



Synthesis and Spectroscopic Studies of Some Lanthanone Complexes of N, O Donor Schiff's Bases (2, 6-Diacetylpyridine-2-Furoyl Salicyldihydrazone)

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ABSTRACT: The 2,6-diacetyl pyridine-2-furoyl salicyldihydrazone Schiff's base synthesized and reacted with LnCl_3 , the molecular formula $[\text{Ln}(\text{H}_2\text{dapfsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}$ has been established for the complexes from analytical molar conductance data. Based on the results and discussion given below, it is concluded that the complexes have 1:1 metal- ligand stoichiometry. The hydrazone is bonded to the metal ions in tetradentate fashion through the carbonyl oxygen, azomethine nitrogens and pyridine nitrogen. A coordination number seven around the Ln (III) ion is evident from stoichiometry of the complexes and also from electronic spectra of the Nd (III) complex. Thus, a pentagonal bipyramidal structure proposed for the complex.

Keywords: Characterisation; complexes; donor; lanthanone; synthesis and spectroscopic.

INTRODUCTION: The Lanthanide complexes and their elements have many uses but quantities consumed relatively small in comparison to other elements. Lanthanides are consumed as catalysts and production of glasses. The application of Lanthanide in phosphors and magnets are more useful. The Lanthanides are used as samarium-cobalt and neodymium-iron-boron high flux rare earth magnets, electronic polishers, magnesium alloys, refining catalyst and hybrid components batteries, magnets and superconductors(1). Lanthanide ions are used as active ions in luminescent materials used in optoelectronics applications. Phosphors with Lanthanide dopants are used in cathode ray tube technology in television sets. Lanthanides are widely used in lasers and as dopants in doped fibre optical amplifiers. Lanthanide metals are particularly useful in technologies that are advantageous in reactivity of specific wavelengths of light. The biological fluids or serum are used in research applications contain many compounds and proteins that are naturally fluorescent. Currently research showing that Lanthanide elements are used as anticancer agents. The main role of Lanthanides to inhibit proliferation of the cancer cells. Lanthanum is used and tested as anticancer agents. It is used in catalytic converters, petroleum refining catalyst, permanent magnets, glass polishing and ceramics, metallurgical and phosphors. Some Lanthanide complexes are used as shift reagents in nmr spectroscopy (2-4). The use of lanthanide compounds in biological studies, material science and in chemical process has produced technological development, scientific and industrial applica-

tions (5-8). Lanthanides offer an interesting series of easily available elements with +3 oxidation state and other common physico chemical properties together with significant differences due to continuous decrease in ionic radius. The ionic radius being close to biologically essential alkaline earth ions and paramagnetism present in the lanthanides except La(III) and Lu(III) make them useful biological probes(9).

MATERIAL AND METHODS:

Preparation of Complexes: The complexes $[\text{Ln}(\text{H}_2\text{dapfsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$ (Ln : La, Pr, Nd, Sm, Eu, Gd, and Dy) were prepared by adding 1mmol of the Ln (III) chloride in 10 ml ethanol to a solution (20ml) of H_2dapfsh (1mmol, 0.405g) in the same solvent. The solution was refluxed for ~4h and concentrated to ~4 ml on a water bath. Acetonitrile (15ml) was added to above solution which resulted in a gummy mass. The microcrystalline compound was obtained by macerating the gummy mass several times with acetonitrile (15ml). The compound was filtered off, washed with ethanol-acetonitrile mixture (1:3 v/v) and dried in a desiccator under reduced pressure.

Analysis of Complexes: The metal content was determined [10] by titrating against EDTA solution after decomposing the organic matter with aqua regia and concentrate sulphuric acid alternatively. Hydrazine was determined [11] by titrating against KIO_3 solu-

tion after hydrolyzing the complex in 6N HCl for ~2h. Chloride was determined gravimetrically as Ag Cl [11]. The analytical data and physical properties of the complexes are given in Table 1.

Table 1: Analytical data and physical properties of Ln (III) complexes of H₂dapfsh.

