

Some Selected Lanthanide Complexes of Schiff Bases Derived from Salicylaldehyde & 2-Quinolinoyl & 8-Quinolinoyl Hydrazines

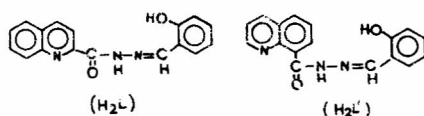
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Lanthanum(III), cerium(III), praseodymium(III), neodymium(III), samarium(III), gadolinium(III), terbium(III), dysprosium(III) and yttrium(III) complexes of schiff bases derived from salicylaldehyde and 2-quinolinoyl hydrazine (H_2L) and salicylaldehyde and 8-quinolinoyl hydrazine (H_2L') have been prepared. The complexes are of the type $[Ln(HL)L](H_2O)_n$, $[Ln(HL')L'](H_2O)_n$, ($n=1-2$) and $[Ln(HL)L']$ and these have been characterised on the basis of elemental analyses, conductance measurements, magnetic moments, thermal analyses, infrared and electronic absorption spectra. Nephelauxetic ratio (β) and covalency factor ($b^{1/2}$) have been determined for neodymium(III) complexes, which indicate some covalent character in these complexes.

Salicylidene 2-quinolinoyl hydrazine† (H_2L) and salicylidene 8-quinolinoyl hydrazine‡ (H_2L') schiff bases have recently attracted attention^{1,2} because of their flexidentate and ambiprotic behaviour. We wish to report a study of complexes of some lanthanides with the following two ligands.



The ligands were prepared by the literature method¹ and the physical measurements were carried out as reported elsewhere³.

General method of synthesis of the complexes

Hydrated lanthanum nitrate (0.001 mol) was dissolved in warm ethanol (10 ml) and mixed with a solution of the schiff base H_2L (0.0025 mol) in warm ethanol (20 ml). The mixture was then refluxed on a steam bath for 90 min. The resulting reddish yellow solution was treated with dilute ammonia (pH 4-4.5) with stirring. The complex formed was collected, washed with ethanol and dried over silica gel. The complexes of H_2L' were obtained without any pH adjustment. In the cases of heavier lanthanides

[Gd(III), Tb(III), Dy(III) and Y(III)] the complexes were immediately formed upon mixing, while in the cases of lighter lanthanides [La(III), Pr(III) and Nd(III)] the products were obtained under refluxing conditions.

The analytical data presented in Table 1 indicate that the complexes have 1:2 (metal:ligand) stoichiometry. The water molecules associated with these complexes are lost at $\sim 110^\circ\text{C}$ in an oven. Thermograms run for these hydrated complexes also indicate loss of water in the temperature range 60° to 110°C , indicating that water molecules are lattice-held and not coordinated. This is also supported by the

Table 1—Characterisation Data of Lanthanide Complexes of Aroyl Hydrazines

Compound	Colour	Found (Calc.) %		μ_{eff} B.M.
		N	Metal	
$[La(HL)L]H_2O$	Deep yellow	11.17 (11.3)	18.69 (18.88)	Dia-magnetic
$[Ce(HL)L]H_2O$	Brown	11.20 (11.35)	19.6 (18.99)	2.3
$[Pr(HL)L]1.5H_2O$	Light yellow	11.21 (11.24)	18.79 (18.87)	3.2
$[Nd(HL)L]2H_2O$	Greenish light yellow	11.15 (11.06)	18.74 (18.97)	3.3
$[Sm(HL)L]H_2O$	Deep yellow	10.98 (11.24)	20.32 (20.1)	1.84
$[Gd(HL)L]H_2O$	Light yellow	10.89 (11.09)	21.0 (20.82)	7.85
$[Tb(HL)L]H_2O$	Deep yellow	11.01 (11.14)	21.02 (20.8)	9.3
$[Dy(HL)L]H_2O$	Pale yellow	11.25 (11.0)	22.0 (21.39)	10.32
$[Y(HL)L]H_2O$	Light yellow	12.8 (12.24)	13.5 (12.97)	Dia-magnetic
$[La(HL')L']H_2O$	Deep yellow	10.98 (11.4)	19.3 (18.9)	Dia-magnetic
$[Pr(HL')L']H_2O$	Deep yellow	11.1 (11.39)	19.52 (19.1)	3.25
$[Nd(HL')L']$	Greenish light yellow	11.44 (11.61)	19.75 (19.9)	3.35
$[Sm(HL')L']1.5H_2O$	Deep yellow	11.42 (11.1)	19.81 (19.84)	1.9
$[Gd(HL')L']$	Deep yellow	11.02 (11.4)	22.0 (21.33)	—
$[Tb(HL')L']$	Deep yellow	11.59 (11.38)	20.89 (21.54)	9.4
$[Dy(HL')L']H_2O$	Deep yellow	10.99 (11.00)	21.52 (21.39)	10.2
$[Y(HL')L']H_2O$	Light yellow	11.95 (12.24)	13.21 (12.97)	Dia-magnetic

H_2L = Salicylidene 2-quinolinoyl hydrazine.

