

Synthesis and Characterization of Lanthanide(III) Complexes of 1-Phenyl-3-Methyl-5-Hydroxy-4-Pyrazolyl Propionyl-2'-Picolinoyl Hydrazone

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The ligand 1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl propionyl-2'-picolinoyl hydrazone (PMHPPr-PHz) was synthesized by condensing 1-phenyl-3-methyl-4-propionyl-5-pyrazolone with 2-picolinic acid hydrazide. The complexes of PMHPPr-PHz with La(III), Ce(III), Nd(III), Sm(III), Gd(III), Dy(III) and Er(III) ions were synthesized. The compositions and properties of the ligand and its complexes were established by elemental analyses, magnetic measurements, molar conductance, IR, ¹H NMR, electronic spectra and thermal analyses.

Key Words: Synthesis, Lanthanide complexes, Bidentate hydrazone ligand.

INTRODUCTION

The hydrazones find wide applications in the treatment of several diseases such as tuberculosis, leprosy and mental disorders, and are also used as herbicides, insecticides, rodenticides and plant growth regulators¹⁻⁸. We have synthesized 1-phenyl-3-methyl-5-hydroxy-4-pyrazolylpropionyl-2'-picolinoyl hydrazone (PMH-PPr-PHz), essentially containing a C=N group which is popularly called Schiff base, a versatile multidentate ligand capable of bonding from several alternate sites resulting in the formation of metal complexes. In this paper, we describe the synthesis and characterization of trivalent lanthanide metal complexes of the title hydrazone.

EXPERIMENTAL

All solvents and chemicals were commercial reagent grade or better and were used without further purification. 1-Phenyl-3-methyl-4-propionyl-5-pyrazolone (PMPPrP) and 2-picolinic acid hydrazide¹⁰ were prepared using a known procedure. Ln(NO₃)₃·6H₂O (Aldrich) was used as received.

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Preparation of hydrazone ligand (PMHPPr-PHz): A quantity of 3.42 g (0.025 M) of 2-picolinic acid hydrazone was dissolved in EtOH (150 mL), then 5.75 g (0.025 M) of PMPrP was added in it. The reaction mixture was refluxed on a water bath for 1 h. The colour of the solution changed from brownish yellow to orange. After cooling to room temperature, a large amount of orange precipitate separated out, which was washed with excess of ethanol and dried over fused CaCl_2 . The product was purified by anhydrous CHCl_3 ; yield 73%; m.p. 182°C. Anal.: found: C, 65.28; H, 5.39; N, 20.42; calcd. for $\text{C}_{19}\text{H}_{19}\text{N}_5\text{O}_2$ (349.36); C, 65.31; H, 5.48; N, 20.04%. ^1H NMR (CDCl_3) δ (ppm): 2.43 (3H, singlet, ring $-\text{CH}_3$); 1.33 (3H, triplet, propionyl, $-\text{CH}_3$); 2.77 (2H, quartet, $-\text{CH}_2$); 7.12-7.98 (5H, multiplet, phenyl ring); 8.01-8.64 (4H, multiplet, pyridine ring); 10.18 (1H, singlet, $-\text{NH}$); 12.6 (1H, singlet, $-\text{OH}$).

Preparation of complexes: A quantity of 2.09 g (0.006 M) of the ligand PMHPPr-PHz was added to DMF (30 mL) and to this was added dropwise a solution of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.002 M) in CH_3OH (10 mL). The pH of the solution was adjusted to 6-7 by constant stirring with the addition of NaOAc dissolved in methanol and then refluxed for 3-4 h. The solid precipitate was collected after the evaporation of the reaction mixture. The complex was recrystallized from DMF solution.

Carbon, hydrogen and nitrogen were analyzed on a Carlo-Erba elemental analyzer. The metal contents of the complexes were determined by complexometric titration with EDTA using xylenol orange as indicator¹¹. The molar conductance of the complexes was recorded in DMF solution on an ELICO Conductivity bridge, type CM82T. Infrared spectra ($4000-400\text{ cm}^{-1}$) were obtained with KBr optics on a Perkin-Elmer-830 FT-IR spectrophotometer. UV/Vis absorption spectra were recorded on a Shimadzu UV-160 spectrophotometer. ^1H NMR spectra were recorded in CDCl_3 and $\text{DMSO}-d_6$ at CDRI, Lucknow and IIT, Powai, Mumbai. The thermal behaviour of the complexes was obtained using a Mettler M3 microbalance with Mettler TC 10A processor from Mantra Institute, Surat.