Complex, % Yield, Mol.Weight	Decomp. Temp. (°C)	Found (Calcd.)%		
		M	Cl	N ₂ H ₄
[La(H ₂ dapfsh)Cl(H ₂ O) ₂]Cl ₂ 65, 670.41	340	20.00 (20.72)	15.30 (15.88)	9.15 (9.54)
[Pr(H ₂ dapfsh)Cl(H ₂ O) ₂]Cl ₂ 60, 672.24	330	20.25 (20.96)	15.25 (15.84)	9.00 (9.52)
[Nd(H ₂ dapfsh)Cl(H ₂ O) ₂]Cl ₂ 52, 675.74	330	21.00 (21.35)	15.18 (15.76)	9.40 (9.47)
[Sm(H ₂ dapfsh)Cl(H ₂ O) ₂]Cl ₂ 50, 681.85	335	21.35 (22.05)	15.40 (15.62)	9.35 (9.39)
[Eu(H ₂ dapfsh)Cl(H ₂ O) ₂]Cl ₂ 55, 683.47	340	21.45 (22.23)	15.00 (15.58)	8.90 (9.36)
[Gd(H ₂ dapfsh)Cl(H ₂ O) ₂]Cl ₂ 53, 688.75	350	22.00 (22.83)	14.80 (15.46)	8.85 (9.29)
[Dy(H ₂ dapfsh)Cl(H ₂ O) ₂]Cl ₂ 55, 694.00	345	23.00 (23.41)	15.15 (15.34)	9.20 (9.22)

Physical Measurements: The molar conductance was determined on a WTW conductivity meter in 10⁻³ M EtOH solution. Infrared spectra of the hydrazone and their complexes were recorded in KBr disc on a Jasco 5300 spectrophotometer. The magnetic susceptibilities were measured at room temperature on a Cahn Faraday electrobalance using Hg[Co(NCS)₄] calibrant and were corrected for diamagnetism [12]. Electronic spectra of the Nd(III) and Dy (III) complexes were obtained in solid (nujol) as well as in 10⁻³ M methanol solution on a Shimadzu uv/vis 160 A spectrophotometer.

RESULTS AND DISCUSSION: The compounds [Ln(H₂dapfsh)Cl(H₂O)₂]Cl₂ obtained by reacting the lanthanide (III) chlorides and ligand (H₂dapfsh)

in ethanol. The complexes are obtained in a good yield in which the lanthanide ion is bonded with the resulting azomethine nitrogen. The complexes are slightly hygroscopic on exposure to the atmosphere and are highly soluble in ethanol, methanol, DMF and DMSO. The molar conductance values (Table 2) in 10⁻³ M ethanol solution indicate 1:2 electrolytic (13) nature of the complexes.

Table 2: Molar conductances of Ln (III) complexes of H₂dapfsh.

Complex	Molar conductances (ohm ⁻¹ cm ² mol ⁻¹)						
	La	Pr	Nd	Sm	Eu	Gd	Dy
[Ln(H ₂ dapfsh)Cl(H ₂ O) ₂]Cl ₂	73.0	77.0	75.0	68.0	74.0	80.0	75.0

Table 3: Experimental magnetic moments for lanthanide sulphates and calculated values of Ln (III) ions.

Ln (III)	Ground term	Experimental μ _{eff} * for Ln ₂ (SO ₄) ₃ ·8H ₂ O	Calculated	
			Hund μ _{eff}	Van Vleck μ _{eff}
La (III)	¹ S ₀	0	0	0
Ce (III)	² F _{5/2}	2.37	2.54	2.56
Pr (III)	³ H ₄	3.47	3.58	3.62
Nd (III)	⁴ I _{9/2}	3.52	3.62	3.68
Pm (III)	⁵ I ₄	--	2.68	2.83
Sm (III)	⁶ H _{5/2}	1.53	0.84	1.55-1.65
Eu (III)	⁷ F ₀	3.42	0	3.40-3.51
Gd (III)	⁸ S _{7/2}	7.81	7.94	7.94
Tb (III)	⁷ F ₆	9.40	9.70	9.70
Dy (III)	⁶ H _{15/2}	10.40	10.60	10.60
Ho (III)	⁵ I ₈	10.30	10.60	10.60
Er (III)	⁵ I _{15/2}	9.60	9.60	9.60
Tm (III)	³ H ₆	7.10	7.60	7.60
Yb (III)	² F _{7/2}	4.40	4.50	4.50
Lu (III)	¹ S ₀	0	0	0

*Calculated by the equation: μ_{eff} = 2.83√χ_mT

The magnetic moment values (Table 4) obtained at room temperature show that except the lanthanum complex, all are paramagnetic and slightly deviate from Van Vleck values (14) This indicates the little participation of 4f- electrons in bonding. In case of the Sm(III) complex a relatively high value was obtained because of low J-J separation (15) which leads to thermal population of the higher energy level and shows susceptibility due to first order Zeeman effect.

Table 4: Magnetic moments of Ln (III) complexes of H₂dapfsh.

