

Some Lanthanide Complexes of 2-Benzoylpyridine Benzoylhydrazone & 2-Benzoylpyridine Salicyloylhydrazone

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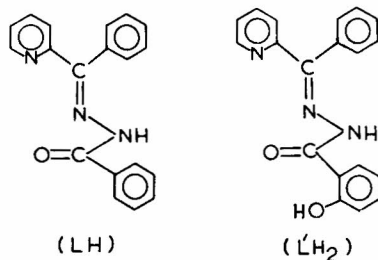
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Received 5 August 1983; revised 12 March 1984; accepted 16 April 1984

Lanthanum(III), praseodymium(III), neodymium(III), samarium(III), gadolinium(III), terbium(III), dysprosium(III) and yttrium(III) complexes of 2-benzoylpyridine benzoylhydrazone (LH) and 2-benzoylpyridine salicyloylhydrazone (L'H₂) have been synthesised and characterised. The complexes conform to the compositions [Ln(L)₃] and [Ln(L'H)₃]. Their magnetic moments, infrared spectra and electronic absorption spectra have been studied in order to establish their structures.

Nephelauxetic ratio (β), covalency factor (b^2) etc have been evaluated wherever possible. A nine-coordinate structure has been proposed on the basis of the shapes of the electronic spectral bands of neodymium(III) complexes in the solid and solution (DMF/DMSO) phases.

Recently, 2-benzoylpyridine benzoylhydrazone (LH) and 2-benzoylpyridine salicyloylhydrazone (L'H₂) have been synthesised via reaction of 2-benzoylpyridine with the appropriate hydrazines¹. Complexes of several lanthanides with these two ligands have now been synthesised and characterised.



Materials and Methods

The ligands were obtained following the reported procedures¹.

Synthesis of complexes

Lanthanide acetates (0.001 mol) were dissolved in water and filtered. The filtrate was added to a solution of the appropriate schiff base (0.003 mol) in boiling ethanol (40 ml). After refluxing for about 45-60 min, the crystalline precipitates obtained were filtered, washed with ethanol and dried over silica gel.

In the cases of Nd(III) and Gd(III) complexes, the preparation was also tried with their nitrate salts. After refluxing in ethanol for 45 min, the pH of the solution was raised to ~5 and it was refluxed further (2-3 hr) to obtain the same products.

The metal contents (Table 1) were estimated as the metal oxides² and in a few cases by complexometric titration by EDTA using xylenol orange indicator³ at pH ~6. Nitrogen was estimated by semimicro

combustion method while carbon and hydrogen were determined at CDRI Lucknow. Other measurements were carried out as described in a previous paper⁴.

Results and Discussion

Analytical data presented in Table 1 show that the complexes have 1 : 3 (metal : schiff base) stoichiometries.

All the samples turned out to be anhydrous. Conductance measurements in DMF ($\Lambda_M = 1-2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) indicate non-electrolytic nature of the complexes. Magnetic moment values are in the usual range expected for lanthanide complexes⁵.

Infrared spectra and bonding sites

The ligands have three potential donor sites in the heterocyclic nitrogen, carbonyl oxygen (in keto or enol form) and the azomethine nitrogen. The lanthanides, on the other hand, are well known for exhibiting a wide array of coordination numbers, from six right up to eleven or twelve. The ligands are capable of exhibiting tridentate (NNO) or bidentate (NO) donor behaviour. In the latter case the pyridine nitrogen may be left out of coordination sphere because of free rotation about C - C single bond. The bands at 3060, 1675 and 1585 cm^{-1} for LH and at 3060, 1645 and 1595 cm^{-1} for L'H₂ are assigned to νNH ; $\nu\text{C}=\text{O}$ (amide-I) and $\nu\text{C}=\text{N}$ modes respectively. The pyridine ring vibrations and phenyl ring vibrations expectedly overlap, making it difficult to identify the bands due to pyridine ring. In fact, the literature is infested with conflicting reports about the assignment of pyridine nitrogen-metal bands⁶. However, in the present study the infrared spectra, run on a high resolution Perkin-Elmer instrument, show a medium intensity sharp band at 1598 cm^{-1} for LH and at 1605 cm^{-1} (shoulder) for

