

Reaction of coordinated ligand-IV. Synthesis and characterization of some lanthanide complexes of 2,6-diacetylpyridine 2-thenoyl salicyl dihydrazone

B SINGH* and T B SINGH

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221 005, India

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Abstract. The complexes of the type $[\text{Ln}(\text{H}_2\text{daphsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}$ and Dy ; $\text{H}_2\text{daphsh} = 2,6\text{-diacetylpyridine 2-thenoyl salicyl dihydrazone}$) have been prepared by reacting salicylhydrazone (sh) with $[\text{Ln}(\text{Hdaphth})\text{Cl}_2(\text{H}_2\text{O})_3]\text{Cl}$ ($\text{Hdaphth} = 2,6\text{-diacetylpyridine mono (2-thenoylhydrazone)}$) in ethanol. The condensation of coordinated acetyl $\text{C}=\text{O}$ with $-\text{NH}_2$ of salicylhydrazone occurs and the resulting azomethine nitrogen is found bonded to the $\text{Ln}(\text{III})$ ions. The compound has been found monomeric from FAB mass spectra. The bonding sites of the dihydrazone and coordination number and symmetry of the ligand field around Ln^{3+} ions have been deduced from IR, electronic and emission spectra.

Keywords. Reaction of coordinated ligand; asymmetrical hydrazone; lanthanide.

1. Introduction

The condensation product of 2,6-diacetylpyridine with various diamines and hydrazides have been found to adopt the pentagonal bipyramidal stereochemistry for the various metal complexes^{1–4}. The chemical properties of the hydrazones have been extensively studied due to their coordinating capability⁵, pharmacological activity⁶ and their use in analytical chemistry as a metal extracting agent⁷. A variety of the lanthanide complexes of symmetrical acyclic and macrocyclic Schiff bases have been synthesized by template effect of Ln^{3+} ion^{8,9}. There are no reports on the complexes of asymmetrical acyclic Schiff bases.

It was therefore worth synthesizing and characterizing the $\text{Ln}(\text{III})$ complexes of asymmetrical H_2daphsh which are obtained by reaction of coordinated acetyl $>\text{C}=\text{O}$ in $(\text{Ln}(\text{Hdaphth})\text{Cl}_2(\text{H}_2\text{O})_3)\text{Cl}$ complexes with salicylhydrazone. The results are presented in the present paper.

2. Experimental

2,6-Diacetylpyridine and 2-thenoylhydrazine (Aldrich, Germany), salicylaldehyde (Spectrochemie, Bombay) and hydrated $\text{Ln}(\text{III})$ chlorides (Indian Rare Earth Ltd., Kerala) were used without purification.

*For correspondence

2.1 Preparation of ligand

Salicylhydrazone was prepared by adding salicylaldehyde (10 mmol, 1.07 ml) to an ice-cold ethanol solution (10 ml) of hydrazine hydrate (10 mmol, 0.49 ml) in drops with continuous stirring. A white precipitate formed immediately which was filtered and washed with ethanol. It was recrystallized from hot chloroform yield, 1.089, 80%. The compound was characterized by m.p. 97–98°C (Lit 98°C; ^{10b}, N₂H₄ 23.35 (23.49))%.

The 2,6-diacetylpyridine 2-thenoylsalicyl dihydrazone (H₂dapthsh) was prepared by adding an ethanol solution (10 ml) of salicylhydrazone (1 mmol, 0.136 g) to a hot solution (30 ml) of 2,6-diacetylpyridine mono (2-thenoylhydrazone) (Hdapth) (1 mmol, 0.287 g) in the same solvent, followed by a catalytic amount of concentrated acetic acid (0.5 ml). The resulting solution was refluxed for ~3 h on a water bath. A yellow compound precipitated and filtered off. The compound was recrystallized from hot ethanol. Yield, 0.071 g, 17%. It was characterized by m.p. 238–240°C, N₂H₄, 15.62 (15.78) %, IR, and mass spectra. The mass spectrum and fragmentation pattern are given in figure 1 and scheme 1, respectively.

