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SYNTHESIS, CHARECTERIZATION OF SCHIFF BASE 2-[(2, 6-DICHLORO-4-IODO-PHENYLIMINO)-METHYL]-4, 6-DIIODO-PHENOL AND ITS INNER TRANSITION METAL COMPLEXES

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ABSTRACT

A New Schiff base 2-[(2,6-Dichloro-4-iodo-phenylimino)-methyl]-4,6-diiodo-phenol has been synthesized from 4,6 diiodosalicilaldehyde and 2, 6 dichloro-4-iodoaniline Metal Complexes of Schiff base were prepared from chloride salt of La(III), Pr (III), Nd(III), Tb(III) , Sm(III).The complexes were electrolytic in DMSO. The Chemical structure of Schiff base ligand and its metal complexes were confirmed by various spectroscopic studies like I.R, UV-visible, ^{1}HNMR, elemental analysis, molar conductance, thermo gravimetric studies and magnetic susceptibility measurement. On basis of elemental and spectral studies six co-ordinate structures is proposed. In the light of these result suggested that this ligand act as neutral and bidentate and Co-ordinate to each metal atom by azomethine nitrogen and oxygen atom of hydroxyl group of diiodosalicylaldehyde. The TGA studies confirm the presence of water molecule in the lattice.

Keywords: 3,5-diiodosalicylaldehyde,4-iodo 2,6 dichloroaniline,Schiff base, Metal Complexes

INTRODUCTION

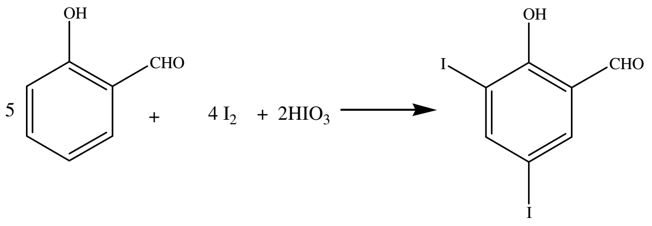
Compounds containing imine group (–CH=N–) known as Schiff base are usually prepared by condensing primary amines with active carbonyl compounds. They are versatile and flexible ligands forming mono and multinuclear transition metal complexes with interesting properties viz. reversible oxygen-binding ability and catalysis for several reactions.[1–4] Considerable attention has focused on the synthesis of new transition metal complexes of Schiff base ligands containing bulky and aromatic groups because of their role in the development of inorganic complexes owing to easy preparation and diversity of structures.[5–16] Moreover, their transition metal complexes have received considerable importance in chemistry and biology for wide spread applications.[5–10] During the recent years, considerable attention has been paid to the thermal behavior of transition metal Schiff base complexes containing substituted salicylaldehyde derivatives, which is one of the important properties of complexes indicating thermal stability and decomposition process under various conditions.[11–16] Lanthanides form a largest series of periodic table. It is 4f inner transition series. Lanthanide (III) ions, because of their size, are the best ions form stable complexes with high coordination number.[17,18] The number of Schiff base complexes of the lanthanide elements is similarly limited to a few reports.[19]

EXPERIMENTAL

All chemicals and solvents are used AR grade. All the metals were used as their chloride salts. UV spectra recorded on UV-vis spectrophotometer 119. Conductance or metal complex was determined in DMSO on conductivity meter quiptronics model NO-EQ665. Melting points were recorded on in recorded by open capillary method and are uncorreded. H^1-NMR spectra or a Schiff base and its metal complex recorded on Brukcer 300 MHz spectrometer in DMSO. Elemental analysis was carried out on Eager 350 analyzer. Magnetic measurement was done on solid complexes using Guoy method. Powder XRD pattern of complexes are recorded Philips Analytical XRD B.V. at CFC Shivaji University Kolhapur.