Table I—Characterisation Data of Lanthanide Complexes of 2-Benzoylpyridine Aroylhydrazones

Compound	Colour	Found (Calc.) %				$\mu_{\text{eff.}}$ (B.M.)
		M	N	C	H	
[La(L) ₃]	Light yellow	13.18 (13.37)	12.23 (12.12)	64.90 (65.80)	4.29 (4.33)	Diamagnetic
[Pr(L) ₃]	Light yellow	13.51 (13.50)	12.31 (12.12)	66.00 (65.70)	4.42 (4.32)	3.39
[Nd(L) ₃]	Greenish yellow	13.83 (13.79)	11.92 (12.00)	—	—	3.38
[Sm(L) ₃]	Deep yellow	14.31 (14.40)	11.75 (11.90)	—	—	1.67
[Gd(L) ₃]	Yellow	14.80 (14.87)	11.72 (11.85)	64.69 (64.69)	4.07 (4.25)	7.80
[Tb(L) ₃]	Yellow	15.32 (15.10)	11.68 (11.89)	—	—	9.58
[Dy(L) ₃]	Yellow	15.52 (15.30)	11.88 (11.88)	63.45 (64.30)	4.16 (4.23)	10.25
[Y(L) ₃]	Deep yellow	9.21 (9.00)	12.69 (12.74)	—	—	Diamagnetic
[Pr(L'H) ₃]	Light yellow	13.04 (12.95)	11.41 (11.50)	—	—	3.49
[Nd(L'H) ₃]	Greenish yellow	13.12 (13.10)	11.42 (11.53)	62.60 (62.60)	4.09 (4.12)	3.40
[Sm(L'H) ₃]	Light yellow	13.35 (13.70)	11.52 (11.47)	62.25 (62.27)	3.97 (4.09)	1.50
[Gd(L'H) ₃]	Deep yellow	14.80 (14.65)	11.41 (11.28)	—	—	—
[Dy(L'H) ₃]	Yellow	14.90 (14.70)	11.26 (11.30)	61.43 (61.59)	3.98 (4.05)	10.21

Abbreviations: LH = 2-Benzoylpyridine benzoylhydrazone; L'H₂ = benzoylpyridine salicyloylhydrazone.

L'H₂ which may be assigned to pyridine ring breathing mode⁷.

In a recent report¹ on the first transition series metal complexes of these ligands from our laboratory, it has been unambiguously demonstrated that the complexes [Ni(L)₂] and [Ni(L'H)₂] are pseudo-octahedral with characteristic magnetic moments (3.1 B.M.), typical electronic spectra coupled with an X-ray crystallographic structure determination of [Ni(L'H)₂]. These information assure that pyridine ring nitrogen is coordinated¹ to Ni(II) along with the azomethine nitrogen and the enolic oxygen. The infrared spectra of the Ni(II) complexes and those of the lanthanides reported herein are similar. The $\nu\text{C}=\text{O}$ (amide-I) of the free ligands is absent in the complexes. Absence of νNH indicates enolisation of the aroyl group. A medium intensity band at 1585 cm^{-1} for LH complexes is assigned⁸ to the skeleton $>\text{C}=\text{N}-\text{N}=\text{C}<$ plus a lowered pyridine ring-breathing mode from 1598 to 1585 cm^{-1} . This latter band is indicative of pyridine nitrogen coordination⁷. The corresponding band for L'H₂ complexes appears at 1590 cm^{-1} . A study of model of L'H₂ reveals that it may function as (NNOO) quadridentate ligand only in the enol form. The appearance of $\nu\text{C}-\text{O}$ (phenolic) at 1250 cm^{-1} in the

spectrum of the ligand L'H₂ and in those of its complexes indicates the non-involvement of the group in coordination with the metal ions.