2.2 Preparation of complexes

The complexes [Ln(H₂dapthsh)Cl(H₂O)₂]₂Cl₂ were synthesized by adding an ethanol solution (10 cm³) of salicylhydrazone (1 mmol, 0.136 g) to a solution of [Ln(Hdapth)Cl₂(H₂O)₃]₂Cl (1 mmol) in the same solvent (25 cm³). The resulting solution was refluxed for ~4 h and concentrated to ~5 ml on a water bath. After addition of acetonitrile, a gummy solid formed which was macerated several times with acetonitrile to give a microcrystalline compound. The compound obtained was filtered, washed with acetonitrile and dried *in vacuo* over fused CaCl₂.

The same compounds were obtained by reacting the lanthanum(III) chlorides and ligand as given below.

The complexes [La(H₂dapthsh)Cl(H₂O)₂]₂Cl₂ and [Pr(H₂dapthsh)Cl(H₂O)₂]₂Cl₂ were prepared by mixing 1 mmol of the La(III) or Pr(III) chlorides in 10 ml of ethanol with 1 mmol of H₂dapthsh (0.405 g) in 20 ml of the same solvent. The solution obtained was concentrated to ~4 ml on a water bath and 15 ml of acetonitrile was added which resulted in a gummy mass. The microcrystalline compound was obtained by