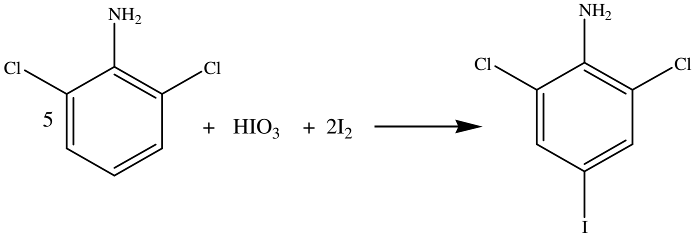
General procedure for iodination of 3,5 diiodosalicylaldehyde by iodine and iodic acid

To a mixture of Salicylaldehyde (0.05 mol) and iodine (0.04 mol) dissolved in ethanol (30 mL), iodic acid (0.02 mol) dissolved in water (2 mL) was added while stirring for 10 min. The reaction mixture was then stirred for 1.5 h at 35-40 ^{0}C. The solid product separates out on dilution with water (15-20mL). It was filtered, washed with saturated sodium thiosulphate solution to remove the excess of iodine, washed with cold water and crystallized from ethyl alcohol.



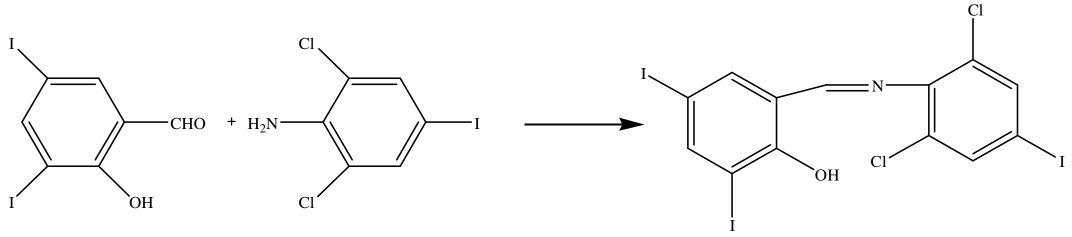
Scheme-1: Synthesis of 2,6 dichloro-4-iodoaniline

To a mixture of 2,6 dichloroaniline (0.05 mol) and iodine (0.02 mol) dissolved in ethanol (30 mL), iodic acid (0.01 mol) dissolved in water (2 mL) was added while stirring for 10 min. The reaction mixture was then stirred for 1.5 h at 35-40 ^{0}C. The solid product separates out on dilution with water (15-20mL). It was filtered, washed with saturated sodium thiosulphate solution to remove the excess of iodine, washed with cold water and crystallized from ethyl alcohol.



Scheme-2: Prepration of Ligand

The Ligand under investigation were performed by condensation of 0.01 M of 3,5-diiodosalicylaldehyde and 0.01 M of 2, 6 dichloro-4-iodoaniline in ethanol and reflux for 5-6 hr. under water condenser. Keep the reaction for overnight, yellow orange colored crystals ,washed it and dry in oven. The formation of Schiff base was monitored by TLC and its purity was checked by melting Point determination and elemental analysis.



Scheme-3: Prepration of Metal complexes

A genral method was used for the synthesis of metal complexes .These metal complexes were prepared by mixing warm ethanolic solution 0.05 mmol of metal salt La(III), Pr (III), Nd(III), Tb(III) , Sm(III) and warm ethanolic solution of ligand (1.0mmol) .The mixture were heated under reflux with continuous shaking for 4-5 hr. after heating add 1:1 alcholic ammonia till the pH 6.8-7.0 during which complex separate out ,filtered washed and dried in oven.

RESULTS AND DISCUSSION

I.R Spectra

The I.R Spectra provide valuable information regarding the nature of a functional group attached to metal atom. The important I.R frequencies exhibited by the Schiff base ligand and their corresponding ligand complex are tabulated in Table-1 .The ligand shows broad band at 3446 cm^{-1} due to phenolic hydroxyl group on free ligand which show shift in frequency in complex indicating co-ordination through metal atom .The Band in range 1616 cm^{-1} indicating the participation of azomethin group in complex formation .This Shift is also due to reduction of double bond character of C=N .The Schiff base ligand show a medium intensity band at 1282 cm^{-1} and 1348 cm^{-1} due to phenolic γ (C-O) is shifted to lower region indicating co-ordination through phenolic oxygen and oxygen γ(C-O) ligand are further evidenced by appearance in complex of non ligand band around 505 cm^{-1} and 449 cm^{-1} are due to M-O and M-N band respectively.

