INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES

(p-ISSN: 2348-5213: e-ISSN: 2348-5221)
www.ijcrcps.com

Research Article

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION STUDIES OF SCHIFF BASE METAL COMPLEXES DERIVED FROM (PYRIDIN-2-YL)METHANAMINE AND 2-HYDROXY-3,5-DIIODOBENZALDEHYDE

V.R.RAJEWAR [1], M.K.DHARMALE[2] AND S.R.PINGALKAR[3]

[1,3]Department of Chemistry N.E.S.Science College ,Nanded (M.S)
[2]Department of Chemistry Yeshwant Mahavidyalaya ,Nanded (M.S)

Corresponding Author: dharmalevaishu@rediffmail.com

Abstract

The Schiff base synthesized from the condensation of (pyridin-2-yl)methanamine and 2-hydroxy-3,5-diiodobenzaldehyde . The prepared Schiff base react with La (III), Nd(III), Pr(III),Sm(III) and Tb(III) Chloride to give complexes with stoichiometric ratio (2 : 1) (ligand : metal). The complexes have been characterized by elemental analysis, molar conductance, electronic absorption, and infrared, ^{1}H-NMR spectral studies. The presence of hydrated and coordinated water molecules is inferred from thermogravimetric analysis. Thermal degradation studies show that the final product is the metal oxide.

Keywords: *Schiff base complexes, IR studies, ^{1}H-NMR, UV-Vis, XRD analysis*

Introduction

Schiff base ligands may contain a variety of substituents with different electron-donating or electron-withdrawing groups, and therefore may have interesting chemical properties. They have attracted particular interest due to their biological activities[1,2] for example acting as radiopharmaceuticals for cancer targeting[3,4]. They have also been used as model systems for biological macromolecules [5,6]. Other applications extent its use in catalysis [7,8], dying processes [9,10] and analytical applications [11].

During the last decade, the coordination chemistry of Schiff bases derived from 2-pyridine carboxaldehyde has received much attention[12]. The Schiff base complexes of pyridine-2-carboxaldehyde and its derivatives have been reported as high super oxide dismutase activities[13]and some of its have been found to be good herbicides are used for the protection of plants[14].

The Schiff bases of salicylaldehyde and amino pyridines have been characterized in solid state and in ligand solution [15,16] and proposed as highly sensitive spectrometric and spectrofluorimetric reagents [17,18.]

Compounds which contain pyridine and its derivatives or Schiff bases as ligands have occupied a central role in the development of coordination chemistry and biochemistry. Schiff base ligands forms a stable complex with different transition metal ions.

The formation of Schiff base intermediate in reactions of biological importance is well documented[19] . Schiff base and their metal complexes have a variety of applications in biological, clinical and analytical fields. Many potent antibacterial and antifungal Schiff base compounds of heterocyclic compounds were reported[20-23] . Some heterocyclic Schiff bases [24,25] can act as antibacterial agent and antifungal agent.

Literature reports show that pyridine containing compounds possess antioxidant[26], antiviral[27,28,29] anticancer[30,31] antibacterial[32,33] antidiabetic[34] antichagagic[35] and antifungal[36] and analgesic[37] activities.

2-Aminopyridine compounds are well known class of compoundes for a long time, and still are interestingly considerable due to their application in various fields.
The primary use of 2-aminopyridine is an intermediate in the manufacture of pharmaceuticals anti-histamines and piroxican.

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 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 (PMDP)schiff base

Schiff base was ligand prepared by condensing of (pyridin-2-yl)methanamine and 2-hydroxy-3,5-diiodobenzaldehyde with 0.01M were mixed in 1:1 ratio into one another and refluxed on water bath for half hour in presence of glacial acetic acid. The reaction mixture was kept for overnight. Yellow precipitate appears. Resultant precipitate was filtered by suction, and washing with distilled water and ethyl alcohol. Then dried in vacuum dessicator, purity of ligand was checked by TLC.