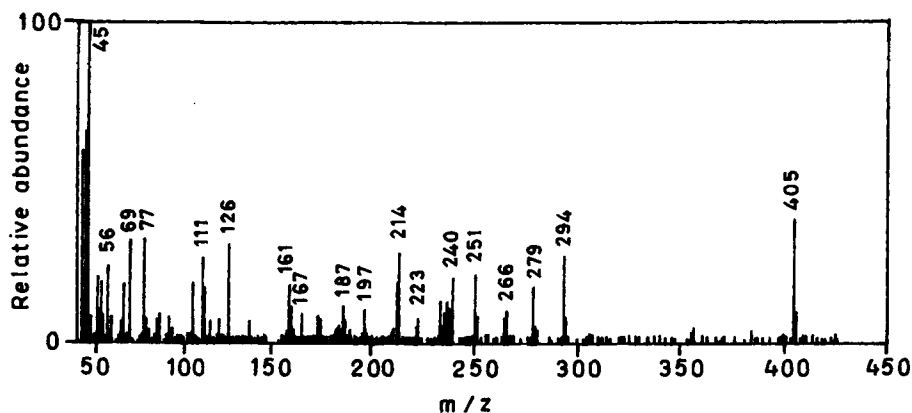
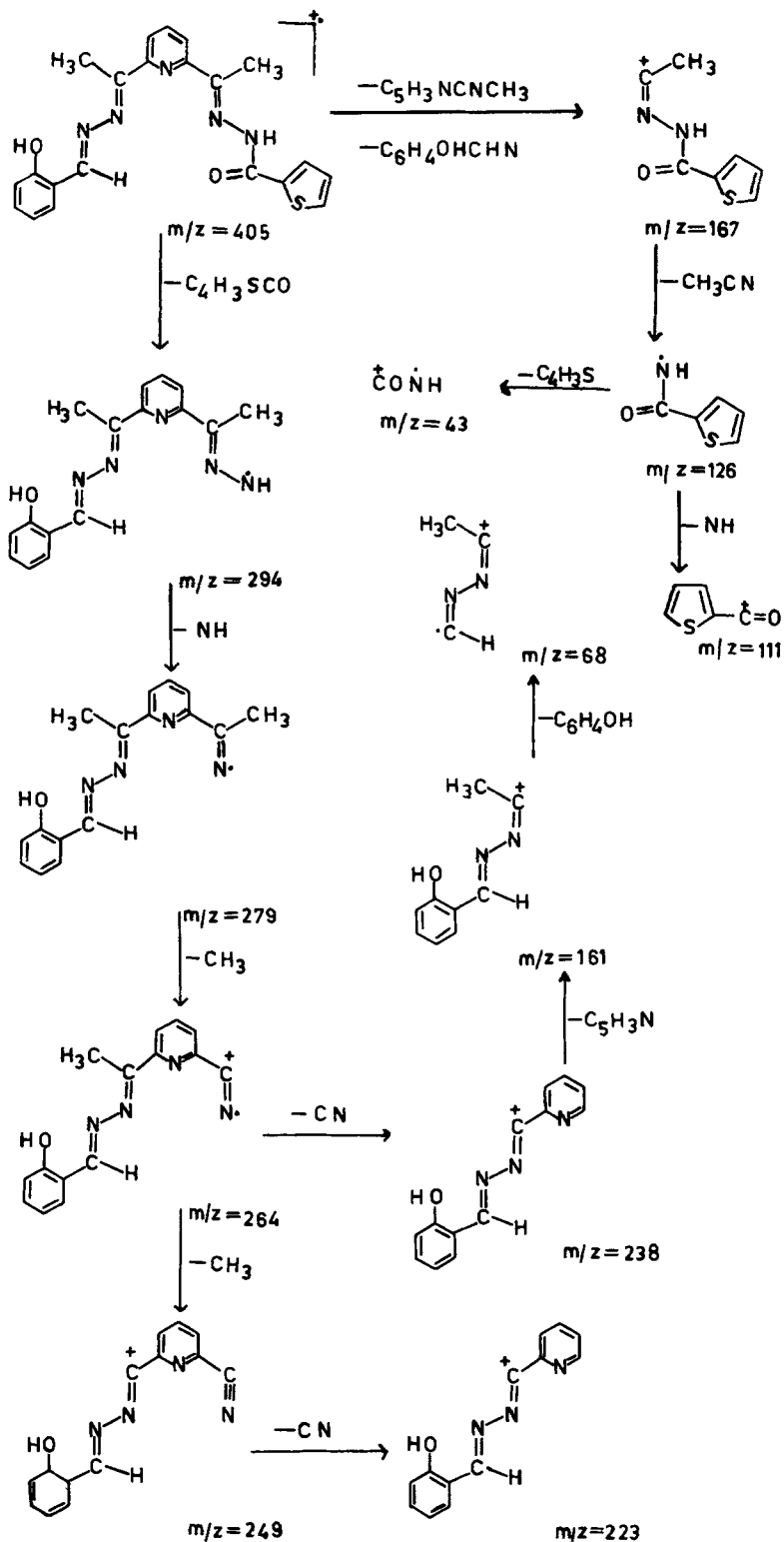


Figure 1. The mass spectrum and fragmentation pattern are given in figure 1 and scheme 1, respectively.



Scheme 1.

macerating the gummy mass several times with acetonitrile (15 cm³). The compound was filtered off, washed with ethanol-acetonitrile mixture (1:3 v/v) and dried in a desiccator under reduced pressure.

Since the ligand H₂dapthsh is obtained in a very low yield, the other compounds were prepared following the former procedure. Thus the compound isolated from above two different methods have the same metal-ligand stoichiometry. The analytical data and physical properties are given in table 1.

2.3 Analysis of complexes

The metal content was determined¹¹ by titrating against EDTA solution after decomposing the organic matter with aqua regia and concentrated sulphuric acid alternatively. Hydrazine was determined¹² by titrating against KIO₃ solution after hydrolysing the complex in 6N HCl for ~ 2 h. Chloride was determined gravimetrically¹² as AgCl.