Electronic Spectra

The electronic spectra of Schiff base ligand and their complexes have been measured in DSMO solution between 200-800nm at room temperature. The spectral data of ligands and its complexes are tabulated in table 1.2 In the spectra of Schiff base ligand the absorption band observed at 272 nm were assigned to a benzene π-π^* transition and the band at 348 nm were assigned due to n-π^* transition associated with azomethine chromophore –(-C=N).The new bands observed near 426-427 nm can assigned to L-M charge transfer band . Colored complexes with metal ion that have a series of overlapping absorption band in the UV part of the spectrum as well as in visible part.

NMR Spectra

Room temperature ^{1}HNMR spectrum of ligand in benzene is presented .The ligand shows two singlet in region 13.28 which are assigned to –OH proton and peak at 7.91 has been assigned to –CH=N (imine Proton) .Spectrum of ligand shows other peak at 6.94,7.15,7.23 for aromatic protons. The signal at 7.91 observed in ligand of azomethine proton which is shifted downfield in spectra of corresponding Nd(III) complex to 12.4.-OH proton singlet at 13.28 is shifted to 15.36 in Nd complex.

Thermo gravimetric Analysis

Thermo gravimetric analysis (TGA and DSC) of metal complexes are used to- (i) get information about the thermal stability of new complexes, (ii) decide whether the water molecules are inside or outside the inner co-ordination sphere of the central metal ion and (iii) suggest a general scheme for thermal decomposition of chelates.

In the present investigation, heating rates were suitably controlled at 10°C min^{-1} under nitrogen atmosphere and the weight loss was measured from the ambient temperature upto 1000°C. The TGA data are presented in Table-5.

The TGA curve of the Pr(III) complexes Figure-1 showed a rapid first step decomposition around 110°C with 6.80 % mass loss (calculated 6.81%) indicating the loss of three lattice chloride molecules. The complex $[Pr(L)_2 2H_2O]Cl_3$ shows a weight loss of 11.68% at a temperature range 225°C which corresponds to the removal of two coordinate water molecule & four chlorine. A weight loss of 48.84% is observed in the temperature range 225 - 450°C which suggests the elimination of four iodine molecules, from 450-800°C loss of 24.82 % organic moiety In the Pr complex the amount of residue is 10.63 %.

The TGA curve of the Tb(III) complexes Figure-2 showed a rapid first step decomposition around 160°C with 3.64 % mass loss (calculated 3.85%) indicating the loss of two coordinated water molecules. The complex $[Tb(L)_1 2H_2O2Cl]Cl$ shows a weight loss of 10.65% at a temperature range 270°C which corresponds to the removal of two chlorine molecule & one lattice chloride molecules . A weight loss of

40.04% is observed in the temperature range 270 - 450°C which suggests the elimination of three iodide molecules. From $450-800^0$C which suggest elimination of two chloride molecules & Organic moiety In the Tb complex the amount of residue is 20.18 %.

The TGA curve of the Nd(III) complexes Figure-3 showed a rapid first step decomposition around 180°C with 2.37 % mass loss (calculated 2.34%) indicating the loss of two coordinated water molecules. The complex $[Nd(L)_2 2H_2O]Cl_3$ shows a weight loss of 6.74% at a temperature range 250°C which corresponds to the removal of three lattice chlorine molecule . A weight loss of 48.99% is observed in the temperature range 250-350°C which suggests the elimination of ic four iodine molecule. A weight loss of 8.94%from350-400 which suggest elimination of four chloride molecule. From 400-725 °C loss of 24.54 % organic moiety. In the Nd complex the amount of residue is 11.21 %.

