

Complexes of some lanthanides with the schiff base derived from 2-acetylpyridine and N-benzoylglycine hydrazide

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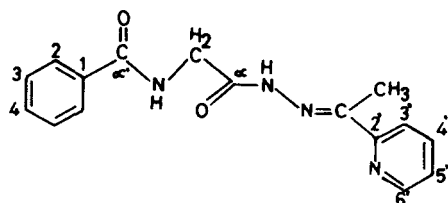
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Complexes of La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III) with the schiff base derived from 2-acetylpyridine and N-benzoylglycine hydrazide have been prepared and characterised on the basis of elemental analyses, molar conductance, magnetic, electronic, infrared, ^1H and ^{13}C NMR spectral techniques. The nephelauxetic ratio (β), the bonding parameter ($b^{1/2}$), Sinha's parameter ($\delta\%$) and angular overlap parameter (η) have been calculated from the electronic spectra of Pr(III), Nd(III) and Sm(III) complexes. Infrared and NMR spectra indicate coordination through azomethine nitrogen, pyridine ring nitrogen and the carbonyl oxygen of the hydrazone moiety. An eight coordinated structure has been proposed for the complexes.

The chemistry of hydrazine derivatives has been intensively investigated in recent years, owing to their coordinative capability¹, their pharmacological activity² and their use in analytical chemistry as metal extracting agents³. In previous papers from our laboratory, the synthesis and structural studies of 3*d*- and 4*f*-metal complexes of L-tyrosine hydrazide⁴ and N-benzoylglycine hydrazide^{5,6} and their derivatives^{7,8} have been reported.

In the present paper we report the synthesis and structural studies of La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III) complexes of the schiff base derived from 2-acetylpyridine and (N-benzoyl) glycylic hydrazines, henceforth abbreviated as 2-ApBzGH (I).



Materials and Methods

Hydrated metal chlorides obtained from M/s Indian Rare Earths Ltd., Kerala, were used without further purification. The ligand (I) was prepared by refluxing ethanolic solutions of (N-benzoyl)glycine hydrazide and 2-acetylpyridine in 1:1 mol ratio for 4 hr. White crystals obtained on slow cooling of the reaction mixture to room temperature were separated by filtration, washed rep-

peatedly with cold ethanol and dried at room temperature. The crude product was recrystallized from ethanol (m.p. 191-3°C) Found: (C, 64.76; H, 5.40; N, 18.88; N_2H_4 , 10.80. Calc. for $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_2$: C, 64.87; H, 5.41; N, 18.91; N_2H_4 , 10.81%.

Preparation of the complexes

[Dichlorobis {2-acetylpyridine (N-benzoyl) glycylic hydrazone} metal (III)] chloride, $[\text{Ln}(2\text{-ApBzGH})_2\text{Cl}_2]\text{Cl}$, [Ln=La, Pr, Nd, Sm, Eu, Gd, Tb and Dy] were prepared by mixing together ethanolic solutions of 2-ApBzGH (2.5 mmol) and the appropriate lanthanide chloride (1.25 mmol) and heating under reflux for 3 hr. The addition of acetonitrile ($\sim 10 \text{ cm}^3$) to the reaction mixture produced a gummy solid which, after decanting the supernatant solution, was redissolved in ethanol and macerated with acetonitrile; successive repetitions of this process yielded crystalline complexes which were filtered, washed with a mixture of acetonitrile and ethanol and dried *in vacuo*.