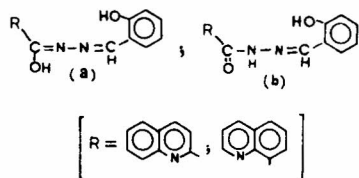
H_2L' = Salicylidene 8-quinolinoyl hydrazine.

†Salicylaldehyde 2-quinolinoyl hydrazine.
‡Salicylaldehyde 8-quinolinoyl hydrazine.

presence of a broad band $\sim 3400\text{ cm}^{-1}$ in the infrared spectra and no new bands in the $600\text{--}700\text{ cm}^{-1}$ region, which is almost absent in the anhydrous samples. All these complexes behave as nonelectrolytes in DMF ($\Lambda_M = 12\text{--}25\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) as compared to $65\text{--}90\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ for 1:1 electrolytes⁴ in DMF. The magnetic moment values are normal and follow the trend of the usual double humped curve⁵.

Infrared spectra and bonding sites

The ligands H_2L and $\text{H}_2\text{L}'$ are capable of functioning as neutral tridentate (ONO), monobasic tridentate (ONO) (in keto form)¹ or dibasic tridentate (ONO) donor (in enol form)². The ligands salicylidene-2-quinolinoyl hydrazine and 8-quinolinoyl hydrazine show characteristic sharp bands at 3300 , 3160 (due to νNH); 1690 , 1670 (due to $\nu\text{C}=\text{O}$ amide-I); 1610 (due to $\nu\text{C}=\text{N}$); and 1265 cm^{-1} due to $\nu\text{C}-\text{O}$ (phenolic) modes respectively. The νOH in the ligands could not be identified with certainty probably due to intramolecular hydrogen bonding with the azomethine nitrogen. On complexation, the νNH band of salicylidene 2-quinolinoyl hydrazine lose both sharpness and intensity and appears at $3240\text{--}3200\text{ cm}^{-1}$, while that of salicylidene 8-quinolinoyl hydrazine complexes appears with diminished intensity at $\sim 3100\text{ cm}^{-1}$. All these complexes show a broad and medium intensity band in the $3350\text{--}3450\text{ cm}^{-1}$ region due to lattice water, which are absent in the anhydrous samples. The sharp strong bands at $1630\text{--}1610\text{ cm}^{-1}$ and $1605\text{--}1610\text{ cm}^{-1}$ in the complexes have been assigned⁶ to the lowered $\nu\text{C}=\text{O}$ (amide-I) and skeleton $-\text{C}=\text{N}-\text{N}=\text{C}-$ vibrations. The band at 1580 cm^{-1} in these complexes may be attributed to the lowered azomethine ($\nu\text{C}=\text{N}$) group. An upward shift of the phenolic $\text{C}-\text{O}$ stretching vibration $\sim 30\text{ cm}^{-1}$ suggests bonding of phenolic oxygen to the metal ion. This indicates that the ligands are attached to the metal ion in two forms; one as a dibasic ONO donor in the enol form (a) while the other as a monobasic ONO donor in the keto form (b). It has been shown earlier from this laboratory that these ligands cannot function as (NONO) quadridentate donor.



Electronic spectra

The electronic spectra of neodymium(III) complexes (Table 2) of salicylidene 2-quinolinoyl and 8-quinolinoyl hydrazines in DMF and DMSO are identical but

Table 2—Electronic Absorption Data for Nd^{3+} Complexes

[Nd(HL)L] $2\text{H}_2\text{O}$		[Nd(HL')L']	
J level	Energy (cm^{-1})	J level	Energy (cm^{-1})
$^4G_{9/2}$	19493 (3.12)	$^4G_{9/2}$	19531 (2.92)
$^4G_{7/2}$	18939 (7.84)	$^4G_{7/2}$	18939 (6.92)
$^4G_{5/2}$	17006 (17.81)	$^4G_{5/2}$	17064 (16.25)
$^2G_{7/2}$	17211 (18.12)	$^2G_{7/2}$	17182 (16.62)