Table-1 : I.R Spectra

Compound	-CH=N	C-O	M-O	M-N	O-H stre H_2O
$C_{13}NOH_{16}Cl_2I_3$(L)	1616	1282	----	----	----
$[La(L)_2 2H_2O]Cl_3$	1633	1209	505	449	3000-3600
$[Pr(L)_2 2H_2O]Cl_3$	1635	1209	507	445	3000-3600
$[Nd(L)_2 2H_2O]Cl_3$	1629	1209	507	437	3000-3600
$[Tb(L)_1 2H_2O2Cl]Cl$	1629	1211	511	418	3000-3600
$[Sm(L)_1 2H_2O2Cl]Cl$	1631	1209	507	424	3000-3600

Table-2 : Electronic Spectral Data

Compound	Electronic Spectral Data			Molar Conductor
	Π- Π*	n- Π*	L-M	
$C_{13}NOH_{16}Cl_2I_3$(L)	272	348	-------	--------
$[La(L)_2 2H_2O]Cl_3$	258	-------	426	117
$[Pr(L)_2 2H_2O]Cl_3$	258	-------	426	114
$[Nd(L)_2 2H_2O]Cl_3$	257	324	427	120
$[Tb(L)_1 2H_2O2Cl]Cl$	258	317	426	66
$[Sm(L)_1 2H_2O2Cl]Cl$	258	319	427	69

Table-3 : Analysis Data of Schiff base Ligand And Its Complexes

Compound	Molecular Formula	Molecular Weight	Color	Yield	M.P
$C_{13}NOH_{16}Cl_2I_3$(L)	$C_{13}NOH_{16}Cl_2I_3$	643	Orange	70 %	220 ^{0}C
$[La(L)_2 2H_2O]Cl_3$	$C_{26}H_{16}Cl_7I_6LaN_2O_4$	1568.92	Faint Yellow	65 %	>300 ^{0}C
$[Pr(L)_2 2H_2O]Cl_3$	$C_{26}H_{16}Cl_7I_6PrN_2O_4$	1569.4	Dull Yellow	60 %	>300 ^{0}C
$[Nd(L)_2 2H_2O]Cl_3$	$C_{26}H_{16}Cl_7I_6N_2NdO_4$	1574.25	Grey	50 %	>300 ^{0}C
$[Tb(L)_1 2H_2O2Cl]Cl$	$C_{13}H_{10}Cl_5I_3NO_3Tb$	945.13	Off white	55 %	>300 ^{0}C
$[Sm(L)_1 2H_2O2Cl]Cl$	$C_{13}H_{10}Cl_5I_3NO_3Sm$	936.56	Cream	55 %	>300 ^{0}C

Table-4 : Elemental Analysis of Ligand and Complexes

Complex	Elemental Analysis ,Found (calculated) %						
	% C	% H	% Cl	% I	% M	% N	% O
Ligand	21.27 (21.25)	1.10 (1.12)	9.66 (9.63)	51.87 (51.90)	9.83 (9.81)	1.91 (1.94)	4.36 (4.35)
La	19.90 (19.92)	1.03 (1.01)	15.82 (15.84)	48.53 (48.51)	8.85 (8.82)	1.79 (1.82)	4.08 (4.09)
Nd	19.84 (19.86)	1.02 (1.00)	15.76 (15.74)	48.37 (48.39)	9.60 (9.58)	1.78 (1.80)	4.07 (4.06)
Pr	19.88 (19.86)	1.09 (1.11)	15.83 (15.85)	48.55 (48.53)	9.09 (9.10)	1.78 (1.76)	4.07 (4.08)
Tb	16.52 (16.50)	1.07 (1.09)	18.76 (18.78)	40.28 (40.26)	16.82 (16.80)	1.48 (1.46)	5.08 (5.09)

Sm	16.67 (16.65)	1.08 (1.10)	18.93 (18.91)	40.65 (40.67)	16.05 (16.07)	1.50 (1.52)	5.12 (5.11)