Complex	Magnetic moments (BM)						
	La	Pr	Nd	Sm	Eu	Gd	Dy
[Ln(H ₂ dapfsh)Cl(H ₂ O) ₂]Cl ₂	0	3.49	3.56	2.25	3.37	7.70	10.30

Electronic Spectral Studies: The electronic spectra of the rare earth ions are consist of closely spaced groups of sharp lines. These spectra arise from transitions between levels of 4fⁿ configurations. The information relating to the crystal field splitting can be obtained from analysis of the absorption spectra. The usual (2J+1) fold degeneracy of terms of 4fⁿ configuration is reduced by crystal field. However, the energy levels of the lanthanide ions in solid state are largely determined by spin orbit interaction, higher than the crystal field influence. The main difference of the transition metal ions from the lanthanide ions is the large contribution of crystal field compared to the spin orbit coupling. On comparing the spectra of lanthanide (III)

complexes with those of aqua ions, three changes are observed which are (i) a red shift of the bands (ii) splitting of certain bands and (iii) alteration of specific absorptivity of individual bands. These changes are related to alteration in the strength and symmetry of the ligand field. The absorption bands which are particularly susceptible to splitting and intensity changes are termed as “hypersensitive transitions” [16] while most of the other bands remain unaffected. The significant shift of the bands towards lower frequency for the lanthanide ions compared with those of lanthanide aqua ions [17] is attributed to the effect of the ligand field to lower interelectronic repulsion among 4f-electrons due to expansion of electron cloud which is known nephelauxetic effect (18) various parameters such as nephelauxetic ratio (β) bonding ($b^{1/2}$), Sinha ($\delta\%$), covalency angular overlap parameter (η) and oscillator strength (P) were evaluated (19-21,22,23) from electronic spectra to draw some informations regarding the nature of metal-ligand bonding. The electronic absorption spectra of the Nd(III) and Dy (III) complexes are recorded, a red shift of the bands is found for the Ln (III) complexes compared to the respective aqua metal ions [17]. The phenomenon of red shift is occurring because of partly expansion of the lanthanide orbit radius due to covalent bonding and partly due to contraction in highly electrostatic bonding on complexation. This effect is known as nephelauxetic effect influenced by the ligand field (18). The various spectral parameters viz nephelauxetic ratio (β), bonding ($b^{1/2}$), Sinha ($\delta\%$) and angular overlap covalency (η) have been calculated from formula. (Table .6) The β values are less than one and positive values of $b^{1/2}$ and $\delta\%$ show weak covalent bonding developed between the metal ion ligand (24). The shape and position of the hypersensitive transition $^4I_{9/2}$, $^4G_{5/2}$, $^2G_{7/2}$ in the Nd (III) complex is similar to that of seven-coordinate complexes [25]. It implies that in these complexes the Ln^{3+} ions have coordination number seven. The solution and solid state spectra of the complexes are similar in appearance and position, suggesting that no change in coordination number occurs due to the solvation effect [26].

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

The intensity of the f-f transitions for the Nd(III) complex has been calculated by area method [25,26]

and presented as oscillator strength. The oscillator strength values (Table.6) obtained for all, the observed bands are larger compared to aqua metal ion (27) indicating metal-ligand interaction. The oscillator strength of hypersensitive transition $^4I_{9/2}$, $^4G_{5/2}$, $^2G_{7/2}$ is larger than that for aqua metal ion which reflects the dynamic coupling between f-electrons quadrupole moment and polarizability of the ligand in the complex (28).

Table 5: Electronic spectral data of Nd(III) and Dy (III) complexes.

*Hypersensitive

Complex	Bands (cm ⁻¹)		S' L' J	Spectral parameters
	Nujol mml	EtOh Soln		
[Nd(H ₂ dapfsh)Cl(H ₂ O) ₂]Cl ₂	11494		$^4F_{3/2}$	$\beta = 0.997$ $b_{1/2} = 0.046$ $\delta\% = 0.432$ $\eta = 0.002$
	12500	12500	$^4F_{5/2}$	
	13495	13568	$^4S_{3/2}$	
	17123	17182	$^4G_{3/2}, ^2G_{7/2}$	
	19083		$^4G_{7/2}$	
	19493		$^4G_{9/2}$	
	22935		$^4P_{1/2}$	
[Dy(H ₂ dapfsh)Cl(H ₂ O) ₂]Cl ₂	11013		$^4F_{3/2}$	$\beta = 0.998$ $b_{1/2} = 0.032$ $\delta\% = 0.200$ $\eta = 0.001$
	12391		$^4F_{5/2}$	
	13192		$^4F_{7/2}$	

Table 6: Oscillator strength of Nd(III) complex of H₂dapfsh.

