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Synthetic and Spectroscopic Studies of Some Lanthanoid Metal Complexes of 2-Acetylpyridine Nicotinoylhydrazone

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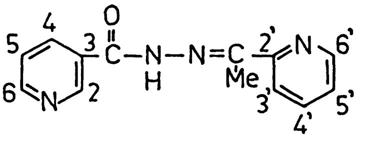
Lanthanoid metal (Ln) complexes of the types, $[Ln(Hapnh)_2Cl_2]Cl \cdot nH_2O$ and $[Ln(apnh)_3]$ have been prepared by reacting 2-acetylpyridine nicotinoylhydrazone (abbreviated to Hapnh) with hydrated lanthanoid metal chlorides. These complexes have been characterized by elemental analysis, molar conductance, magnetic susceptibility, electronic, infrared, NMR, and mass spectral studies. Various spectral parameters have been calculated from the electronic spectra of praseodymium(III), neodymium(III), samarium(III), and dysprosium(III) complexes while the neodymium(III) complexes have been subjected to detailed investigations with respect to the hypersensitive band profile and its oscillator strength's dependence on temperature and pH. On the basis of IR and NMR spectral studies, Hapnh is believed to act as a neutral tridentate species in the adduct complexes and as a uninegative tridentate one in the neutral complexes. Electrical conductance data indicate 1 : 1 electrolytic nature of the adducts and nonelectrolytic nature of the neutral complexes. On the basis of these studies, eight- and nine-coordination numbers have been proposed around Ln(III) in the $[Ln(Hapnh)Cl_2]Cl \cdot nH_2O$ and $[Ln(apnh)_3]$ respectively.

Coordination chemistry of lanthanoids has developed rapidly during the last few years. Lanthanoid complexes of N, O-donor ligands are of biological importance[1] and used as NMR shift reagents and in vapor phase chromatography.[2] Reactions of lanthanoid metal ions with hydrazides and their derivatives[3—8] have attracted much attention within recent years because of their wide variety of products presenting varied bonding and stereochemical possibilities and their potential applications as antitubercular and antifungal agents. 2-Acetylpyridine nicotinoylhydrazone has three active bonding sites forming complexes with lanthanoid metal ions, having coordination numbers often more than six. The present paper reports our investigations on synthetic and spectral studies of lanthanoid metal complexes of 2-acetylpyridine nicotinoyl hydrazone, abbreviated to Hapnh (I).



I

Experimental

Materials and Methods. All the hydrated lanthanoid metal chlorides (99.9% purity), obtained from Indian Rare Earths Ltd., Kerala (India), were used as such. All other chemicals used, were of BDH or S. Merck. 2-Acetylpyridine nicotinoylhydrazone was prepared by refluxing, together ethanolic solutions (20 cm^3 each) of 25 mmol of nicotinoylhydrazide (3.42 g) and 30 mmol of 2-acetylpyridine (3.63 g) for ca. 4 h. The cream colored product obtained on slow cooling of the reaction mixture, was recrystallized from hot ethanol, which had mp 175 °C (Anal. Found: C, 65.15; H, 5.00; N, 23.30; N_2H_4, 13.35%, Calcd for $C_{13}H_{12}N_4O$: C, 65.00; H, 5.00; N, 23.33; N_2H_4, 13.33%]. Yield, 4.38 g (73%).

Table 1. Analytical Data and Magnetic Moments of Lanthanoid Metal Complexes of Hapnh

Sl.[a)] No.	Found (Calcd)/%				μ_{eff} (B.M.)
	M	Cl	N	N_2H_4	
I	18.69 (18.68)	14.31 (14.33)	15.04 (15.06)	8.58 (8.61)	Diamag.
II	18.98 (18.90)	14.28 (14.29)	15.00 (15.02)	8.56 (8.58)	3.28
III	19.81 (19.74)	14.56 (14.57)	15.32 (15.33)	8.82 (8.76)	3.44
IV	20.36 (20.40)	14.37 (14.45)	15.16 (15.20)	8.54 (8.68)	2.30
V	20.04 (20.08)	14.10 (14.08)	14.75 (14.80)	8.43 (8.46)	3.19
VI	20.60 (20.64)	13.94 (13.98)	14.68 (14.70)	8.34 (8.40)	7.69
VII	20.79 (20.81)	13.94 (13.95)	14.67 (14.67)	8.36 (8.38)	9.63
VIII	21.12 (21.19)	13.83 (13.88)	14.60 (14.60)	8.32 (8.34)	10.05
IX	12.80 (12.82)	15.30 (15.36)	16.11 (16.15)	9.29 (9.23)	Diamag.
X	16.20 (16.21)	—	19.58 (19.61)	11.21 (11.20)	Diamag.
XI	16.40 (16.42)	—	19.60 (19.58)	11.20 (11.19)	3.58
XII	16.71 (16.75)	—	19.55 (19.51)	11.20 (11.15)	3.54
XIII	17.35 (17.33)	—	19.35 (19.37)	11.10 (11.07)	2.14
XIV	17.45 (17.49)	—	19.30 (19.33)	11.00 (11.05)	3.98
XV	17.96 (17.99)	—	19.21 (19.22)	11.00 (10.98)	8.05
XVI	18.20 (18.14)	—	19.15 (19.18)	11.00 (10.96)	9.97
XVII	18.50 (18.48)	—	19.06 (19.10)	10.98 (10.92)	10.29
XVIII	11.06 (11.03)	—	20.81 (20.85)	11.90 (11.91)	Diamag.