Table-5 : Thermal Analysis data for metal complexes

Complex	Decomposition Temp°C	Lost fragment	Weight loss %	
			Experimental	Theoretical
$[Pr(L)_2 2H_2O]Cl_3$	110	three lattice chloride molecules	6.80	6.81
	110-225	two coordinate water molecule & four chlorine	11.68	11.48
	225-450	Four iodine	48.84	49.19
	450-800	Organic moiety	24.82	24.78
	800-1000	Metal oxide	10.63	10.67
$[Tb(L)_1 2H_2O2Cl]Cl$	160	two coordinated Water molecules	3.64	3.85
	160-270	two chlorine molecule & one lattice chloride molecules	10.65	11.39
	270-450	three iodide molecules	40.04	40.77
	450-800	two chloride molecules & Organic moiety	28.34	28.53
	800-1000	Metal oxide	20.18	19.57
$[Nd(L)_2 2H_2O]Cl_3$	180	coordinated two water molecules	2.37	2.34
	180-250	three lattice chlorine	6.74	6.80
	250-350	four iodine	48.99	49.01
	350-400	four chlorine	8.94	9.01
	400-725	Organic moiety	24.54	24.73
	725-1000	Metal oxide	11.21	10.80

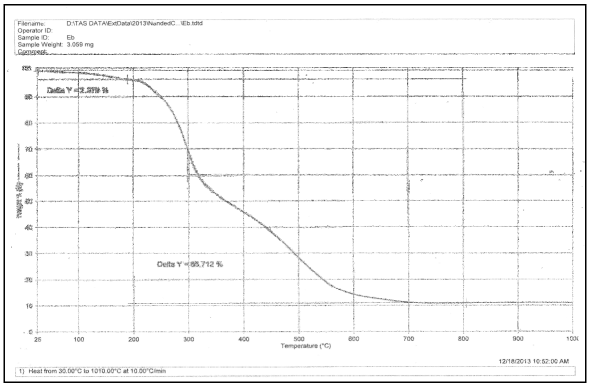


Fig.-1: $[Nd(L)_2 2H_2O]Cl_3$

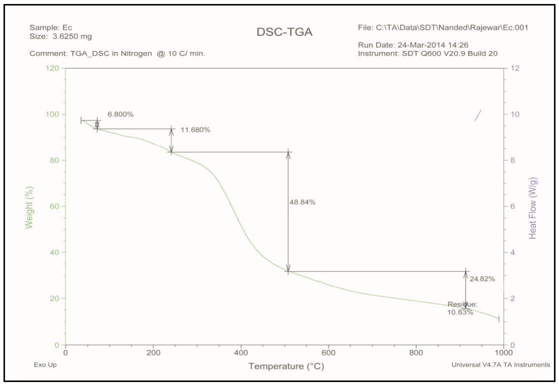


Fig.-2: $[Pr(L)_2 2H_2O]Cl_3$

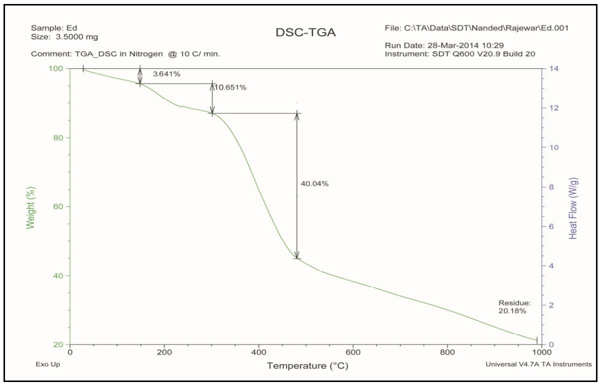


Fig.-3: $[Tb (L)_1 2H_2O2Cl] Cl$

X-ray diffraction study

The X-ray diffractgram of a representative metal complex of Nd (III) was scanned in the range 5-100^o at wavelength 1.54 Å (Figure-4, Table-6). The diffractogram and associated data depict 2θ values for each peak, relative intensity and inter planar spacing (d-values). The diffractogram of Nd (III) complex showed ten reflections with maxima at 2θ (21.03885) corresponding to d value 2.14551Å. The X-ray diffraction pattern of the complex with respect to major peaks having relative intensity greater than 10% have been indexed by using computer programme [20]. The above indexing method also yields Miller indices (h, k, l), unit cell parameters and volume. The unit cell of Nd (III) complex yielded values of lattice constants, a= 15.04501 A^0 b=12.43458A^0 c= 5.22645 A^0 and unit cell volume, V = 165.39 (Å)^3. In concurrence with these cell parameters of Nd (III) complex, the condition such as $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^o$ required for the compounds to be Orthorhombic were tested and found to be satisfactory. The above values indicate that the metal complex has orthorhombic crystal system.