Complex	Spectral range (cm ⁻¹)	S' L' J	Oscillator strengths (P x 10 ³)
[Nd(H ₂ dapfsh)Cl(H ₂ O) ₂]Cl ₂	11261-11655	$^4F_{3/2}$	18.17
	12330-12886	$^4F_{5/2}, ^4H_{9/2}$	47.83
	13495-13947	$^4S_{3/2}, ^4F_{7/2}$	35.88
	16366-17730	$^4G_{3/2}, ^2G_{7/2}$	68.88

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

REFERENCES:

1. C. Pelizzi, G. Pelizzi, G. Predieri and S. Resola, J. Chem. Soc. Dalton Trans., 1349 (1982).
2. A. N. Kokerill, G. L. O. Devies, R. C. Harden and D. M. Rackan, Chem Rev, 73, 55(1973).
3. R. E. Sievers,(Ed) “NMR Shift Reagents”, Academic Press ,New York,1973.
4. G. R. Sullivan, “Topics in Stereochemistry” 10, 287(1978).
5. G. J. McCarty, J. J. Rhyne and H. B. Silber, “The Rare Earth in Modern Science and Technology” Vol. 1, 2 and 3 Plenum Press, 1977, 1979, 1981.

6. A. Mazzei, in T. J. Marks and R.D.Fischer (Eds), "Organometallics of the f-Elements", D. Riedel Dordrecht, p. 379, (1979).
7. H. B. Kagan, in T. J. Marks and I. I. Fragala (Eds), "Fundamental and Technological Applications of Organo f-Elements Chemistry", D. Riedel Dordrecht, p. 49, (1985).
8. M. Bruzzone and A. Carbonaro, in T. J. Marks and I. I. Fragala (Eds). "Fundamental and Technological Applications of Organo f-Elements Chemistry", D.Riedel, Dordrecht, p. 387, 1985.
9. M. N. Hughes, "The Inorganic Chemistry of Biological Processes" 2nd Edn, Wiley, New York, p. 68, 273,279, (1981).
10. S. J. Lyle and M. Md. Rahman, *Talanta*, 10, 1177 (1963).
11. A.I. Vogel, "A Text Book of Quantitative Inorganic Analysis", 3rd Edn., Longman, London, p. 380, 460, (1969).
12. B. N. Figgis and J. Lewis, "Modern Inorganic Chemistry", (Eds) J. Lewis and R.G. Wilkins, Interscience, New York, (1960).
13. W. J. Geary, *Coord. Chem. Rev.*, 7, 81 (1971).
14. J. H. Van Vleck and A. Frank, *Phys. Rev.*, 34, 1494, 1625 (1929).
15. B. N. Figgis and J. Lewis, "Techniques of Inorganic Chemistry", Interscience New York, Vol. 4, p. 137 (1965).
16. (a) T. Moeller, in K.W. Bagnall (Ed) "MTP International Review of Science". Series One, Buterworth, London, vol. 7, p. 275, 1972.
(b) D. L. Kepert, *Prog Inorg. Chem.*, 24, 179 (1978).
(c) D. L. Kepert *Prog. Inorg. Chem.*, 25, 41 (1979).
(d) M. C. Favas and D. L. Kepert, *Prog. Inorg. Chem.*, 28, 309 (1981)
17. W. T. Carnall, P. R. Fields and K. Rajnak, *J. Chem. Phys.* 49, 4424 (1968).
18. C. E. Schaffer and C. K. Jorgensen, *J. Inorg. Nucl. Chem.*, 8, 143 (1958).
19. C. K. Jorgensen "Modern Aspects of Ligand Field theory" North Holland, Amsterdam, p. 293 (1971).
20. D. E. Henrie and G. R. Choppin, *J. Chem. Phys.*, 49, 477 (1968).
21. M. Singh, S. N. Mishra and R. D. Verma, *J. Inorg. Nucl. Chem.*, 40, 1939 (1978).
22. S. P. Sinha, *Spectrochim. Acta*, 22, 57 (1966).
23. W. T. Carnall. P.R. Fields and B.G. Wybourn, *J. Chem Phys.*, 42, 3797 (1965).
24. S. P. Tandon and P. C. Mehta, *J. Chem. Phys.*, 52, 4896 (1970).
25. D. G. Karraker, *Inorg. Chem.*, 6, 1863 (1967).
26. D. G. Karraker, *Inorg. Chem*, 7, 473 (1968).
27. K. Iftikhar, *Inorg. Chim. Acta*, 129, 261 (1987).
28. G. Blasse A. Bril and W. C. Nieuwpoort, *J. Phys. Chem. Solids*, 27, 1587 (1966).