The metal ions were estimated volumetrically by EDTA titration⁹ using Eriochrome Black-T as indicator. Chloride was determined gravimetrically as AgCl. Hydrazine was estimated volumetrically after subjecting the complexes to acid hydrolysis. C, H and N were determined using a Perkin-Elmer 240C Elemental Analyser. The molar conductances of the complexes were measured at room temperature on a WTW conductivity meter. Magnetic susceptibility measurements were carried out on a Cahn-Faraday electrobalance using

Table 1—Characterization data of the complexes

Complex (colour)	Decomp temp. (°C)	Found (Calc) %				μ_{eff} (B.M.)
		N	M	Cl	N ₂ H ₄	
[La(2-ApBzGH) ₂ Cl ₂]Cl (White)	248	13.29 (13.37)	16.80 (16.58)	12.66 (12.71)	7.66 (7.64)	diamag
[Pr(2-ApBzGH) ₂ Cl ₂]Cl (Green)	245	13.31 (13.34)	16.80 (16.79)	12.23 (12.69)	7.34 (7.62)	3.78
[Nd(2-ApBzGH) ₂ Cl ₂]Cl (Blue)	242	13.25 (13.29)	17.14 (17.12)	12.42 (12.64)	7.50 (7.59)	3.97
[Sm(2-ApBzGH) ₂ Cl ₂]Cl (Light Yellow)	264	13.20 (13.19)	17.42 (17.71)	11.98 (12.55)	7.33 (7.54)	2.65
[Eu(2-ApBzGH) ₂ Cl ₂]Cl (Cream)	228	13.10 (13.16)	17.89 (17.87)	12.25 (12.52)	7.30 (7.53)	3.36
[Gd(2-ApBzGH) ₂ Cl ₂]Cl (Cream)	256	13.11 (13.08)	18.25 (18.39)	12.44 (12.45)	7.25 (7.49)	7.26
[Tb(2-ApBzGH) ₂ Cl ₂]Cl (Cream)	262	13.00 (13.05)	18.64 (18.54)	12.36 (12.42)	7.26 (7.46)	8.56
[Dy(2-ApBzGH) ₂ Cl ₂]Cl (Cream)	266	13.00 (13.01)	18.95 (18.87)	12.43 (12.37)	7.60 (7.43)	8.63

Hg[Co(NCS)₄] as the calibrant. The electronic spectra were recorded on a Cary-14 spectrophotometer while the IR spectra were obtained on a Perkin-Elmer 783 spectrophotometer. The ¹H and ¹³C NMR spectra were recorded on a Jeol FX-90Q multinuclear NMR spectrometer.

Results and Discussion

The analytical data (Table 1) indicate that 2-ApBzGH reacts with Ln(III) chlorides to form complexes of the type [Ln(2-ApBzGH)₂Cl₂]Cl. The complexes are hygroscopic and are soluble in water, methanol, ethanol, pyridine, DMF and DMSO. The electrical conductance values of the complexes in 0.001 M DMF solution at room temperature (88.5–105.0 ohm⁻¹cm²mol⁻¹) indicate that the complexes behave as 1:1 electrolytes¹⁰.

The magnetic moments of the complexes show very little deviation from Van Vleck values¹¹ indicating little participation of the 4*f* electrons in bond formation. The slightly higher values observed in case of Sm(III) complexes may presumably be due to temperature-dependent magnetism on account of low *J*-separation¹².

The electronic absorption spectra of lanthanide ions have been subject of several investigations^{13–16}. The spectral data of Pr(III), Nd(III) and Sm(III) complexes along with various calculated parameters are given in Table 2. The spectral features of the hypersensitive bands (Fig. 1) corresponding to the ⁴I_{9/2} → ⁴G_{5/2}, ²G_{7/2} transition in Nd(III) com-

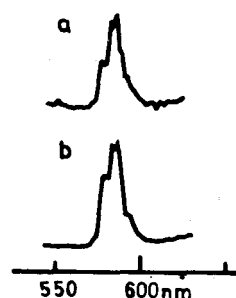


Fig. 1—Hypersensitive bands of [Nd(2-ApBzGH)₂Cl₂]Cl (a) in nujol; (b) in MeOH

plex are similar in both the solid as well as in methanol solution spectra indicating that the complex maintains identical stereochemistry and coordination number in the solid and the solution phases. An eight coordination may be assigned around the metal ion based on the striking resemblances of the hypersensitive bands with that of eight coordinate Nd(thd)₃·2HFAA [thd = (CH₃)₃CCOCHCOC(CH₃)₃; HFAA = CF₃COCHCOCF₃] reported by Karraker¹⁷. There is a shift in the position of the hypersensitive band compared to that of the aquo neodymium ion^{18,19} and such a shift has been attributed by Jørgensen²⁰ to the effect of crystal field upon interelectronic repulsion among the 4*f* electrons, i.e., the lowering of interelectronic repulsion parameter (β) in the complex. The covalency (δ), the bonding parameter ($b^{1/2}$) and the covalency angular over-