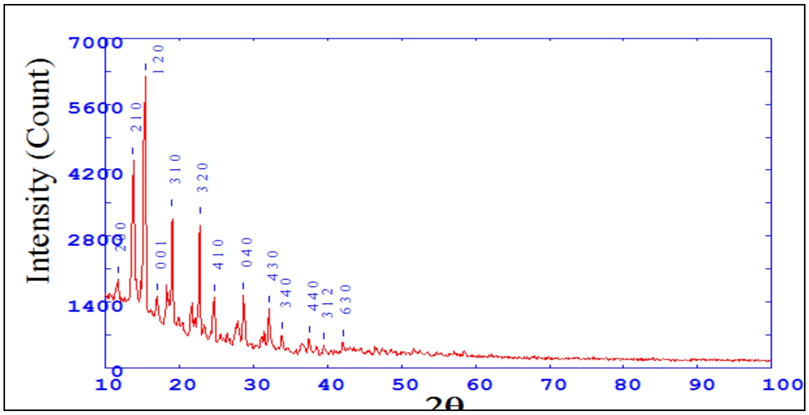


Fig.-4: $[Nd(L)_2 2H_2O]Cl_3$
Crystal system: Lattice Type: Orthorhombic
Lattice Parameter: a= 15.04501 b= 12.43458 c= 5.22645 A^0
Lattice Parameter: Alpha= 90.000 Beta=90.000 Gama=90.000

Table-6

h k l			2θ (cal)	2θ (Obs)	d(cal)	d (obs)
2	0	0	5.87601	5.84714	7.52421	7.55903
2	1	0	6.87286	6.89494	6.43705	6.41496
1	2	0	7.70534	7.69414	5.74513	5.75218
0	0	1	8.48063	8.49618	5.22325	5.21272
3	1	0	9.53171	9.52786	4.65175	4.65278
3	2	0	11.38082	11.38263	3.90362	3.90243
4	1	0	12.35230	12.34982	3.60084	3.60106
0	4	0	14.35005	14.35279	3.10798	3.10704
4	3	0	16.05403	16.05632	2.78545	2.78478
3	4	0	16.95159	16.92578	2.64196	2.64561
4	4	0	18.75259	18.76922	2.39609	2.39383
3	1	2	19.77063	19.75951	2.27727	2.27831
6	3	0	21.03877	21.03885	2.14568	2.14551

The X-ray diffractgram of a representative metal complex of Pr (III) was scanned in the range 5-100^o at wavelength 1.54 Å (Figure-5, Table- 7). The diffract gram and associated data depict 2θ values for each peak, relative intensity and inter planar spacing (d-values). The diffractogram of Pr (III) complex showed ten reflections with maxima at 2θ (38.33803) corresponding to d value 1.24175Å. The X-ray diffraction pattern of the complex with respect to major peaks having relative intensity greater than 10% have been indexed by using computer programme[20]. The above indexing method also yields Miller indices (hkl), unit cell parameters and volume. The unit cell of Pr (III) complex yielded values of lattice constants, a= 16.28383A^0 b= 8.60044A^0 c= 3.80777 A^0 and unit cell volume, V = 165.39 (Å)^3. In concurrence with these cell parameters of Pr (III) complex, the condition such as $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^o$ required for the compounds to be Orthorhombic were tested and found to be satisfactory. The above values indicate that the metal complex has orthorhombic crystal system.