2.4 Physical measurement

The molar conductance was determined on a WTW conductivitymeter in 10⁻³ M EtOH solution. Mass spectrum of the ligand and FAB mass spectrum of the Tb (III) complex were obtained on Jeol D-300C and Jeol SX-102/DA-6000 mass spectrometer respectively. 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 Cahn-Faraday electrobalance and Hg[Co(NCS)₄] using a calibrant and was corrected for diamagnetism¹³. Electronic spectra of the complexes were obtained in solid (nujol) as well as in 10⁻³ M methanol solution on a Shimadzu UV-VIS 160 A spectrophotometer. Solid state emission spectra of Sm(III), Eu(III) and Tb(III) complexes were recorded at LNT on a Perkin-Elmer MPF-44B fluorescence spectrophotometer.

3. Results and discussion

The compounds [Ln(H₂dapthsh)Cl(H₂O)₂]₂Cl₂ were obtained either by reacting the lanthanide (III) chlorides and ligand (H₂dapthsh) or by reacting salicylhydrazone with [Ln(Hdapth)Cl₂(H₂O)₃]₂Cl in ethanol. The latter method was followed to prepare the complexes, because H₂dapthsh was obtained in a very low yield. This is considered an example of reaction of the coordinated ligand in which -NH₂ group of salicylhydrazone is condensed with 2,6-diacetylpyridine C=O which is bonded with the metal ions. This gives a good yield of the complexes in which the lanthanide ion is bonded with the resulting azomethine nitrogen. The complexes are slightly hygroscopic on prolonged exposure to the atmosphere and are highly soluble in ethanol, methanol, DMF and DMSO. The molar conductance (table 1) in 10⁻³ M ethanol solution, indicate 1:2 electrolytic nature of the complexes¹⁴.

3.1 Mass spectra

The FAB mass spectrum of [Tb(H₂dapthsh)Cl(H₂O)₂]₂Cl₂ shows base peak at m/z = 604 corresponding to the fragment H₂dapthsh TbCl]⁺. The highest mass peak (M⁺) obtained at m/z = 640 is attributed to the monomeric nature of

Table 1. Analytical data, melting points, magnetic moments and molar conductance of Ln(III) complexes of H₂dapthsh

Complex, % yield, formula wt.	Decomposition temperature (°C)	Found (Calculated)%			Magnetic moment BM	Molar conductance ohm ⁻¹ cm ² mol ⁻¹
		M	Cl	N ₂ H ₄		
[La(H ₂ dapthsh)Cl(H ₂ O) ₂]Cl ₂ 65, 686·82	340	20·00 (20·23)	15·30 (15·48)	9·15 (9·32)	0	73·0
[Pr(H ₂ dapthsh)Cl(H ₂ O) ₂]Cl ₂ 60, 688·82	330	20·15 (20·46)	15·25 (15·44)	9·00 (9·29)	3·45	77·0
[Nd(H ₂ dapthsh)Cl(H ₂ O) ₂]Cl ₂ 52, 692·15	330	21·00 (20·84)	15·18 (15·37)	9·40 (9·25)	3·55	75·0
[Sm(H ₂ dapthsh)Cl(H ₂ O) ₂]Cl ₂ 50, 698·27	335	21·35 (21·53)	15·40 (15·23)	9·35 (9·17)	2·25	68·0
[Eu(H ₂ dapthsh)Cl(H ₂ O) ₂]Cl ₂ 55, 699·87	340	21·45 (21·71)	15·00 (15·19)	8·90 (9·14)	3·37	74·0
[Gd(H ₂ dapthsh)Cl(H ₂ O) ₂]Cl ₂ 53, 705·16	350	22·00 (22·29)	14·80 (15·08)	8·85 (9·08)	7·70	80·0
[Tb(H ₂ dapthsh)Cl(H ₂ O) ₂]Cl ₂ 58, 706·84	338	22·20 (22·48)	14·80 (15·05)	9·35 (9·05)	9·60	78·0
[Dy(H ₂ dapthsh)Cl(H ₂ O) ₂]Cl ₂ 55, 710·41	345	23·00 (22·87)	15·15 (14·97)	9·20 (9·00)	10·35	75·0

the complex. The FAB mass spectrum and most favourable fragments are given in figure 2 and scheme 2, respectively.