a) I—IX, adduct complexes $[Ln(Hapnh)_2Cl_2]Cl \cdot nH_2O$; X—XVIII, neutral complexes $[Ln(apnh)_3]$; where Ln=La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), and Y(III), respectively in each series.

Table 2. Electronic Spectral Data of Neodymium(III) Complexes of Hapnh

Complex	Band area/cm^{-1}		Band assignments	$P \times 10^6$	Parameters
	Solid	Solution (DMSO)			
III	11428—11765	11111—11614	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	3.01	
	12121—12903	11933—12870	$\rightarrow {}^4H_{9/2}$	10.23	$\overline{\beta}=0.9957$
	13316—13763	13004—13680	$\rightarrow {}^4S_{3/2}$	8.61	$b^{1/2}=0.0464$
	14598—14925	14286—14771	$\rightarrow {}^4F_{9/2}$	1.07	$\%\delta=0.4319$
	16949—17391[a)]	16667—17575	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	17.78	$\eta=0.0022$
	18587—18832	18587—19120	$\rightarrow {}^2K_{13/2}$	2.05	
	18832—20000	19120—19685	$\rightarrow {}^4G_{7/2}$	1.17	
XII	11287—11415	11312—11507	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	3.72	
	11415—11574	11507—11614	$\rightarrow {}^4F_{5/2}$	2.59	$\overline{\beta}=0.9825$
	12195—12642	12151—12626	$\rightarrow {}^4H_{9/2}$	15.98	$b^{1/2}=0.0935$
	13123—13736	13141—13626	$\rightarrow {}^4S_{3/2}, {}^4F_{7/2}$	24.96	$\%\delta=1.7812$
	14598—14815	14451—14948	$\rightarrow {}^4F_{9/2}$	10.38	$\eta=0.0089$
	16447—17575[a)]	16260—17575	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	61.74	
	18692—19011	18587—19120	$\rightarrow {}^2K_{13/2}$	21.87	
	19194—19960	19418—19685	$\rightarrow {}^4G_{9/2}$	15.11	

a) Hypersensitive band from which spectral parameters are calculated.

Table 3. NMR Spectral Bands of Hapnh and Its Complexes

Proton/Carbon	Hapnh	Lanthanum complex, I (Yttrium complex, IX)	Lanthanum complex, X (Yttrium complex, XVIII)
$-N\underline{H}-$	11.20_s	11.44_b (11.47_b)	—
$-C\underline{H}_3$	2.59_s	2.48_s (2.48_s)	2.74_s (2.78_s)
Py($\underline{H}$)	7.60—9.16	7.57—9.13 (7.63—9.21)	7.53—9.13 (7.63—9.22)
$-\underline{C}=O$	161.98	169.15 (169.26)	173.26 (171.24)
$-\underline{C}=N-$	145.53	149.17 (148.16)	148.54 (148.45)
Py($\underline{C}$)	120.19—154.94	120.96—157.42 (121.97—156.64)	121.91—156.46 (121.84—155.38)

s=singlet; b=broad.

Preparation of the Complexes: $[Ln(Hapnh)_2Cl_2]Cl \cdot nH_2O$ were prepared by mixing together ethanolic solutions of 4 mmol of 2-acetylpyridine nicotinoylhydrazone (0.96 g) and 2 mmol of the appropriate hydrated lanthanoid chloride (ca. 0.40 g) and digesting the reaction mixture on a water bath for ca. 1/2 h. The reaction mixture was cooled to room temperature and precipitation was induced by addition of ca. 10 cm^3 of acetonitrile. The precipitated complexes were filtered off, washed several times with a mixture of ethanol and acetonitrile (25:75, v/v), and dried in vacuo. $[Ln(apnh)_3]$ were prepared by mixing together aqueous solutions of 2 mmol of metal chloride, 6 mmol of Hapnh (1.63 g) and 6 mmol of KOH (0.30 g) and adjusting the pH of the solution, if necessary, to ca. 7.5. The precipitated complexes were digested on a water bath for ca. 1 h, filtered off, washed successively with water followed by ethanol and dried at room temperature.