Nephelauxetic ratio, $\beta = 0.9879$ $\beta = 0.9884$

Covalency factor, $h^{1/2} = 0.0776$ $h^{1/2} = 0.0761$

Sinha parameter $\delta_{(\text{percent})} = 1.224$ $\delta = 1.170$

The values in parentheses denote molar extinction coefficient.

are slightly different from the solid state spectra, indicating a substantial influence of the solvents on the symmetry around the central ion. The spectra of all the other lanthanides are exactly similar both in solution and solid state. The spectral shape of the hypersensitive transition ($^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$) of neodymium(III) complexes compare well with the shapes of the bands of 6-coordinated Nd(III) complexes reported by Karakar⁷ and other authors⁸. The band due to $^4I_{9/2} \rightarrow ^2P_{1/2}$ transition of Nd(III) at $\sim 23000\text{ cm}^{-1}$ was not resolved possibly due to the strong charge transfer band at 24000 cm^{-1} . Compared to the spectra of the aquoneodymium(III) complex, the hypersensitive band mentioned above shows a significant red shift ($\Delta\nu = 200\text{--}250\text{ cm}^{-1}$). For other important bands (e.g. $^4I_{9/2} \rightarrow ^2H_{9/2}$, $^4F_{5/2}$; $^4I_{9/2} \rightarrow ^4S_{3/2}$, $^4F_{7/2}$; $^4I_{9/2} \rightarrow ^4G_{7/2}$, $^2K_{13/2}$) the red shift is much less. The nephelauxetic ratio β , ($\beta = \text{average value of } \nu \text{ complex} / \nu \text{ aquo}$) (ref. 9), the covalent factor $b^{1/2}$, ($b^{1/2} = [\frac{1}{2}(1 - \beta)^{1/2}]$ (ref. 10) and Sinha parameter δ (metal-ligand covalency per cent) $\delta (\text{per cent}) = [(1 - \beta)/\beta] \times 100$, (ref. 9) were calculated from the hypersensitive transition of the neodymium(III) spectra (Table 2). The values obtained are close to those calculated for similar other neodymium(III) chelates. The β values in both the complexes are close to unity showing only a slight covalent character of the Nd(III) $\rightarrow$ ligand interaction; the $b^{1/2}$ values suggest a small participation of $4f$ orbitals in bonding and along with δ values indicate relatively low covalent character of the bond.

The spectra of praseodymium(III) complexes in both solid and solution (DMF and DMSO) exhibit two bands ~ 17120 and 20495 cm^{-1} in the visible region, which may be due to the hypersensitive $^3H_4 \rightarrow ^1D_2$ and $^3H_4 \rightarrow ^3P_0$ transitions respectively¹¹. These bands show some red shift compared to the aquopraseodymium(III) ion. The other important bands in this region are not resolved.

The electronic spectra of samarium(III) and dysprosium(III) complexes of the same ligand in both solution and solid state are very nearly the same: [Sm(HL)L]H₂O: 24390, 28901, 39940, 31055; [Dy(HL)L]H₂O: 24630, 28901, 30030, 31010; [Sm(HL')L']H₂O: 24630, 29761, 31446, 34013; [Dy(HL')L']H₂O: 24752, 29678, 31446, 33783 cm⁻¹. This is expected because these two ions are hole equivalent of each other. The molar extinction coefficient (ϵ) values of these complexes over the range 250-460 nm are very high, indicating a charge transfer origin.

Thermal analysis

The neodymium(III) complexes were subjected to thermal analysis in nitrogen atmosphere. The DTA curves for complexes with H₂L show an endothermic effect at 110 °C due to dehydration of the samples. The water loss of [Nd(HL)(L)]2H₂O corresponds to two molecules of water (Found, 4.7; Calc, 4.7%). At 250 °C the DTA curve shows a deep endothermic effect due to incongruent fusion of the complex with H₂L which on subsequent heating begins to decompose followed by highly exothermic two step oxidative loss (250-500 °C)

of the tridentate ligands. The final solid product remaining is invariably Nd₂O₃ (Found Nd₂O₃, 22.1; Calc. 22.2%). The H₂L' complex [Nd(HL')(L')], however, is found to be stable up to 350 °C. The complex is decomposed at ~355 °C with a highly exothermic loss over a very narrow temperature range (5-10 °C). The total loss over this temperature range corresponds to one mol of the tridentate ligand (Found 40.0, Calc. 40.2%). A two step exothermic loss of the remaining ligand follows, giving Nd₂O₃ at 610 (Found, Nd₂O₃, 23.5; Calc. 23.2%).

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