Table 2—Electronic spectral data of the complexes

Complex	Solid	Band max (cm ⁻¹)		Assignments	Calculated ^a Parameters
		Solution (MeOH)	Aqueous ^b		
[Pr(2-ApBzGH) ₂ Cl ₂]Cl	16780	—	16840	³ H ₄ → ¹ D ₂	$\bar{\beta} = 0.996$
	20575	—	20710	→ ³ P ₀	$b^{1/2} = 0.047$
	21275	—	21330	→ ³ P ₁	$\eta = 0.002$
	22421	—	22440	→ ³ P ₂	$\delta\% = 0.442$
[Nd(2-ApBzGH) ₂ Cl ₂]Cl	12510	—	—	⁴ I _{9/2} → ⁴ F _{5/2}	
	13425	13440	13500	→ ⁴ F _{7/2}	
	13585	13550	13500	→ ⁴ S _{3/2}	
	—	16225	—	→ ² H _{11/2}	$\bar{\beta} = 0.992$
	17150	17240 ^c	17300	→ ⁴ G _{5/2} , ² G _{7/2}	$b^{1/2} = 0.066$
	19050	19120	19160	→ ⁴ G _{7/2}	$\eta = 0.004$
	19520	19610	19550	→ ⁴ G _{9/2}	$\delta\% = 0.867$
	—	21280	21300	→ ² G _{9/2}	
	—	22220	—	→ ² K _{5/2}	
	—	22470	—	→ ² P _{1/2}	$\bar{\beta} = 0.996$
[Sm(2-ApBzGH) ₂ Cl ₂]Cl	21010	—	2110	⁶ H _{5/2} → ⁴ I _{11/2}	$b^{1/2} = 0.047$
	21645	—	21600	→ ⁴ I _{13/2}	$\eta = 0.002$
	24155	—	24050	→ ⁴ P _{5/2}	$\delta\% = 0.432$

a) Parameters calculated from solid state spectrum

b) The aqueous solution spectral bands of Pr³⁺, Nd³⁺ and Sm³⁺ are taken from Ref. 19.

c) ϵ_{\max} value of the band corresponds to 0.85.

 Table 3—22.49 MHz proton noise decoupled ¹³C NMR spectral data* of 2-ApBzGH and its La(III) complex (in ppm)

Carbon atoms	2-ApBzGH	[La(2-ApBzGH) ₂ Cl ₂]Cl
C _α	170.73	172.03
C _{α'}	166.98	167.00
-CH ₂ -	41.30	41.23
-N=C	152.98	155.42
-CH ₃	11.76	12.24, 13.50
C ₁	131.32	131.43
C ₂	128.23	128.26
C ₃	127.26	127.43
C ₄	134.08	133.95
C _{2'}	154.88	152.35
C _{3'}	123.85	124.46
C _{4'}	135.46	137.14
C _{5'}	119.95	120.65
C _{6'}	148.55	147.91

* Measured in ppm w.r.t. DMSO-*d*₆ (39.50 ppm).

lap parameter (η) have been calculated. The parameters support the idea of a partial covalent bond between metal and the ligand, 2-ApBzGH²¹.