Analyses and Physical Measurements: The details of the analysis and physicochemical techniques used are the same as reported earlier.[9)] The relevant analytical and physicochemical data are given in Tables 1—3.

Results and Discussion

The analytical data indicate the formation of lanthanoid metal complexes of the general formulae $[Ln(Hapnh)_2Cl_2]Cl \cdot nH_2O$ and $[Ln(apnh)_3]$. The reactions may be represented by the following equations:

$$[1]\quad LnCl_3 \cdot mH_2O + 2(Hapnh) \xrightarrow[\frac{1}{2}\ h]{EtOH} [Ln(Hapnh)_2Cl_2]Cl \cdot nH_2O + (m-n)H_2O$$

$$[2]\quad LnCl_3 \cdot mH_2O + 3(Hapnh) + 3\ KOH \xrightarrow[ca\ 1\ h]{pH\ ca.\ 7.5} [Ln(apnh)_3] + 3KCl + (m+3)H_2O$$

where

Ln=La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), and Y(III); Hapnh=2-Acetylpyridine nicotinoylhydrazone.

All the adduct complexes are soluble in methanol, ethanol and coordinating solvents such as *N,N*-dimethylformamide and dimethylsulfoxide whereas the neutral complexes are soluble only in coordinating solvents such as pyridine, *N,N*-dimethylformamide and dimethylsulfoxide. All the complexes are stable at room temperature. Most of them are yellow while some are fluorescent yellow in color. The adduct complexes decompose below 300 °C while the neutral complexes are nonmelting below 300 °C. The electrical conductance data of the adduct complexes (88.39—108.91 $ohm^{-1} cm^2 mol^{-1}$) are compatible with their 1 : 1 electrolytic behavior while those of the neutral complexes (1.12—4.52 $ohm^{-1} cm^2 mol^{-1}$) suggest their nonelectrolytic behavior.[10)]

Magnetic and Spectroscopic [Electronic, Infrared and (^1H and ^{13}C) NMR] Studies: The room-temperature magnetic moments corrected for diamagnetism show a slight deviation from van Vleck values[11)] indicating a little participation of 4f electrons in bond formation.

Electronic spectra of Pr(III), Nd(III), Sm(III) and Dy(III) complexes were recorded both in solid and solution states. The nephelauxetic parameter ($\bar{\beta}$), the covalent factor ($b^{1/2}$), Sinha's parameter (%δ), and angular overlap parameter (η), were calculated from the Nujol mull absorption spectra, and the absorption intensity, presented as oscillator strength (P), was calculated from the solution spectra using appropriate equations.[12,13)] The electronic spectral data of only representative complexes, say, the Nd(III) complexes are shown in Table 2. Increased oscillator strengths of the present complexes are most likely due to a lower molecular symmetry[14,15)] around the metal ion. The $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ band (hypersensitive band) in Nd(III) complexes is commonly used to calculate the change in oscillator strength with temperature/pH and to consider the coordination number around Nd(III) ion. The oscillator strengths (P) of the present Nd(III) complexes are found to increase at values of pH>6, which is most likely due to a change in the geometry and 'effective' symmetry of the ligand field about the Nd(III) ion.[16)] With increasing temperature there is, however, a negligible change in the oscillator strengths of the complexes. The spectral profile of the hypersensitive bands suggests eight-coordination in the Nd(III) adduct and nine-coordination in the Nd(III) neutral complex.[17)]

The Nujol mull infrared spectrum of Hapnh showed bands at 3190, 1660, 1618, 1545, 1322, and 1040 cm^{-1}, which may be assigned to the $\nu(\text{-NH})_{\text{symm.}}$, amide I, ν(C=N), amide II, amide III, and ν(N–N) modes. In the spectra of $[Ln(Hapnh)_2Cl_2]Cl$, the amide I and amide II bands were found to undergo bathochromic shifts (1630 and 1535—1532 cm^{-1}) and amide III a hypsochromic shift (1340—1338 cm^{-1}) suggesting coordination through the carbonyl oxygen. However, the amide I, II, and III bands totally disappeared from the spectra of $[Ln(apnh)_3]$ while a sharp band, diagnostic of $\rangle$C=N–N=C$\langle$ group,[18)] appeared at 1580 cm^{-1}, which indicated the transformation of the carbonyl group to enolic form through amide $\rightleftarrows$ imidic acid tautomerism and subsequent coordination of the imidic acid oxygen after deprotonation. Appearance of new bands characteristic of $\nu(NCO^-)$ at 1510—1500 and 1375—1365 cm^{-1} regions, further supported the imidic acid oxygen coordination.[19)] The ν(N–N) modes underwent a hypsochromic shift of 55—48 cm^{-1} in the spectra of all the complexes indicating azomethine nitrogen coordination.[20)] Coordination of 2-acetylpyridine ring nitrogen is suggested on the basis of the observed changes in the ring skeletal mode [ligand, 990; complexes 1030—1020], in-plane-ring deformation mode [ligand, 640; complexes, 670—660 cm^{-1}] and out-of-plane ring deformation mode [ligand, 435; complexes, 470—460 cm^{-1}].[21)] The corresponding bands associated to the nicotinoyl ring moiety show no changes suggesting non-coordinating nature of the nicotinoyl ring nitrogen.

