



Synthesis and Spectral Characterization of Lanthanide Complexes Derived from 2-[(4-bromo-2,6-dichlorophenylimino)-methyl]-4,6-diiodo-phenol

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ABSTRACT

The solid complexes of La(III), Pr (III), Tb(III) ,Sm(III) and Nd(III) were prepared from bidentate Schiff base, 2-[(4-bromo-2,6-dichloro-phenylimino)-methyl]-4,6-diiodo-phenol. The Schiff base ligand was synthesized from 3,5 diiodosalicylaldehyde and 4-bromo-2,6-dichlorobenzeneamine. These metal complexes were characterized by molar conductivity, magnetic susceptibility, thermal analysis, X-ray diffraction, FTIR, ¹H-NMR and UV-Vis. The analytical data of these metal complexes showed metal:ligand ratio of 1:2 La(III), Pr (III), Tb(III) ,Sm(III) and 1:1 for Nd(III) complexes. The physico-chemical study supports the presence of octahedral geometry around La(III), Pr (III), Tb(III) ,Sm(III) and Nd(III) ions. The IR spectral data reveal that the ligand behaves as bidentate with ON donor atom sequence towards central metal ion. The molar conductance values of metal complexes suggest their electrolyte nature except Nd(III) complex. The X-ray diffraction data suggest monoclinic crystal system for Pr (III), Nd (III) complexes. Thermal behavior (TG/DTA) shows breakdown of complexes.

Key words: Bidentate Schiff base, Metal complexes, Thermal analysis. XRD,

INTRODUCTION

Schiff bases derived from aromatic amines and aldehydes have a wide variety and an important class of ligands in coordination chemistry and find extensive applications in different fields, e.g., biological, inorganic and analytical chemistry^{1,2}. Many biologically important Schiff bases have been reported in the literature possessing, antimicrobial, antibacterial, antifungal, anti-inflammatory,

antitumor and anti HIV activities^{3,4}. Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions⁵.

The interaction of these donors ligands and metal ions give complexes of different geometries and these complexes are potentially biologically active⁶. Several research papers reported the synthesis and characterization of

transition metal complexes of Schiff bases derived from salicylaldehyde^{7,8}.

Metal complexes with Schiff base ligands containing salicylaldehyde and its derivatives; have been extensively studied. Metal complexes with such ligands are quite common and also reflect their facile synthesis, accessibility of diverse structural modifications and wide applications in different fields, such as catalysis, biological systems and material chemistry^{9, 10}.

Transition metal complexes with Schiff base as ligand have been amongst the widely studied co-ordination compounds in the past few years, since they are found to be widely applicable in many fields such as biochemical, analytical and antimicrobial fields¹¹⁻¹⁵. It is well known from the literature that much work have been done on the synthesis and characterization of this compounds¹⁶⁻¹⁸ with Schiff base ligand formed from salicylaldehyde or substituted salicylaldehyde and various aromatic amines¹⁹⁻²³.

Salicylaldehyde is called 2-hydroxybenzaldehyde and ortho-hydroxy benzaldehyde and is an organic compound with the formula $C_7H_6O_2$. Part of the class hydroxy aromatic aldehydes, aromatic nucleus contains two functional groups: a hydroxyl and aldehyde one. This colorless liquid has a bitter almond odor at higher concentrations The natural oils found in *Spiraea* [*Filipendula (Spiraea) ulmaria (Rosaceae)*].

Sweet-smelling flowers containing salicylaldehyde and methyl salicylate, glycosides form. Was also identified as a component of the characteristic flavor of buckwheat.²⁴ Salicylaldehyde is used as an important intermediate in the chemical industry, in medicine. It is used in perfume, fragrances, dyes, pharmaceuticals, etc.²⁵ Salicylaldehyde and its derivatives can be used as

preservatives in cosmetic products,²⁶ fragrances, essential oils in various biological applications.²⁷ Also get in formulation of perfumes and fragrances. Salicylic aldehyde is an important intermediate in the manufacture of herbicides and pesticides.²⁸ Also, salicylaldehyde and its derivatives are used for various reactions for the production of polymers and fibers.