Synthesis of metal chelates

Synthesis of 2-(((Pyridin-2-Yl) Methylimino)Methyl)-4,6-Diiodophenol (PMDP) complexs

0.02M solution of 2-(((Pyridin-2-Yl)Methylimino)Methyl)-4,6-Diiodophenol were prepared in warm ethyl alcohol. The Merck make 0.01M Metal chloride solution was also prepared in ethyl alcohol. Metal ion solution was added drop wise with constant stirring.

The P^H of reaction mixture was maintained about 6.9 to 7.1 by adding alcoholic ammonia solution drop by drop. The reaction mixture was refluxed for about four hours on water bath. Appearance of coloured precipitate was allowed to digest for half an hour. It is filtered through whatmann filter paper. The complex was purified by washing with distilled water and little hot ethanol to apparent dryness. The complex is dried and yield was recorded.

Results and Discussion

Physical parameters and analytical data of complexes synthesized from PMDP ligand presented in the table 1.1.

Complexes prepared are intensely colored, insoluble in water, ethanol, chloroform, carbon tetra chloride and acetone. Decomposition points are relatively higher than ligand in La(III), Pr (III), Nd (III), Tb(III) and Sm(III) metal complexes indicating good stability at normal condition[38].

Molar conductivity in DMSO varies in the range of λ60 to 80$\Omega^{-1}cm^2$ mol^{-1} implies that complexes are electrolytic nature[39-41]. Magnetic moments values as usual indicated that all the metal complexes were paramagnetic in nature except La(III) complex. On the basis of elemental analysis, empirical formula of the complexes and metal ligand ratio was deduced (table 1.2).

Electronic spectra

UV-Visible plots of ligand PMDP and its complexes recorded in the range of 200 nm to 1000 nm on spectrometer 119-Pc based instrument in DMSO solvent from pharmacy College Nanded are presented in figures 4.1 to 4.6. Ligand PMDP shows strong absorption band at 37453 cm^{-1} assignable for π-π* transition. Absorption bands and corresponding transition are given the table No. 1.3.

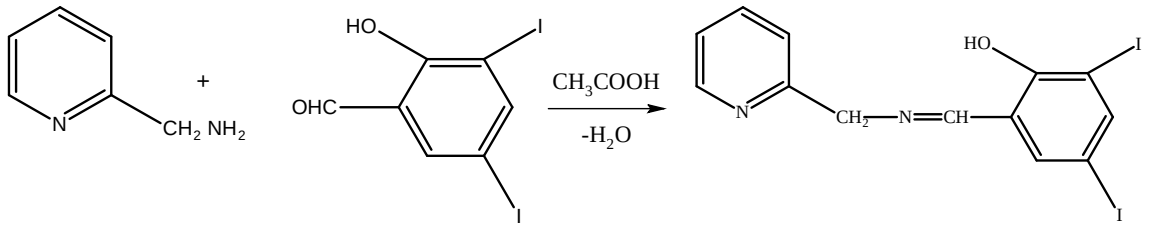
The UV electronic spectra of La (III), Pr (III), Nd(III), Tb(III) and Sm(III) metal ion complexes indicates, the transition is shifted towards higher or lower frequencies which confirm the coordination of the ligand to the metal ions.

Infrared spectrum study of complexes

IR spectra of PMDP Ligand

Infrared spectra of ligand PMDP exhibits medium band is obtained at 3061cm^{-1} due to the presence of ν(OH). A band was observed around 1389cm^{-1} is due to the bond bending vibration of - OH group [42]. Similarly phenolic ν C-O) stretching frequency found in ligand at 1201cm^{-1} Table no.1.4.

The spectra of Schiff base shows a (C=N) stretching band at 1625cm^{-1}. Significant changes in wave numbers of the coordinating atoms involved in coordination.