3.2 Infrared spectra

The diagnostic IR bands of the ligand and their Ln(III) complexes are shown in table 2. The infrared absorption bands of the ligand appeared at 3425, 3150, 1640, 1515 and 1030 cm^{-1} , which are assigned to $\nu(\text{O-H})$, $\nu(\text{N-H})$, amide I, amide II and $\nu(\text{N-N})$ modes, respectively. The absorption due to amide I and amide II shift to lower frequencies at 1620–1615 and 1505–1500 cm^{-1} , respectively and that due to $\nu(\text{N-N})$ shift to higher frequencies at 1052–1045 cm^{-1} . In free H_2 dapthsh the band due to $\nu(\text{C=N})$ is well splitted and is observed at 1625 and 1610 cm^{-1} because of two different environments around C=N group. The absorption due to $\nu(\text{C=N})$ also shift to the lower frequencies and are observed as a composite band at 1605–1600 cm^{-1} in the complexes. These spectral features are characteristics of coordination of H_2 dapthsh with the metal ions through the carbonyl oxygen and azomethine nitrogens¹⁵. The pyridine ring vibrations at 995 (breathing), 640 (in-plane) and 420 cm^{-1} (out-of-plane) are observed at higher wave numbers at 1010–1005, 655–650 and 433–427 cm^{-1} respectively, in the complexes and indicated by the bonding of the pyridine nitrogen to the metal ions¹⁶. The bands due to thiophene ring appearing at 1420, 1250 and 900 cm^{-1} in free ligand are assigned to the ring stretching, C–H bending and $\text{C}_{\text{ring}}-\text{C}_{\text{exo}}$ modes respectively,¹⁷. These bands are obtained almost at the same position in the complexes, showing non-involvement of the thiophene sulphur in bonding. The coordinated nature of water molecules are shown from a presence of bands at 850–855 and 560–570 cm^{-1} due to $\rho_r(\text{H}_2\text{O})$ and $\rho_w(\text{H}_2\text{O})$ modes, respectively, in the Ln(III) complexes¹⁸.

3.3 Magnetic moment

The magnetic moment values (table 1) obtained at room temperature for the $[\text{Ln}(\text{H}_2\text{dapthsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$ complexes show that except La(III), all are