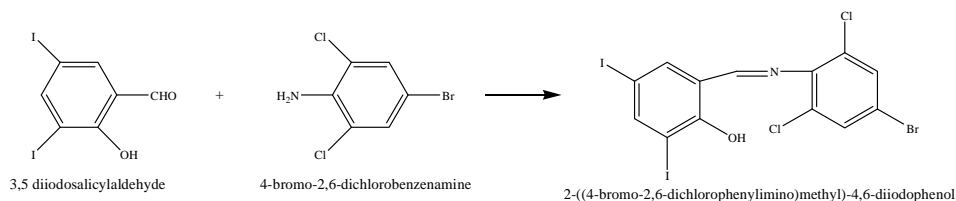
EXPERIMENTAL

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 uncorrected. H^1 -NMR spectra or a Schiff base and its metal complex recorded on Bruker 300 MHz spectrometer in DMSO. Elemental analysis was carried out on Eager 350 analyser. Magnetic measurement were done on solid complexes using Guoy method. Powder XRD pattern of complexes are recorded Philips Analytical XRD B.V. at CFC Shivaji University Kolhapur.

Synthesis of ligand

Synthesis of 2-[(4-Bromo-2,6-Dichloro-Phenylimino)-Methyl]-4,6-Diiodo-Phenol (BDPDP) Schiff base

Schiff base ligand were synthesized by refluxing of 3,5 diiodosalicylaldehyde (0.01M) and 4-bromo-2,6-dichlorobenzeneamine (0.01 M) in 50ml ethanol on water bath for 4-5 hours in presence of 2-3 drops of glacial acetic acid. The reaction mixture was kept for overnight, where yellow color precipitate was obtained. It was filtered by whatmann paper, washed with distilled water then alcohol, dried in vacuum dessicator. Pure Schiff base was recrystallized from ethanol. The purity of ligand was checked by TLC.



Synthesis of metal Complexes

The ethanolic solution of Metal chloride (0.01M) was added to hot ethanolic solution of BDPDP (0.02 M) La(III), Pr (III), Tb(III) ,Sm(III) and (0.01 M) in Nd(III) complexes drop wise with constant stirring. PH of the reaction mixture was adjusted to 7 -7.2 with alcoholic ammonia solution. Resulting reaction mixture refluxed for 5 to 6 hours on water bath.

Colored complexes was allowed to digest and collected by filtration. Then washed with sufficient quantity of distilled water and little hot

ethanol to apparent dryness and dried in vacuum desiccators.

RESULTS AND DISCUSSION**Physical and analytical parameters**

Empirical formulae of the complexes were deduced on the basis of elemental analysis, metal ligand ratio and thermal analysis (table No. 1.1 and 1.2). Complexes possess different colors, metal complexes of ligand BDPDP are insoluble in common organic solvents, dissolve freely in DMSO/DMF High melting points of complexes suggest that

Table 1: Physical and analytical data of BDPDP metal complexes

Compound	F.W.	Yield	M.L ratio	M.P. decom. Temp °C	Color	Molar Conductance W ⁻¹ cm ² mol ⁻¹	%of Cl cal. (obs)	Magnetic Moment
BDPDP(L)	596.81	67 %	-	190°C	Yellow	-	-	-
[La(L) ₂ 2H ₂ O]Cl	1404.01	58 %	1:2	>270 °C	Muddy Yellow	66	12.63 (12.59)	Dimagnetc
[Pr(L) ₂ 2H ₂ O]Cl	1408.03	62 %	1:2	>270 °C	Brown	71	12.59 (12.57)	Paramagnetic
[Nd(L) ₁ 2H ₂ O2Cl]	847.99	58 %	1:1	>270 °C	Grey	14	16.72 (16.74)	Paramagnetic
[Tb(L) ₂ 2H ₂ O]Cl	1426.05	51 %	1:2	>270 °C	Dark Yellow	78	12.43 (12.41)	Paramagnetic
[Sm(L) ₂ 2H ₂ O]Cl	1412.33	61 %	1:2	>270 °C	Faint Yellow	64	12.52 (12.48)	Paramagnetic