(pyridin-2-yl)methanamine 2-hydroxy-3,5-diiodobenzaldehyde 2-(((pyridin-2-yl)methylimino)methyl)-4,6-diiodophenol

Compound	F.W.	Yield	M. L ratio	M.P. decom. Temp °C	Color	Molar Conductance t^{-1} cm^2 mol^{-1}	%of Cl cal. (obs)	Magnetic Moment
PMDP (L)	465.5	67%	----	192^0C	Yellow	-----	-------	----------
$[La(L)_2]$ $Cl2H_2O$	1138.47	54%	1:2	>270 ^{0}C	Brown	71	3.11 (3.20)	Dimagnetic
$[Pr(L)_2]$ $Cl2H_2O$	1140.47	61%	1:2	>270 ^{0}C	Muddy Brown	76	3.11 (3.15)	Paramagnetic
$[Nd(L)_2]Cl2H_2O$	1143.8	55%	1:2	>270 ^{0}C	Dull Brown	66	3.10 (3.20)	Paramagnetic
$[Tb(L)_2]$ Cl $2H_2O$	1158	59%	1:2	>270 ^{0}C	Brownish Yellow	65	3.06 (3.10)	Paramagnetic
$[Sm(L)_2]$ $Cl2H_2O$	1149.92	47%	1:2	>270 ^{0}C	Brown	68	3.08 (3.12)	Paramagnetic

Table 1.1: Physical and analytical data of PMDP metal complexes.

Compound	Empirical Formula	%C (calcd)	%H (calcd.)	%N (calcd.)	% O (calcd.)	% I (calcd.)	%M (calcd)
PMDP (L)	$C_{13}H_{10}I_2N_2O$	33.6 (33.12)	2.17 (2.01)	6.04 (5.86)	3.45 (3.41)	54.70 (54.34)	----
$[La(L)_2]$ $Cl2H_2O$	$C_{26}H_{24}ClI_4LaN_4O_4$	27.43 (27.21)	2.12 (2.04)	4.92 (4.46)	5.62 (5.23)	44.59 (44.32)	12.20 (12.08)
$[Pr(L)_2]$ $Cl2H_2O$	$C_{26}H_{24}ClI_4N_4O_4Pr$	27,38 (27.25)	2.12 (2.03)	4.91 (4.76)	5.61 (5.34)	44.51 (44.32)	12.36 (12.12)
$[Nd(L)_2]$ $Cl2H_2O$	$C_{26}H_{24}ClI_4N_4NdO_4$	27.30 (27.12)	2.11 (2.04)	4.90 (4.57)	5.60 (5.36)	44.38 (44.21)	12.61 (12.53)
$[Tb(L)_2]$ Cl $2H_2O$	$C_{26}H_{24}ClI_4N_4O_4Tb$	26.96 (26.64)	2.06 (2.12)	4.84 (4.63)	5.52 (5.35)	43.82 (43.46)	13.72 (13.24)
$[Sm(L)_2]$ $Cl2H_2O$	$C_{26}H_{24}ClI_4N_4O_4Sm$	27.16 (27.26)	2.10 (2.02)	4.87 (4.64)	5.57 (5.28)	44.14 (44.05)	13.08 (13.21)

Table 1.2: Percent C, H, N,O and metal ion in PMDP metal complexes.

Ligand / Complex	Absorbance nm	ν/cm^{-1}	Transition
PMDP (L)	267	37453	$\pi - \pi^*$
$[La(L)_2]$ $Cl2H_2O$	272	36764	$\pi - \pi^*$
	392	25510	$n - \pi^*$
$[Pr(L)_2]$ $Cl2H_2O$	259	38610	$\pi - \pi^*$
	362	27624	$n - \pi^*$
$[Nd(L)_2]Cl2H_2O$	360	27777	$n - \pi^*$
$[Tb(L)_2]$ Cl $2H_2O$	362	27624	$n - \pi^*$
$[Sm(L)_2]$ $Cl2H_2O$	261	38363	$\pi - \pi^*$

Table 1.3: Electronic spectral data of (PMDP) complexes.

IR spectra of Metal complexes

In the spectra of Metal complexes, A band at 3061cm^{-1} is observed in ligand due to ν(OH) stretching vibration. This band is disappeared in the complex shows deprotonation of this group[43].