RESULTS AND DISCUSSION

All complexes are greenish yellow in colour, insoluble in CCl_4 , water, ethanol and benzene but are soluble in DMF, DMSO and CHCl_3 . The molar conductance of the complexes in 10^{-3} M DMF solutions were found to be very low values (Table-1), indicating that the complexes are non-electrolytic in nature. The magnetic susceptibility of the complexes was measured by Gouy method at room temperature; the effective magnetic moment (μ_{eff}) values are most comparable with the expected values.

The elemental analyses data of the complexes (Table-1) show the formula of the complexes as $[\text{Ln}(\text{PMHPPr-PHz})_3]$ (Ln = trivalent lanthanides such as La, Ce, Nd, Sm, Gd, Dy and Er), with three ligand moieties coordinate to the metal ion.

TABLE-I
ANALYTICAL DATA OF HYDRAZONE LIGAND AND ITS
LANTHANIDE METAL COMPLEXES

Compound	Color (m.p. °C)	Elemental analysis (%), Found (Calcd.)				χ_m (U) ^b	μ_{eff} (BM)
		C	H	N	Metal		
[PMHPPr-PHz] C ₁₉ H ₁₉ N ₅ O ₂	Greenish yellow (180)	65.28 (65.31)	5.39 (5.48)	20.42 (16.82)	—	—	—
[La(PMHPPr-PHz) ₃] La C ₅₇ H ₅₄ N ₁₅ O ₆	Greenish yellow (191)	56.14 (56.11)	4.82 (4.79)	17.26 (17.22)	11.62 (11.73)	11.40	Diamag
[Ce(PMHPPr-PHz) ₃] Ce C ₅₇ H ₅₄ N ₁₅ O ₆	Greenish yellow (202)	56.12 (56.05)	4.76 (4.78)	17.25 (17.20)	11.86 (11.82)	14.80	2.20
[Nd(PMHPPr-PHz) ₃] Nd C ₅₇ H ₅₄ N ₁₅ O ₆	Greenish yellow (222)	55.92 (55.86)	4.81 (4.76)	17.18 (17.14)	12.16 (12.12)	10.20	2.68
[Sm(PMHPPr-PHz) ₃] Sm C ₅₇ H ₅₄ N ₁₅ O ₆	Greenish yellow (212)	55.61 (55.69)	4.77 (4.74)	17.12 (17.06)	12.64 (12.57)	10.60	3.87
[Gd(PMHPPr-PHz) ₃] Gd C ₅₇ H ₅₄ N ₁₅ O ₆	Greenish yellow (190)	55.31 (55.28)	4.73 (4.71)	16.98 (16.96)	13.12 (13.07)	14.70	8.56
[Dy(PMHPPr-PHz) ₃] Dy C ₅₇ H ₅₄ N ₁₅ O ₆	Greenish yellow (206)	55.12 (55.04)	4.68 (4.69)	16.92 (16.89)	13.52 (13.45)	12.20	10.45
[Er(PMHPPr-PHz) ₃] Er C ₅₇ H ₅₄ N ₁₅ O ₆	Greenish yellow (199)	54.86 (54.83)	4.72 (4.68)	16.87 (16.82)	13.82 (13.79)	14.60	9.97

(U)^b = mol⁻¹ ohm⁻¹ cm²

The main stretching frequencies of the IR spectra of the ligand (PMHPPr-PHz) and its complexes are discussed. The peak at 1625 cm⁻¹ in the free ligand is due to ν (C=N) azomethine stretching. This band shifts to 1610 cm⁻¹ or so on complex formation, indicating that coordination takes place *via* azomethine nitrogen. The absorption bands at 3190 and 1700 cm⁻¹ in the free ligand have been attributed to ν (—NH) and ν (C=O), respectively. In the spectra of complexes these bands disappeared, indicating that the ligand exists in tautomeric enol form by the loss of —NH proton *via* carbonyl oxygen.

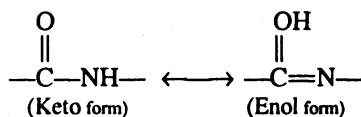


Fig. 1. Amide-imidol form of the ligand

After enolization, the new band appearing at *ca.* 1360 cm^{-1} was diagnostic of $\nu(\text{C}=\text{O})$ group¹². In the spectra of complexes, the bands around 460 cm^{-1} and 420 cm^{-1} are assigned to $\nu(\text{Ln}=\text{O})$ and $\nu(\text{Ln}=\text{N})$, respectively¹³.

The ^1H NMR spectra of ligand and its Ce and Er complexes were recorded. The spectra of $[\text{Er}(\text{PMHPPr-PHz})_3]$ only are discussed. In the spectra of complex compared with the free ligand the $-\text{NH}$ proton of hydrazide moiety was found to be absent, presumably on account of enolization and subsequent loss of $-\text{NH}$ proton by coordination with the metal ion through carbonyl oxygen. The $-\text{OH}$ proton of 5-pyrazolone group in the free ligand exhibited signal at δ 12.6 ppm, which remained intact in the spectra of complex, indicating non-participation of this group. In the spectra of free ligand, the picoline ring ($\text{C}_5\text{H}_4\text{N}$)¹⁴ protons appeared as multiplet in the region of δ 8.01–8.64 ppm, which remained unaltered in the spectra of complexes suggesting the non-involvement of this group.