Table 2: Percent C, H, N,O and metal ion in BDPDP metal complexes

Compound	Empirical Formula	%C obs (calcd.)	%H obs (calcd.)	%N obs (calcd.)	%O obs (calcd.)	% I obs (calcd.)	% Br obs (calcd.)	%M obs (calcd.)
BDPDP(L)	C ₁₃ H ₆ BrCl ₂ I ₂ NO	26.16 (26.12)	1.01 (0.92)	2.35 (2.24)	2.68 (2.46)	42.53 (42.42)	13.39 (13.12)	-
[La(L) ₂ 2H ₂ O]Cl	C ₂₆ H ₁₆ Br ₂ Cl ₅ I ₄ LaN ₂ O ₄	22.24 (22.14)	1.15 (1.11)	2.00 (1.98)	4.56 (4.31)	36.15 (36.23)	11.38 (11.23)	9.89 (9.78)
[Pr(L) ₂ 2H ₂ O]Cl	C ₂₆ H ₁₈ Br ₂ Cl ₅ I ₄ N ₂ O ₄ Pr	22.18 (22.09)	1.29 (1.14)	4.55 (4.34)	4.55 (4.43)	36.05 (35.95)	11.35 (11.27)	10.01 (9.67)
[Nd(L) ₁ 2H ₂ O2Cl]	C ₁₃ H ₁₀ BrCl ₄ I ₂ NNdO ₃	18.41 (18.31)	1.19 (1.04)	1.65 (1.45)	5.66 (5.45)	29.93 (29.84)	9.42 (9.31)	17.01 (16.47)
[Tb(L) ₂ 2H ₂ O]Cl	C ₂₆ H ₁₈ Br ₂ Cl ₅ I ₄ N ₂ O ₄ Tb	21.90 (21.87)	1.27 (1.16)	1.96 (1.89)	4.49 (4.38)	35.60 (35.49)	11.21 (11.14)	11.14 (11.03)
[Sm(L) ₂ 2H ₂ O]Cl	C ₂₆ H ₁₆ Br ₂ Cl ₅ I ₄ N ₂ O ₄ Sm	22.06 (21.89)	1.14 (1.08)	1.98 (1.78)	4.52 (4.43)	35.86 (35.73)	11.29 (11.18)	10.62 (10.54)

Table 1.3: Electronic spectral data of BDPDP complexes

Ligand / Complex	Absorbance nm	n/cm ⁻¹	Transition
BDPDP(L)	293	34160	$\pi - \pi^*$
[La(L) ₂ 2H ₂ O]Cl ₃	261	38314	$\pi - \pi^*$
	431	23201	LMCT
[Pr(L) ₂ 2H ₂ O]Cl	261	38314	$\pi - \pi^*$
	431	23201	LMCT
[Nd(L) ₁ 2H ₂ O2Cl]	259	38610	$\pi - \pi^*$
	431	23201	LMCT
[Tb(L) ₂ 2H ₂ O]Cl	261	38314	$\pi - \pi^*$
	429	23310	LMCT
[Sm(L) ₂ 2H ₂ O]Cl	261	38314	$\pi - \pi^*$
	429	23310	LMCT

Table 4: Infrared spectral data of the ligand (DPMDI) and their La(III), Pr (III), Nd(III), Tb(III) and Sm(III) metal complexes

Compound	$\nu(\text{CH}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{H}_2\text{O})$ Rocking	$\nu(\text{H}_2\text{O})$	$\nu(\text{OH})$
BDPDP(L)	1616	1204	-	-	-	-	3447
[La(L) ₂ 2H ₂ O]Cl	1596	1212	520	432	853	3134	-
[Pr(L) ₂ 2H ₂ O]Cl	1627	1209	505	432	860	3477	-
[Nd(L) ₁ 2H ₂ O2Cl]	1629	1211	507	435	869	3448	-
[Tb(L) ₂ 2H ₂ O]Cl	1627	1211	507	441	889	3437	-
[Sm(L) ₂ 2H ₂ O]Cl	1631	1211	509	435	867	3473	-