Electronic spectra

The electronic spectra of neodymium(III) complexes of these ligands remain invariant in the solid state, in DMSO and in DMF solutions. The same stereochemistry persists in both the phases. These spectra are characterised by three closely spaced peaks in the range $575\text{ nm}-590\text{ nm}$ arising out of the hypersensitive transition⁹ ($^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$). The spectral profiles of the neodymium(III) complexes are similar to those of the nine coordinated tris[antipyrilaldehyde acetylhydrazone (APACET)] and tris[antipyrilaldehyde benzoylhydrazone (APABZ)] complexes¹⁰ of neodymium(III), as well as to those of neodymium(III) complexes of N, N, N', N'-tetramethylpyridine dicarboxamide¹¹ (TMPD) and dipicolinic acid¹² (DPA), for which X-ray crystallographic studies have established¹³ nine-coordination. A similar correlation between spectral profile and nine coordination had earlier been high-lighted by Karrekar¹⁴. Compared to the spectra of the aquoneodymium(III) complex, the hypersensitive band mentioned have shows red shift

Table 2—Electronic Spectral Data of Nd³⁺ Complexes
[Nd(L)₃] [Nd(L'H)₃] ϵ

J level	Energy(kK)	J level	Energy(kK)	ϵ
⁴ G _{9/2}	19.493	⁴ G _{9/2}	19.569	2.70
⁴ G _{7/2}	18.939	⁴ G _{7/2}	18.975	6.39
⁴ G _{5/2}	17.094	⁴ G _{5/2}	17.035	16.80
² G _{7/2}	17.301	² G _{7/2}	17.152	17.80
$\beta = 0.98489$		$\beta = 0.98748$		
$b^{1/2} = 0.08691$		$b^{1/2} = 0.07912$		
$\delta\% = 1.530$		$\delta\% = 1.267$		

($\Delta\nu = 200\text{--}270\text{ cm}^{-1}$). For the other spectral bands (e.g. ⁴I_{9/2} → ²H_{9/2}, ⁴F_{5/2}; ⁴I_{9/2} → ⁴S_{3/2}, ⁴F_{7/2}; ⁴I_{9/2} → ⁴G_{7/2}, ²G_{9/2} etc.) the red shift is much less. The red shift of the hypersensitive bands has been used to calculate the nephelauxetic effect ratio¹⁵ β (β = average value of $\nu_{\text{complex}}/\nu_{\text{aquo}}$) in these chelates. From the β values, covalency factor¹⁶ $b^{\frac{1}{2}}\{b^{\frac{1}{2}} = [\frac{1}{2}(1-\beta)]^{\frac{1}{2}}\}$ and Sinha parameter¹⁵ δ (metal-ligand covalency percent) $\{\delta(\text{percent}) = [(1-\beta)/\beta] \times 100\}$ were also calculated (Table 2). The β , δ , and $b^{\frac{1}{2}}$ values are close to those calculated for similar other nine-coordinated chelates¹⁵. Small positive values of $b^{\frac{1}{2}}$ are indicative of a slight involvement¹⁷ of the 4f orbitals in bonding with the Schiff bases.

The electronic spectra of Pr³⁺ complexes in solid and solution (DMF and DMSO) phases are also similar. The spectra of these complexes exhibit two bands around 16890 and 20490 cm⁻¹ in the visible region, which may be due to¹⁸ ³H₄ → ¹D₂ and ³H₄ → ³P₀ transitions. Compared to the spectra of the aquo praseodymium(III) complex, these bands show a slight red shift ($\Delta\nu = \sim 130\text{ cm}^{-1}$; $\sim 160\text{ cm}^{-1}$). The other bands in this region cannot be located as these bands are presumably buried underneath the strong metal-ligand charge-transfer band around 24000 cm⁻¹.

The electronic spectra of samarium(III) and dysprosium(III) complexes of the same ligand run in solid state and solution (DMF) are almost identical: [Sm(L)₃], 26737, 30959, 30487; [Dy(L)₃], 26881, 30864,

30489; [Sm(L'H)₃], 26595, 31250, 33257; [Dy(L'H)₃], 26525, 31250, 33333 cm⁻¹. This is only to be expected because these ions are hole-equivalents to each other. All the complexes are characterised by very intense bands over the range (250–450 nm), which have charge transfer origin.

In the absence of any definite correlation between X-ray crystallographic structure and electronic spectra, no definite conclusion about the geometry of Pr(III), Sm(III) and Dy(III) complexes can be drawn. Sm(III) and Dy(III) have no bands in the visible region which are sensitive to ligand environment and overall geometry of the complex. However, the infrared spectra of Nd(III) complex on the one hand and those of Pr(III), Sm(III) and Dy(III) on the other are similar. Nine coordination may be tentatively assigned to these complexes.

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