrobenzene and dimethyl formamide. The molar conductance values reveal their non-electrolytic nature⁹. The room temperature magnetic moments of the lanthanide complexes with PBB are compared with the theoretical spin orbit coupling values¹⁰ (the Hund values) of the respective lanthanide ions and they agree with each other with the exception of samarium(III) complexes. However, it is found that the experimental values of all the complexes including those of samarium(III) agree with the theoretical values calculated from Van Vleck formula¹⁰. The discrepancies in the case of samarium(III) complexes may be attributed to the fact that the first excited J states of Sm³⁺ are sufficiently close to their ground states so that these states mix with each other even at room temperature causing increase in magnetic moments. This is the reason for the breakdown of the spin orbit coupling models for samarium(III) complexes. The fact that the observed magnetic moments of the present complexes show very little deviation from the Van Vleck values suggests the non-participation of 4f electrons in the bond formation with the ligands.

The mass spectrum of the ligand was recorded. The base peak observed at m/z 122 shows the presence of benzamide moiety. The molecular ion peak for the ligand is observed at m/z = 280 (C₁₈H₂₀N₂O). Other important peaks at m/z = 120 and 105 correspond to the presence of C₆H₅CONH and C₆H₅CO respectively.

The infrared spectrum of the Mannich base PBB shows $\nu(\text{NH})$ modes at 3460 (asymmetric) and 3360 cm^{-1} (symmetric). The carbonyl and C—N—C stretching frequencies of PBB appear at 1650 and 1160 cm^{-1} respectively. The $\nu(\text{NH})$ bands appearing at 3460 and 3360 cm^{-1} remain unaltered in the spectra of the complexes showing the nonparticipation of nitrogen of NH₂ in coordination. The band at 1160 cm^{-1} in the ligand¹¹, which is due to C—N—C stretching frequency, shifts to 1142–1130 cm^{-1} , in the spectra of the complexes. This indicates the coordina-

tion through the tertiary nitrogen of pyrrolidine ring. The spectra of the complexes show negative shifts of the carbonyl band at 1650 to 1635–1620 cm^{-1} showing the coordination through the carbonyl oxygen. The additional bands in the regions 440–420 and 540–515 cm^{-1} are assigned to $\nu(\text{Ln—O})$ and $\nu(\text{Ln—N})$ respectively.

The X-ray powder patterns of Nd(III) and Sm(III) complexes were analyzed to determine their structure¹². The unit cell dimensions of Nd(III) complexes are: $a = 17.5454 \text{ \AA}$, $b = 14.9178 \text{ \AA}$ and $c = 11.9621 \text{ \AA}$ respectively. These values correspond to the orthorhombic system. For Sm(III) complex, the unit cell dimensions are $a = 18.272 \text{ \AA}$, $b = 14.9182 \text{ \AA}$ and $c = 10.6984 \text{ \AA}$ respectively. These values also correspond to orthorhombic system. The number of molecules per unit cell was found to be four for both the Nd(III) and Sm(III) complexes.

All the metal chelates were tested for their antibacterial activity against *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Escherichia coli* and *Pseudomonas aeruginosa* by using well diffusion method. The zone of inhibition values of the ligand and the complexes against the growth of microorganisms are summarized in Table-2. All the complexes were found to be active towards these bacteria. The metal chelates exhibit higher activity than the free ligand and the control (ampicillin). The order of activity towards *S. aureus* is $\text{Sm} > \text{Nd} > \text{Gd} > \text{Dy} > \text{Pr}$; *P. aeruginosa* is $\text{Sm} > \text{Gd} > \text{Nd} > \text{Dy} > \text{Pr}$; *K. pneumoniae* and *E. coli* is $\text{Sm} > \text{Gd} > \text{Nd} > \text{Pr} > \text{Dy}$.

TABLE-2
ANTIBACTERIAL ACTIVITY OF THE LIGAND AND THEIR COMPLEXES:
ZONE OF INHIBITION (in mm)

Compound	<i>S. aureus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>K. pneumoniae</i>
Ampicillin	10	12	15	12
PBB	8	9	7	6
[Sm(PBB) ₃]	18	22	20	21
[Nd(PBB) ₃]	15	16	15	17
[Pr(PBB) ₃]	10	13	11	14
[Gd(PBB) ₃]	14	17	18	18
[Dy(PBB) ₃]	12	10	13	11

Thermal studies were conducted on [Dy(PBB)₃] and [Gd(PBB)₃]. For the complex [Dy(PBB)₃] the TG plateau up to 180°C shows that the complex is stable up to this temperature. The DTG curve has two peaks at 198.9° and 741.5°C. The TG curve shows a second plateau after 780°C indicating the completion of decomposition. At 198.9°C the complex shows a weight loss of 61.8%. This weight loss is due to the release of $\text{C}_6\text{H}_5\text{CO—NCH—C}_6\text{H}_5$ parts of the organic moiety. A constant weight is obtained at 780°C. The residual weight is about 18.78% which is due to Dy_2O_3 .¹³ For [Gd(PBB)₃], the plateau up to 195°C shows its stability up to this temperature. The DTG curve shows two peaks at 321.8° and 580.9°C showing the decomposition of the complex in two stages. At 321.8°C the observed weight loss is 62.1% which is due to the release of the $\text{C}_6\text{H}_5\text{CONCHC}_6\text{H}_5$ parts of the organic moiety. The TG curve shows the second

plateau at 648.5°C. This indicates the completion of decomposition. The residual mass is about 18.48% showing that the decomposition product is Gd_2O_3 . Independent pyrolysis also confirms that Gd_2O_3 is the decomposition product.

On the basis of the above studies, the structure of the complexes may be represented as in Fig. 2 in which a coordination number of six is assigned to lanthanide ions.

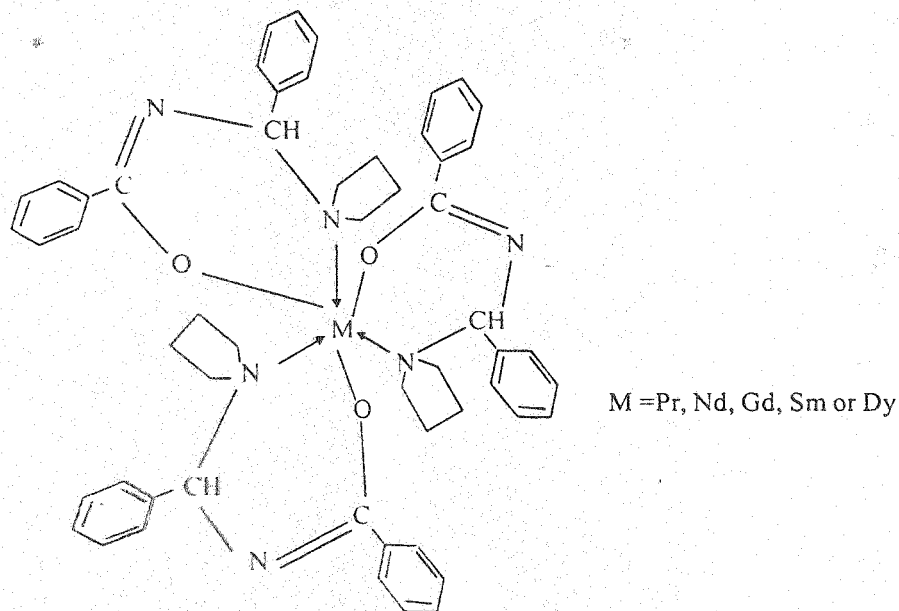


Fig. 2

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