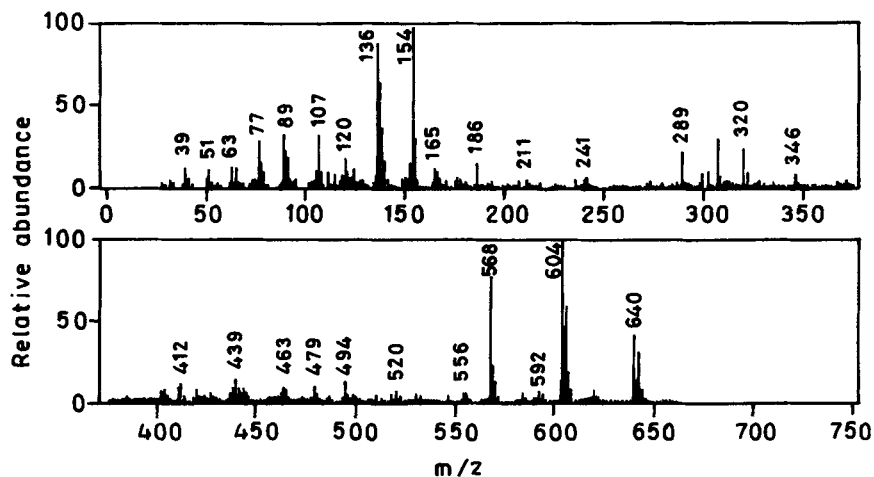
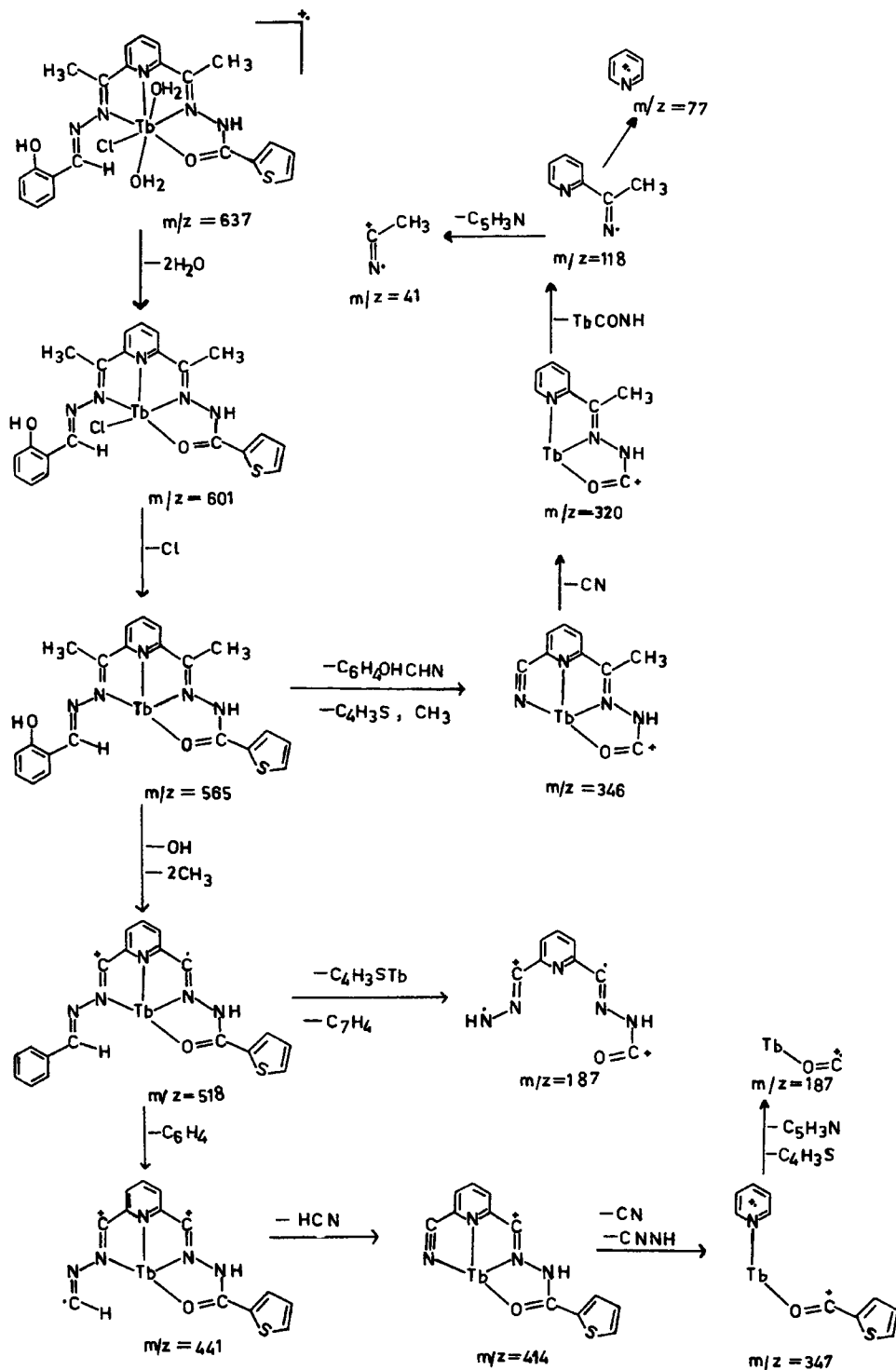


Figure 2. The FAB mass spectrum and most favourable fragments are given in figure 2 and scheme 2, respectively.



Scheme 2.