Table 5: Thermal Analysis data for metal complexes

Complex	Decomposition Temp °C	Lost fragment	Weight loss %	
			Experimental	Theoretical
[Tb(L) ₂ 2H ₂ O]Cl	140 °C	two coordinate water molecule	2.44	2.56
	140-280 °C	one lattice chlorine	2.42	2.53
	280-310 °C	Four iodine	38.04	36.22
	310-600 °C	Four chlorine two bromine	18.16	21.53
	600-800 °C	Organic moiety	28.12	27.23
	800-1000 °C	Metal oxide	12.44	13.04
[Pr(L) ₂ 2H ₂ O]Cl	160 °C	two coordinated Water molecules	2.32	2.60
	160-390 °C	one lattice chloride molecules four iodine, four chloride, two bromine	61.32	61.02
	390-800 °C	Organic Moiety	27.68	26.64
	800-1000 °C	Metal oxide	11.87	11.91
[Nd(L) ₁ 2H ₂ O2Cl]	160 °C	coordinated two water molecules	4.25	4.30
	160-430 °C	Two iodine, One bromine	36.71	39.89
	430-800 °C	four chlorine, Organic moiety	33.64	32.60
	800-1000 °C	Metal oxide	19.58	20.09

complexes are stable at normal temperatures²⁹. Molar conductivity ($1m$ 71 to $82 W^{-1}cm^2mol^{-1}$) reveals electrolytic nature of the complexes³⁰ except Neodymium metal ion complex ($1m$ $14W^{-1}cm^2mol^{-1}$) reveals nonelectrolytic nature of the complex.(table 1.1).

Electronic spectra

Plots of UV-Visible spectra of ligand BDPDP and its metal complexes were recorded on UV-Visible spectrophotometer 119-Pc based instrument are presented in figure 6.1, 6.2, 6.3 , 6.4,6.5 and 6.6. Ligand (BDPDP) shows strong absorption band at $34160cm^{-1}$ assigned for $p - p^*$ transition. Absorption bands and corresponding transition are given in the table No. 1.3.

The UV electronic spectra of La(III), Pr (III), Nd(III), Tb(III) and Sm(III)complexes have indicates absorption bands at $23201cm^{-1}$, $23201cm^{-1}$, $23201cm^{-1}$, $23310cm^{-1}$ and $23310cm^{-1}$ assigned as charge transfer^{31,32}.

Infrared spectra

Determination of coordinating atoms in the complex is made on the basis of comparison of IR spectra of the ligand and their metal complexes.