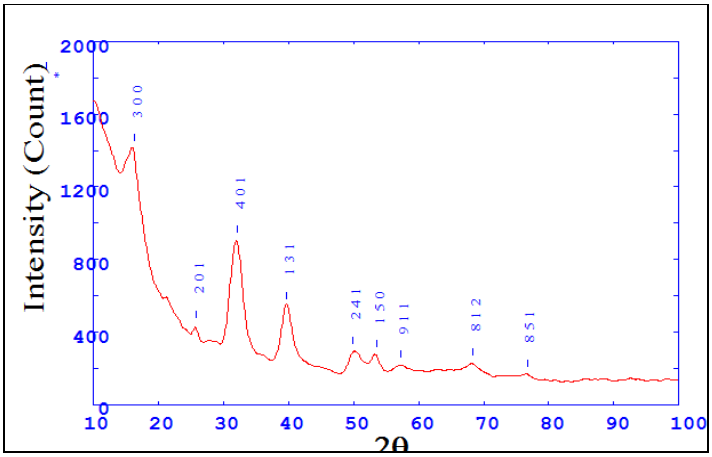
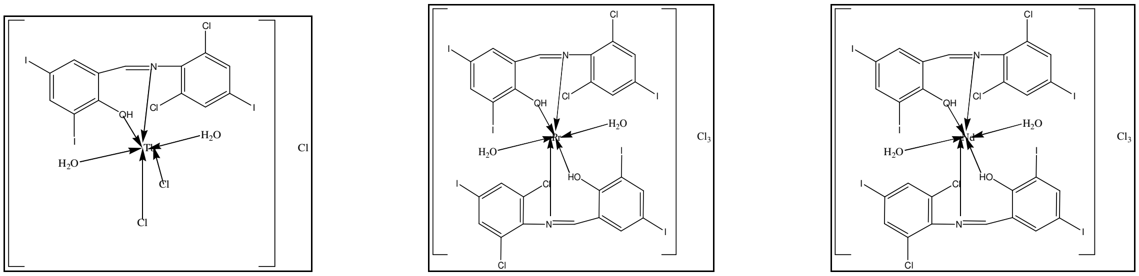


Fig.-5: $[Pr(L)_2 2H_2O]Cl_3$
Crystal system: Lattice Type: Orthorhombic
Lattice Parameter: a= 16.28383 b= 8.60044 c= 3.80777 A^0
Lattice Parameter: Alpha= 90.000 Beta= 90.000 Gama= 90.000

Table-7

h k l	2θ (cal)	2θ (Obs)	d(cal)	d (obs)
0 3 0	8.15849	8.15317	5.42801	5.42999
2 0 1	12.90672	12.90669	3.44862	3.44801
4 0 1	16.08281	16.07570	2.78060	2.78140
1 3 1	19.85899	19.87852	2.26754	2.26515
2 4 1	24.97604	24.94894	1.82432	1.82601
1 5 0	26.76890	26.77113	1.71028	1.71001
9 1 1	28.67291	28.67254	1.60543	1.60533
8 1 2	34.14215	34.13909	1.37248	1.37250
8 5 1	38.33778	38.33803	1.24182	1.24175



$[Tb(L)_1 2H_2O2Cl]Cl$ $[Pr(L)_2 2H_2O]Cl_3$ $[Nd(L)_2 2H_2O]Cl_3$

Fig.-6: Based on above result probable structure have been proposed.

CONCLUSION

Synthesis of Schiff base (DPMDI) and analysis of various physical, chemical and spectral parameters is given. High decomposition points of the complexes suggest good thermal stability at normal conditions. Molar conductivities of the complexes in DMSO suggest that La (III), Pr (III), Nd (III), Tb (III) and Sm (III) complexes are electrolytic in nature .Electronic spectra and molar absorptivity values of the chelates are supportive evidences to charge transfer band (LMCT). ^{1}H NMR spectra supports involvement of azomethine, phenolic oxygen in coordination and presence of coordinated water molecule in Lanthanum complex. Thermal studies also support presence of coordinated water molecule in Lanthanum complex .Powder XRD results indicate that Pr(III) and Nd(III) complexes are orthorhombic with P-type.

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