

ELECTRONIC SPECTRAL STUDIES OF SOME LANTHANON COMPLEXES OF 2,6-DIACETYLPIRIDINE -2-FUROYL- ISONICOTINOYL DIHYDRAZONE

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ABSTRACT

The molecular formula $[Ln(H_2dapfhh)Cl(H_2O)_2]Cl_2$ has been established for the complexes from the analytical and molar conductance data. The Schiff base $H_2dapfhh$ is bonded to metal ions in pentadentate fashion through carbonyl oxygens, azomethine nitrogens and disubstituted pyridine nitrogen. The coordination number eight around the metal ions is inferred from the electronic spectra of the Nd (III) complex. The single crystal structure could not be determined because crystal could not be developed due to insolubility in the suitable solvents. In absence of this study a tentative square antiprismatic structure for the Ln (III) complexes of $H_2dapfhh$ is shown in Fig 1.

Keywords: Lanthanon complexes, electronic spectral studies, Schiff's bases.

I. INTRODUCTION

Some lanthanide complexes are used as shift reagents in nmr spectroscopy (1-3). The Eu^{3+} and Tb^{3+} complexes induced downfield proton nmr shifts where as those of Pr^{3+} and Dy^{3+} induced upfield shifts. The Yb^{3+} and Dy^{3+} shift reagents have been used in ^{13}C , ^{15}N and ^{19}F nmr experiments. Dysprosium bis(triposphate) has been used as shift reagent for ^{23}Na and ^{39}K nmr in wide range of biological preparations for yeast cells (4), plant cells (5), frog skin (6), amphibian oocytes (7) and human red cells (8). The use of this compound has also been made in studies of model membrane systems and phosphatidyl choline liposomes (9). The applications of these reagents for the determination of configuration of nonrigid molecules (10) have also been reported. Some sulphonated porphyrine complexes (11) are employed as water soluble shift reagents. The efficiency of gadolinium cryptate has been demonstrated for ^{15}N , ^{89}Y , ^{111}Cd and ^{183}W nmr measurements. The resistance of porphyrine (11) and macrocyclic (12) complexes to hydrolysis has allowed the introduction of lanthanide complexes of naturally occurring porphyrine into heme proteins, via reconstitution reactions. The use of lanthanide compounds in biological studies, material science and in chemical processes has produced technological development, scientific and industrial applications (13-16). The rare earth alkoxides and related

complexes have been used in electroceramics for synthesis of superconductors as $\text{LaBa}_2\text{Cu}_3\text{O}_{7-x}$ (17) and $\text{La}_2\text{Sr}_x\text{Cu}_{4-x}\text{O}_4$ (18) and piezoelectricssuch as LaCuO_2 (19). They represent a suitable solid lubricant due to its smaller hexagonal structures and ionic conducting properties. High purity of neodymium derivatives are of interest for optical fibers (20),non-linear optical materials (21) and high temperature superconductors (22). Neodymium alkoxide, β -diketonate and relative derivatives often display highest activity among the rare earth catalyst for polymerization reaction (23).

II.EXPERIMENTAL

2.1Electronic Spectral Studies:

The electronic spectral bands of the Nd(III), Sm(III) and Dy(III) complexes show red shift compared to the aqua metal ions [24]. This may be explained in terms of nephelauxetic effect arising from metal- ligand interaction [25]. The spectra were analysed and various spectral parameters viz. nephelauxetic ratio (β), bonding ($b^{1/2}$), Sinha ($\delta\%$) and covalency (η) have been calculated using eqns. 1- 4 from the solid spectra.

$$\beta = \nu_{\text{comp}}/\nu_{\text{aqua}} \quad [1]$$

$$b^{1/2} = \frac{1}{2} (1 - \beta)^{1/2} \quad [2]$$

$$\delta\% = [(1 - \beta) / \beta] \times 100 \quad [3]$$

$$\eta = (1 - \beta^{1/2}) / \beta^{1/2} \quad [4]$$

The absorption bands of the complexes with their assignments and the spectral parameter are given in Table 1

Table 1.Electron spectral data of Nd(III) complex of H₂dapfhh.

Complex	Bands (Cm ⁻¹)		S' L'J'	Spectral parameters
	Nujol mull	EtOH Soln		
[Nd(H ₂ dapfhh)Cl(H ₂ O) ₂]Cl ₂	11507	-	⁴ F _{3/2}	$\beta = 0.985$
	12547	12468	⁴ F _{5/2}	$B^{1/2} = 0.095$
	13280	-	⁴ F _{7/2}	$\delta\% = 1.833$
	13550	-	⁴ S _{3/2}	$\eta = 0.009$
	14534	-	⁴ F _{9/2}	
	14814	-		
	15822	-	² F _{11/2}	
	17123	17152	* ⁴ G _{5/2} , ² G _{7/2}	
	18656	-	² K _{13/2}	
	19011	-		