Various nonligand bands have been located in the far-infrared spectra of the Nd(III) and Tb(III) complexes. In the adduct complexes of Nd(III) and Tb(III) the intense bands observed at 426 and 423 cm^{-1} are assignable to ν(M–O) mode and those at 325 and 323 cm^{-1} are due to ν(M–N) mode while the medium intense bands around 199 and 196 cm^{-1} indicate ν(M–Cl) mode.[22,23)] The presence of a single ν(M–Cl) band represents the trans nature of the two chloro ligands. The neutral complexes of Nd(III) and Tb(III) show intense bands at 426 and 427 cm^{-1} due to ν(M–O) and medium intense band at 321 and 315 cm^{-1} due to ν(M–N) mode.

The proton NMR spectrum of Hapnh shows signals at $\delta=11.20_s, 2.59_s$, and (7.62—9.16) due to imine proton, methyl proton, and ring protons respectively. The proton NMR spectra of $[La(Hapnh)_2Cl_2]Cl$ and $[Y(Hapnh)_2Cl_2]Cl$ show downfield shifts in the imine proton signal suggesting coordination through carbonyl oxygen or azomethine nitrogen.[24)] The slight downfield shift of the methyl group signal supports coordination of azomethine nitrogen. The spectra of $[La(apnh)_3]$ and $[Y(apnh)_3]$ however, do not show imine proton signals owing to apparently the deprotonation of the enolic form and subsequent bonding through the azomethine nitrogen and imidic acid oxygen atoms.

The ^{13}C NMR spectrum of Hapnh shows signals at δ=163.76, 145.53, 12.63, and 154.94—120.17 due to $\rangle\underline{C}$=O, $-N=\underline{C}(CH_3)$, $-\underline{C}H_3$, and pyridine ring carbon atoms respectively. The ^{13}C NMR spectra of the adduct complexes show downfield shifts in the carbonyl and $-N=\underline{C}(CH_3)$ resonances, suggesting coordination through carbonyl oxygen and azomethine nitrogen.[25)] The azomethine bonding is further supported by the downfield shift of the $-\underline{C}H_3$ signal. In the neutral complexes coordination of carbonyl oxygen and azomethine nitrogen was suggested on the basis of downfield shift of the $\rangle\underline{C}$=O and $-N=\underline{C}(CH_3)$ signals. The downfield shifts of the 2-acetylpyridine ring carbon signals (in both adduct and neutral complexes) are due to coordinating nature of the ring nitrogen.[26)] The relatively larger shift observed in the $\underline{C}_3$ signal of the nicotinoyl ring may be due to direct bonding of this carbon atom with carbonyl carbon, i.e., the coordinating site.

These observations clearly indicate the formation of two different types of complexes from the reaction of hydrated lanthanoid metal chlorides with 2-acetylpyridine nicotinoylhydrazone ligand. The empirical formula of the eight-coordinated adduct complexes has been found to be $[Ln(Hapnh)_2Cl_2]Cl \cdot nH_2O$ and that of the nine-coordinated neutral complexes is $[Ln(apnh)_3]$.

Conclusion

On the basis of the various spectral studies made, the following conclusions are drawn regarding the present series of the complexes:

(1) Analytical and molar conductance determinations show the formation of two classes of complexes, viz., the adducts, $[Ln(Hapnh)_2Cl_2]Cl \cdot nH_2O$ and the neutral complexes, $[Ln(apnh)_3]$.

(2) A little deviation of magnetic susceptibility from van Vleck values suggests little participation of 4f-electrons in bond formation.

(3) Infrared spectral studies indicate tridentate nature of the ligand in both the adducts and the neutral complexes.

(4) Electronic and IR spectral data indicate eight-coordination number in the adduct complexes and nine-coordination in the neutral complexes of particularly Nd(III).

(5) NMR data clearly indicate two types of the complexes; Hapnh acts as a neutral tridentate and uninegative tridentate species in the adducts and neutral complexes respectively.

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