Table 2. Infrared spectral bands (cm^{-1}) and their assignments in H_2 dapthsh and its Ln(III) complexes.

Complex	Pyridine ring vibration						
	Amide I	$\nu(\text{C}=\text{N})$	Amide II	$\nu(\text{N}-\text{N})$	Breathing	In-plane	Out-of-plane
H_2 dapthsh	1640	1625, 1610	1515	1030	995	640	420
$[\text{La}(\text{H}_2\text{dapthsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$	1620	1605	1503	1045	1005	655	430
$[\text{Pr}(\text{H}_2\text{dapthsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$	1620	1605	1503	1045	1005	650	435
$[\text{Nd}(\text{H}_2\text{dapthsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$	1618	1600	1500	1055	1010	655	435
$[\text{Sm}(\text{H}_2\text{dapthsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$	1622	1595	1503	1050	1010	655	430
$[\text{Eu}(\text{H}_2\text{dapthsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$	1622	1590	1505	1042	1005	655	430
$[\text{Gd}(\text{H}_2\text{dapthsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$	1620	1590	1500	1045	1005	655	433
$[\text{Tb}(\text{H}_2\text{dapthsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$	1620	1590	1505	1040	1010	650	430
$[\text{Dy}(\text{H}_2\text{dapthsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$	1620	1590	1503	1060	1010	650	432

paramagnetic and slightly deviate from VanVleck value¹⁹. This indicates the little participation of 4f-electrons in bonding. In case of the Sm(III) complex relatively high value was obtained, because of low J-J separation²⁰ which leads to thermal population of the higher energy level.

3.4 Electronic spectra

The electronic absorption bands of the Nd(III) and Dy(III) complexes are depicted in table 3. A red shift of the bands are found for the Ln(III) complexes compared to the respective aqua metal ions²¹. The phenomenon of red shift is partly because of the expansion of the lanthanide orbit radius due to covalent bonding and partly due to contraction in highly electrostatic bonding on complexation. This effect known as nephelauxetic effect is influenced by the ligand field²². The various spectral parameters viz. nephelauxetic ratio(β), bonding ($b^{1/2}$), Sinha ($\delta\%$) and angular overlap covalency parameter (η) have been calculated. The β values are less than one and positive values of $b^{1/2}$ and $\delta\%$ (percentage covalency) show weak covalent bonding developed between the metal and ligand²³. The shape and position of the hypersensitive transition ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ in the Nd(III) complex is similar to that of seven coordinated complexes²⁴. It means that in these complexes the Ln³⁺ ions have coordination number seven.

The intensity of the $f-f$ transitions for the Nd(III) complex has been calculated by the area method²⁵ and are presented as oscillator strength. The oscillator strength values (table 4) obtained for all the observed bands are larger compared to aqua metal ion²⁶, indicating metal-ligand interaction. The oscillator strength of hypersensitive transition ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ is larger than aqua metal ion which reflects that complex possesses a lower molecular symmetry. The solution and solid state (nujol mull) spectra of the complexes are similar in appearance and position, suggesting that no change in coordination number occurs around the Ln(III) ions due to solvation effect²⁵.

Table 3. Electronic spectral bands and their assignments for Nd(III) and Dy(III) complexes.

Complex	Bands (cm ⁻¹)			Spectral parameter
	Nujol	EtOH	S'L'J'	
[Nd(H ₂ dapthsh)Cl(H ₂ O) ₂]Cl ₂	11494		${}^4F_{3/2}$	$\beta = 0.9957$
	12500	12500	${}^4F_{5/2}$	$b^{1/2} = 0.0464$
	13495	13568	${}^4S_{3/2}, {}^4F_{7/2}$	$\delta\% = 0.4319$
	17123	17182	${}^{*4}G_{5/2}, {}^2G_{7/2}$	$\eta = 0.0022$
	19083		${}^4G_{7/2}$	
	19493		${}^4G_{9/2}$	
	22935		${}^2P_{1/2}$	
[Dy(H ₂ dapthsh)Cl(H ₂ O) ₂]Cl ₂				$\beta = 0.9980$
	11013		${}^6F_{7/2}$	$b^{1/2} = 0.0316$
	12391		${}^6F_{5/2}$	$\delta\% = 0.2004$
	13192		${}^6F_{3/2}$	$\eta = 0.0015$

Table 4. Oscillator strength of Nd(III) complex.