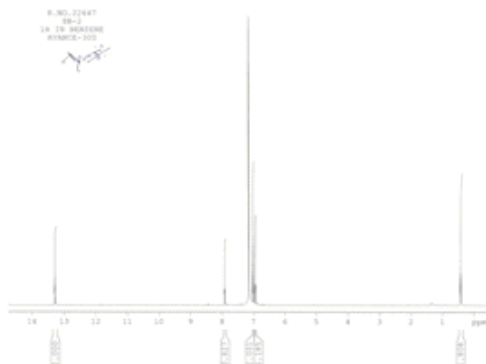


Fig. 1: ¹H NMR ligand BDPDP

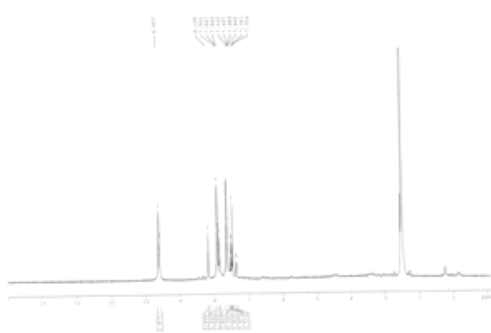


Fig. 2: ¹H NMR Metal complex

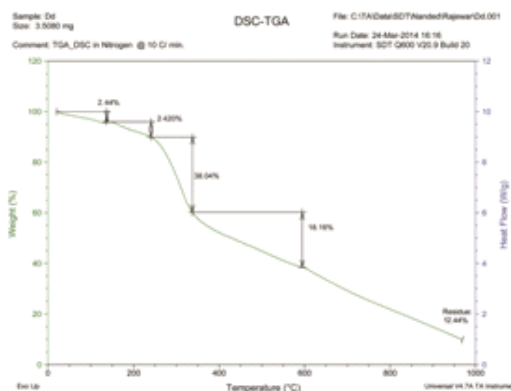


Fig. 3: TG/DSC [Tb(L)₂·2H₂O]Cl

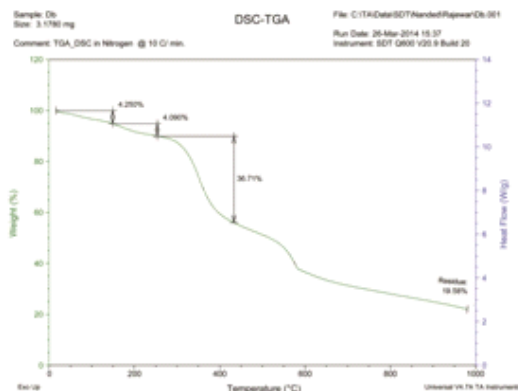


Fig. 4: TG/DSC [Nd(L)₁·2H₂O2Cl]

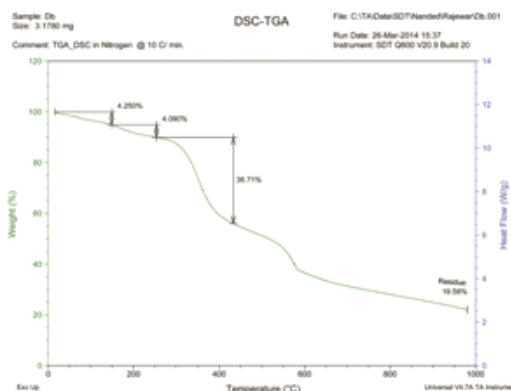


Fig. 5: TG/DSC [Pr(L)₂·2H₂O]Cl

Significant changes in wave numbers of the coordinating atoms involved in coordination are summarized in the table No. 1.4.

IR spectral study of BDPDP Ligand

Ligand BDPDP contains phenolic -OH and azomethine group. In spectra of ligand exhibits strong ν (O-H) stretching at 3447 cm^{-1} , corresponding to n (OH) of phenol. The band at 1204 cm^{-1} is due to presence of ν (C-O) group. It also indicate ν (C=N) stretching frequency at 1616 cm^{-1} . On complexation significant changes in wave numbers are observed.

IR spectral study of La(III) complex

The IR spectra of Metal complexes is compared with IR spectra of ligand (BDPDP), there are certain shifts in the bands. In complex deprotonation of -OH in phenolic group and indicating involvement of phenolic group in coordination³³. The band stretching vibration in ligand due to phenolic n (OH) group observed at 3447 cm^{-1} , Which is disappear in complex.

Besides, ligand exhibits stretching of ν (C=N) stretching at 1616 cm^{-1} which on complexation shifted to lower wave number at $1596\text{-}1631\text{ cm}^{-1}$ suggesting that azomethine nitrogen are involved in coordination³⁴⁻³⁵. A new broad band at $3134\text{-}3477\text{ cm}^{-1}$ suggested the presence of coordinated water molecule³⁶.

The appearance of new bands in the spectra of metal ion complex at $432\text{-}441\text{ cm}^{-1}$ and $505\text{-}520\text{ cm}^{-1}$ due to new bonding i.e. ν (M-N) and ν (M-O)^{37,38}.

Thus the ligand BDPDP exhibits uninegative bidentate behaviour and coordinates to the metal ion through azomethine nitrogen and phenoxide oxygen for La(III), Pr (III), Tb(III) and Sm(III) complexes, Nd(III) complex behave neutral in nature.

¹H NMR Spectra

¹H NMR spectral studies of ligand BDPDP indicated signals at δ 6.9- 7.2 ppm corresponding to aromatic protons (m, 4H, Ar-H) and at δ 7.9 ppm due to azomethine group (CH=N). A strong signal at δ 13.3 ppm assignable (S, 1H) due to phenolic

OH group (fig. 1.1).

In the metal complex signal corresponding to phenolic OH group at δ 13.3 ppm has disappeared³⁹⁻⁴¹ (fig.1.2) may be attributed to deprotonation of -OH group on involvement of ν (O-H) in bonding. A new peak due to presence of coordinated water at δ 2.5 ppm is observed in metal complex⁴². The shift in azomethine group from δ 7.9 ppm to δ 9.6 ppm indicate coordination through water molecule azomethine group.

Thus, BDPDP molecule seems to be coordinated to the metal through phenoxide oxygen and azomethine group in Pr (III) metal complex.