*Hypersensitive transtition ; ground state of Nd (III) is ⁴I_{9/2}

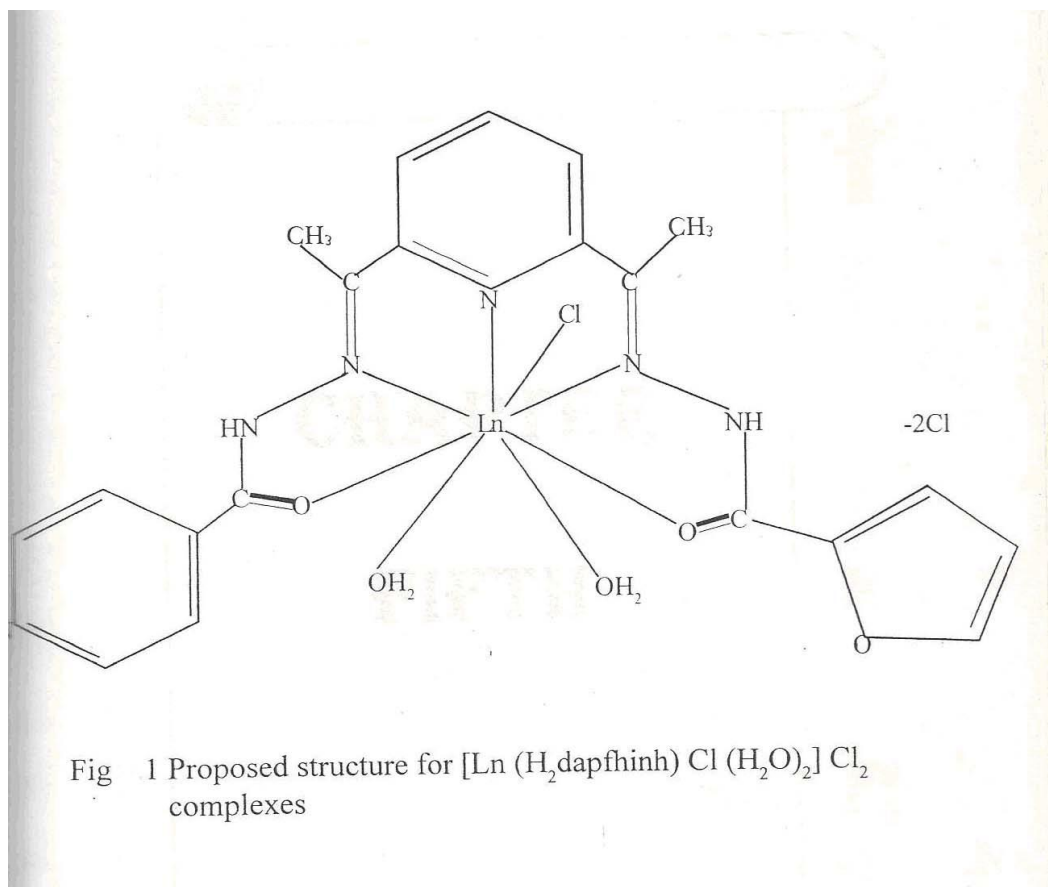
The β value are less than unity and $b^{1/2}$ and $\delta\%$ values are positive. These suggest weak covalent bonding between Ln(III) and the hydrazone (30). The band at 17182 cm⁻¹ in the spectrum of the Nd(III) complex is

assigned to the hypersensitive transition ($^4I_{9/2}$, $^4G_{5/2}$, $^2G_{7/2}$). The spectral profile is similar to that of the eight- coordinate complex, $Nd(thd)_3 \cdot 2HFAA$ ($thd = (CH_3)_3 CCOCHCOC(CH_3)_3$; $HFAA = CF_3COCH_2COCF_3$) (27) suggesting that metal ions have same coordination number in this complex also. The nujol mull and ethanol solution spectra of the Nd(III) complex have similar appearance in position and shape. It may therefore, be inferred that there is no change in coordination number due to solvation effect [26]. The oscillator strengths (Table- 2) have been calculated by evaluating the absorption intensities from the area beneath the absorption curve by using the literature procedure [26,27]. The oscillator strengths of the hypersensitive transition of the Nd(III), Sm (III) and Dy (III) complexes display a large change while the other f-electron transitions show little changes compared to aqua metal ions (28). The large increase in the oscillator strength value for the hypersensitive transition is due to dynamic coupling between transient induced electric dipoles in the ligand and the f-electron quadrupole moments of the metal ion (29). This indicates partial overlapping of metal-ligand orbitals.

Table2.Oscillator strengths of Nd(III), Sm(III) and Dy (III) complexes of H₂dapfhh

Complex	Spectral range (cm ⁻¹)	S 'L'J'	Oscillator strengths (px10 ⁶)
[Nd(H ₂ dapfhh)Cl(H ₂ O) ₂]Cl ₂	11415-11890	$^4F_{3/2}$	4.05
	12330-12787	$^4F_{5/2}$	11.83
	13089-13605	$^4S_{3/2}$, $^4F_{7/2}$	9.56
	16666-17730	$^{*4}G_{5/2}$, $^2G_{7/2}$	18.19
[Sm(H ₂ dapfhh)Cl(H ₂ O) ₂]Cl ₂	9140-9216	$^6F_{9/2}$	2.05
	11547-11890	$^6F_{11/2}$	0.99
	17182-17730	$^4G_{5/2}$	1.49
[Dy(H ₂ dapfhh)Cl(H ₂ O) ₂]Cl ₂	10764-11806	$^6F_{7/2}$	3.50
	11890-12690	$^6F_{5/2}$	2.55
	13089-13495	$^6F_{3/2}$	0.59

*Hypersensitive transition, ground state of Nd(III), Sm (III) and Dy(III) are $^4I_{9/2}$, $^6H_{5/2}$ and $^6H_{15/2}$ respectively.



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