The infrared spectral data reveal that amide I (ligand 1630; complexes 1630-1640), amide II (li-

gand 1550; complexes 1550) and amide III (ligand 1310; complexes 1305-1310) bands arising from the benzamide moiety remain almost unchanged in the spectra of all the complexes indicating noninvolvement of the benzamide carbonyl group in coordination. The amide I (ligand 1695; complexes 1650-1660), and amide II (ligand 1580; complexes 1550-1560), of the hydrazide moiety are lowered on complex formation while the amide III band (ligand 1360; complexes 1395-1400) shifts to higher frequency side indicating coordination of carbonyl oxygen of the hydrazido amide moiety²². The coordination of the azomethine nitrogen is suggested on the basis²³ of the lowering by 20 cm⁻¹ of the ν (C=N) mode (ligand 1610; complexes 1590). The coordination of the pyridine ring nitrogen is suggested on the basis of the observed changes in the ring skeletal mode (ligand 990; complexes 1000-1005), in-plane ring deformation mode (ligand 595; complexes 630-635) and out-of-plane ring deformation mode (ligand 405; complexes 445-450 cm⁻¹)²⁴.

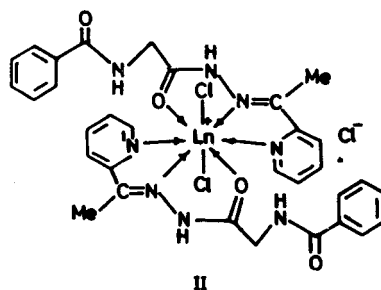
The ¹H NMR spectra of 2-ApBzGH and its La(III) complex were recorded in DMSO-*d*₆ solutions. 2-ApBzGH: 4.52d (-CH₂-), 2.38s (-CH₃), 10.85s (hydrazide NH), 8.71s (benzamide

NH), 7.52 m, 7.91 m, 8.57d (ring protons); La(III) complex: 4.52 d ($-\text{CH}_2-$), 2.38s ($-\text{CH}_3$), 11.07s (hydrazide NH), 8.71s (benzamide NH), 7.67m, 8.07m, 8.57d (ring protons). The observed down-field shift (0.226) of the imino proton signal of hydrazide moiety in the spectrum of La(III) complex suggests coordination of the hydrazide carbonyl group and azomethine nitrogen with the metal ion. The signal due to the imino proton of the benzamide moiety remains unchanged in the complex, thereby indicating the non-involvement of the benzamide moiety in coordination with the metal ion.

The 22.49 MHz proton noise-decoupled ^{13}C NMR spectra of the ligand and the La(III) complex were recorded in $\text{DMSO}-d_6$ solutions and the peak positions along with the assignments are listed in Table 3. The assignments for the ligand have been deduced taking into account the shifts of the carbon atoms of the fragments which form the 2-ApBzGH molecule. The effect of coordination is to strongly influence the carbon shifts particularly of those groups which directly interact with the metal ion²⁵. The signal due to the carbonyl carbon of the hydrazide moiety undergoes a significant down-field shift (1.30 ppm) compared to its position in that of 2-ApBzGH. Similarly, the azomethine carbon signal observed at 152.98 ppm in 2-ApBzGH undergoes a down-field shift in that of the La(III) complex presumably as a result of coordination of the nitrogen atom²⁶. The up-field shifts of the C_2 and C_6 and the down-field shifts of the C_3 , C_4 and C_5 , carbon atoms of pyridine ring suggest coordination of the pyridine ring nitrogen²⁵ thereby supporting the inference drawn from the infrared spectra. The signal due to the carbonyl carbon of the benzamide moiety appears almost at the same position in the spectra of the parent ligand and the La(III) complex suggesting non-coordination of the particular carbonyl group.

Thus, the ^1H and ^{13}C NMR spectral data support the inference drawn earlier on the basis of IR spectra about the non-involvement of the benzamide carbonyl group and the participation of the azomethine nitrogen and the carbonyl oxygen of the hydrazide moiety in coordination with the metal ions.

Based on the elemental analyses and various physico-chemical studies the empirical formula $[\text{Ln}(2\text{-ApBzGH})_2\text{Cl}_2]\text{Cl}$ (Structure II) has been tentatively proposed for the present complexes in-



volving a neutral tridentate functional ligand and an eight-coordinate metal ion.

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