Thermal study

Nd(III), Pr(III) and Tb(III) complexes were studied by thermogravimetric analysis from ambient temperature to 1000°C in nitrogen atmosphere. The range of temperature, experimental and calculated mass losses of the decomposition reaction are given in the table No. 1.5. TGA/DSC scans are depicted in figures 1.3, 1.4 and 1.5.

Thermal study of [Tb(L)₂2H₂O]Cl

The thermogram of Tb(III) complex shows weight loss 2.44% corresponding to two coordinated water molecule in the range from room temperature to 140°C . Decomposition reaction corresponds to an experimental mass 2.42 % occurs in the temperature range 140°C - 280°C attributed loss of one lattice chlorine⁴³ part of the complex.

In the temperature range 280°C - 310°C Four iodine part is lost and this loss corresponds to 38.04%. As the temperature increases to $310\text{-}600^\circ\text{C}$ there is of 18.16 % indicating loss of four chloride, two bromine, part of metal complex. From $600\text{-}800^\circ\text{C}$ loss of organic moiety which is 28.12 %. Finally 800°C - 1000°C residue is obtained corresponding to Tb₂O₃ as stable residue⁴⁴ 12.44%.

Thermal study of [Pr(L)₂2H₂O]Cl

The TGA of Pr(III) complex indicates loss in weight in the range from room temperature to 160°C corresponding to 2.32 % indicates the loss of coordinated water-molecule.

Decomposition beyond this temperature in the range 160°C -390°C corresponds to mass loss of 61.32 % in the TG curve assigned to expulsion of one lattice chloride molecules four iodine, four chloride , two bromine part of the complex. The decomposition occurs in the temperature 390°C - 800°C indicates the loss of Organic Moiety 27.68 %. Further at 800°C-1000°C losses of 11.87 % were occurs indicating presence of thermally stable residual metal oxide⁴⁵.

Thermal study of [Nd(L)₁2H₂O2Cl]

TGA of Nd (III) complex shows weight loss corresponding to mass loss 4.25 %. This loss corresponds to loss of coordinated water molecule in the range from room temperature to 160°C⁴⁶. Further decomposition at 160°C-430°C loss of 36.71 % was occurs indicating loss of Two iodine, One bromine of the complex. From 430-800°C loss

of four chlorine , Organic moiety which is 33.64 %.The end product of decomposition is formation of Nd₂O₃ weight corresponds to 19.58 percent which is equal to theoretical value 20.09.

Powder x-ray studies

X-ray diffractograms of the metal complexes were recorded in the 2θ range from 10- 90° at a wave length of 1.5405 Å and using Cu Kα radiation source. Results of miller indices, lattice parameters and unit cell volume are computed from programmer. Data has been summarized in the following tables.

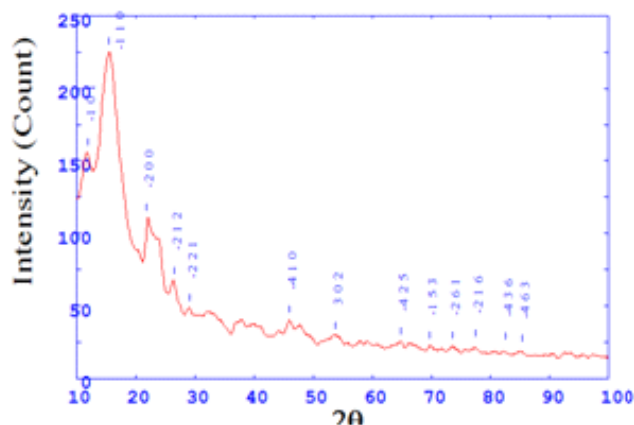
[Nd(L)₁2H₂O2Cl]