The electronic spectra of the complexes have been recorded in DMF solution (Table-2). In the electronic spectra of Nd and Er complexes the absorption intensity was evaluated from the area beneath the absorption curve and the oscillator strengths corresponding to the observed bands of Nd and Er complexes are much larger than those reported for the aquo ion¹⁵. The nephelauxetic parameter (β), bonding parameter ($b^{1/2}$), covalency parameter ($\delta\%$) and covalency-angular overlap parameter (η) for the complexes of Nd, Dy and Er are listed in Table-2. The nephelauxetic parameter¹⁶ of these complexes (Table-2) was less than 1 and bonding and covalency parameters are positive indicating the covalent nature of the metal-ligand bond.

TABLE-2
ELECTRONIC SPECTRAL DATA OF LANTHANIDE(III) COMPLEXES

Complexes	Transition ($\text{S}^1 \text{L}^1 \text{J}^1$)	Energy (cm^{-1}) ^a	$P \times 10^6$	
			Aqua ions	Complexes
[Nd(PMHPPr-PHz) ₃]	$^4\text{I}_{9/2} \rightarrow ^4\text{G}_{7/2}$	19011(19175.4)	—	—
	$\rightarrow ^4\text{G}_{7/2}$	17152(17391.00)	2.37	3.245
	$\rightarrow ^4\text{F}_{7/2}$	13458(13513.51)	1.52	2.037
	$\rightarrow ^4\text{F}_{5/2}$	12492(13210.04)	1.78	1.982
[Dy(PMHPPr-PHz) ₃]	$^6\text{H}_{15/2} \rightarrow ^6\text{F}_{3/2}$	12461 (13210.04)	—	—
[Er(PMHPPr-PHz) ₃]	$^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$	19193(19238.75)	—	—
	$\rightarrow ^4\text{F}_{9/2}$	15325(15327.67)		
Covalency Parameters				
	β	$b^{1/2}$	δ (%)	η
[Nd(PMHPPr-PHz) ₃]	0.9914	0.0655	0.867	0.0044
[Dy(PMHPPr-PHz) ₃]	0.9432	0.1685	6.020	0.0297
[Er(PMHPPr-PHz) ₃]	0.9949	0.0504	0.512	0.0026

The thermal data of $[\text{Sm}(\text{PMHPPr-PHz})_3]$ were recorded and discussed. In general, the water of hydration may be with water of crystallization or coordinated water. According to Nikolaev¹⁷ water eliminated below 150°C can be considered as water of crystallization and water eliminated above 150°C may be due to water. This complex does not show the presence of water moiety either in or outside the coordination sphere. In this complex, the first step of decomposition occurs between $290\text{--}405^\circ\text{C}$ with weight loss of 18.73%. This loss corresponds to some of the ligand fragments. The second and third steps of the decomposition occur between $430\text{--}498^\circ\text{C}$ and $500\text{--}715^\circ\text{C}$, respectively. Beyond 730°C , a plateau is obtained, which indicates the formation of stable Sm_2O_3 . The weight of Sm_2O_3 agrees well with the weight of the oxide excepted from the metal complex.

On the basis of analytical and physical data, the probable structure of lanthanide complexes is as shown in Fig. 2

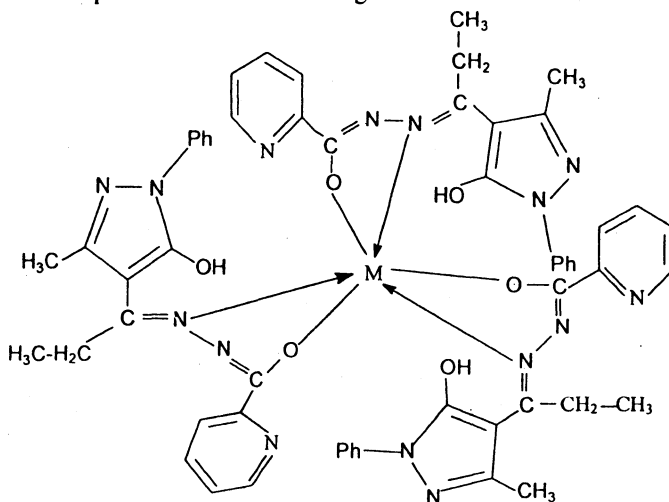


Fig. 2. The probable structure of the complexes

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