Complex	Spectral range (cm^{-1})	S'JL'	Oscillator strength ($\text{p} \times 10^6$)
[Nd(H ₂ daphthsh)Cl(H ₂ O) ₂] ₂ Cl ₂	11655–11261	⁴ F _{3/2}	18.17
	12886–12330	⁴ F _{3/2} , ² H _{9/2}	47.83
	13947–13495	⁴ S _{3/2} , ⁴ F _{7/2}	35.88
	17730–16366	* ⁴ G _{5/2} , ² G _{7/2}	68.88

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

3.5 Emission spectra

The complex [Eu(H₂daphthsh)Cl(H₂O)₂]₂Cl₂ shows strong emission lines when excited with 350 nm radiation at 77 K. No lines were observed in the region of ⁵D₀ → ⁷F₀ transition showing that the complex does not have C_n, C_{nv} or C_s site symmetry²⁷. An emission line is observed at 594 nm corresponding to the transition ⁵D₀ → ⁷F₁ (magnetic dipole-allowed transition). This line is split into a doublet with energy separation of 114 cm^{-1} . A line due to the ⁵D₀ → ⁷F₂ transition (electric dipole-allowed transition) is observed at 630 nm. The ⁵D₀ → ⁷F₃ transition consists of a single broad line at 654 nm and that of ⁵D₀ → ⁷F₄ transition appears at 700 nm with a weak component at 690 nm, respectively. The split nature of the ⁵D₀ → ⁷F₁ transition is in agreement with D_{5h} site symmetry for the Eu(III) ion²⁸.

The emission lines in the Tb(III) complex are observed at 544, 592, and 616 nm corresponding to the ⁵D₄ → ⁷F₅, ⁵D₄ → ⁷F₄ and ⁵D₄ → ⁷F₃ transitions, respectively. In the spectrum the number of lines associated with the ⁵D₄ → ⁷F₄ and ⁵D₄ → ⁷F₃ transitions are rather small indicating high symmetry around seven coordinate cation²⁹.

Emission spectrum of Sm(III) complex shows the ⁴G_{5/2} → ⁶H_{7/2} as the most populated transition at 615 nm with two lines at lower wavelengths (600 and 608 nm). A very weak broad band at 562 nm appears in the region of ⁴G_{5/2} → ⁶H_{5/2} while the ⁴G_{5/2} → ⁶H_{9/2} transition consists of a broad component at 648 nm. These spectral features are characteristics of a high symmetry for the electrostatic field surrounding the Sm(III) ion³⁰.

4. Conclusion

Based on the above results and discussion it is concluded that the complexes have 1:1 metal-ligand stoichiometry and are monomeric in nature. The hydrazone is bonded to the metal ions in tetradentate fashion through the carbonyl oxygen, azomethine and pyridine nitrogen(s). 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. A D_{5h} site symmetry for the Eu(III) complex and a high symmetry for Tb(III) and Sm(III) complexes are inferred from their emission spectra. Single crystal could not be developed in spite of the continued efforts and hence single crystal analysis could not be drawn. Thus, a tentative structure for the complexes is shown in figure 3.

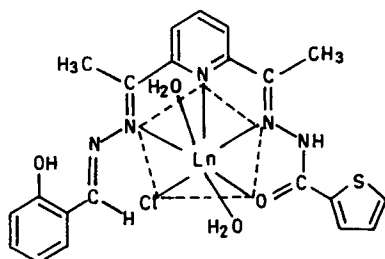


Figure 3. A tentative structure of $[\text{Ln}(\text{H}_2\text{daphsh})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$.

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