Crystal system: **Monoclinic** Lattice Type: **P**

Lattice Parameter: a= 9.53034 b= 8.00951 c= 7.79302 Å

Lattice Parameter: Alpha= 90.000 Beta= 121.572 Gama=90.000

h	k	l	θ (cal)	θ (Obs)	d(cal)	d (obs)
-1	0	1	6.00366	6.01408	7.36480	7.34506
-1	1	0	7.76464	7.75704	5.70152	5.70286
-2	0	0	10.94017	10.92606	4.05882	4.06188
-2	1	2	13.31070	13.30282	3.34576	3.34628
-2	2	1	14.58616	14.57042	3.05874	3.06078
-4	1	0	23.05168	23.04753	1.96725	1.96712
3	0	2	26.85357	26.85035	1.70529	1.70514
-4	2	5	32.39762	32.39613	1.43768	1.43751
-1	5	3	34.86598	34.85211	1.34748	1.34775
-2	6	1	36.83277	36.83274	1.28494	1.28477
-2	1	6	38.73699	38.73415	1.23101	1.23093
-4	3	6	41.28170	41.26937	1.16754	1.16769
-4	6	3	42.69762	42.69542	1.13592	1.13584



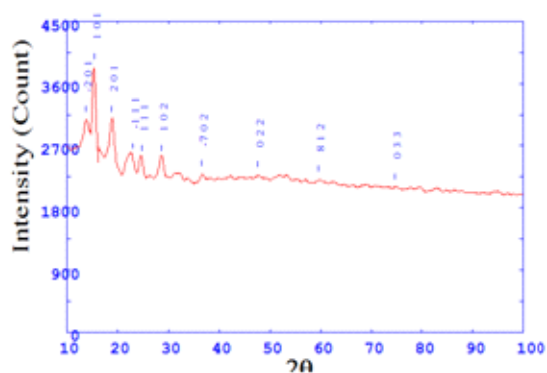
The cell data and crystal parameters of [Nd(L)₂H₂O₂Cl] complex is given in the tables indicates that complex have monoclinic crystal system⁴⁷, with lattice type-P.
[Pr(L)₂2H₂O]Cl

7.04556 Å⁰
Lattice Parameter: Alpha= 90.000 Beta= 108.476
Gama=90.000

Crystal system: **Monoclinic** Lattice Type: **P**
Lattice Parameter: a= 19.06907 b= 4.64343 c=

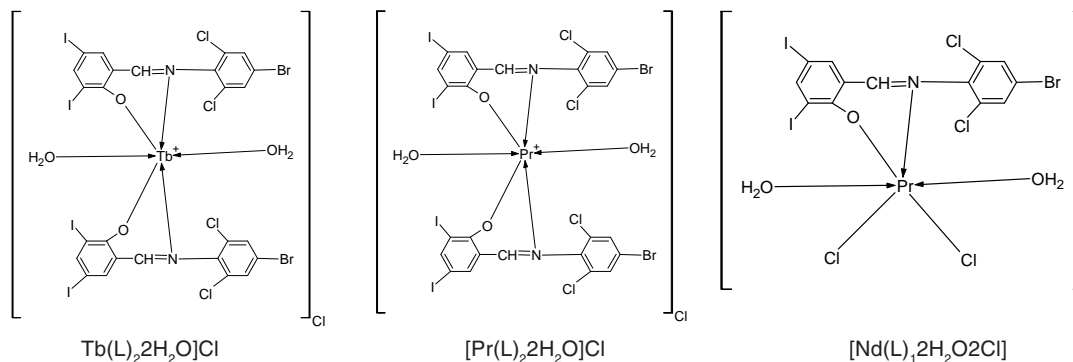
Cell data and crystal lattice parameters of [Pr(L)₂2H₂O]Cl complex attributed to monoclinic crystal system⁴⁸, with lattice type-P.

h	k	l	θ, (cal)	θ (Obs)	d(cal)	d (obs)
-2	0	1	6.87288	6.88556	1.27114	6.43274
1	0	1	7.75612	7.75704	5.70775	5.71298
2	0	1	9.41625	9.42077	4.70827	4.71002
-1	1	1	11.46505	11.48063	3.87533	3.87282
1	1	1	12.34822	12.35211	3.60201	3.60321
1	0	2	14.32149	14.33275	3.11405	3.11337
-7	0	2	18.28842	18.29401	2.45474	2.45506
0	2	2	23.82950	23.83979	1.90660	1.90644
8	1	2	29.77117	29.78169	1.55134	1.55123
0	3	3	37.30260	37.30810	1.27107	1.27114



Proposed structures of the chelates

Based on above result probable structure have been proposed



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