New broad band at 3133 to 3394 cm^{-1} have appeared, this band indicated the presence of coordinated water molecule[44]. A band of medium intensity at 867cm^{-1} (OH rocking) indicates presence of coordinated water. Similarly band at 1201cm^{-1} in ligand due to phenolic ν(OH) shifted at 1215- 1219 cm^{-1} indicates involvement in coordination.

Further, the band observed at 1625cm^{-1} due toν(C=N) azomethine group in ligand and is shifted towards lower frequency at 1594-1624 cm^{-1} attributed to involvement in coordinate bond. The band observedi at 1587cm^{-1} due toν(CH=N) pyridine in ligand and is shifted towards lower frequency at 1400 -1450 cm^{-1} attributed to involvement in coordinate bond[45].Appearance of new bands in the complex ν (M-N) at 410- 490 cm^{-1} and ν(M-O) at 550-560 cm^{-} [146,47]. Thus, IR data it is conclude that the complexes are having ML_1 structure. Also three coordination through azomethine group, phenoxide oxygen and water molecule. The ligand (PMDP) shows uninegative bidentate nature.

^{1}HNMR spectra

The ^{1}HNMR spectral studies of ligand PMDP indicated signals at δ7.3-8.1 (m, 6H) due to aromatic protons and pyridine ring proton , δ8.6ppm (s, 1H) for azomethine proton, δ14.82 (s, 1H) for Ar-OH[48] . δ3.4 ppm for CH_2 (S, 2H) (fig. 1.1).

A signal corresponding to azomethine in free ligand at δ8.62 ppm is shifted to down field region[49] to δ13.3ppm. The disappearance of peak at δ 14,82 ppm due to phenolic OH may be attributed to deprotonation of OH group on involvements in bonding[50](fig. 1.2). A new peak observed at δ 2.0 ppm in Pr(III) complex due to corresponding water molecule[51]. Thus, PMDP molecule seems to be coordinated to the metal ions through azomethine and phenolic oxygen.

Thermal study of prepared complexes

Nd(III), Pr(III), Tb(III) complexes were studied by thermo gravimetric analysis from ambident temperature to 1000°C in nitrogen atomosphere. The range of temperature and the experimental and calculated mass losses of the decomposition reaction are given in the table No. 1.5 and figures 1.3, 1.4 and 1.5.

Thermal study of $[Nd(L)_2]Cl2H_2O$

The TGA study of 2-(((Pyridin-2-Yl)Methylimino)Methyl)-4,6-Diiodophenol Nd(III) chloride complex indicates decomposition in four steps. There is a loss in mass 6.35% at 210^{0}C indicates the first loss of two lattice water[52] and then coordinated chloride molecule[53]. The second step of complex decomposition indicates loss in weight in the temperature range 210-450^{0}C corresponding to 57.38% indicates the loss of two diiodobenzene ring .

Decomposition reaction corresponds to an experimental mass 23.79 % occurs in the temperature range 450-680^{0}C attributed loss of azomethine and pyridine with organic moiety of the complex. Finally 680-1000^{0}C residue is obtained corresponding to Nd_2O_3 as a stable residue 14.71%.

Compound	¬ÉCH=N) azomethine	¬ÉC=N) pyridine	¬ÉC-O)	¬ÉM-O)	¬ÉM-N)	¬ÉH_2O)	¬ÉOH)
PMDP (L)	1625	1587	1201	----	----	----	3061
[La$(L)_2$] Cl2H_2O	1623	1438	1218	551	410	3394	----
[Pr$(L)_2$] Cl2H_2O	1624	1436	1219	545	412	3373	----
[Nd$(L)_2$]Cl2H_2O	1594	1400	1215	525	416	3133	----
[Tb$(L)_2$] Cl 2H_2O	1623	1440	1216	509	485	3411	----
[Sm$(L)_2$] Cl2H_2O	1621	1450	1216	549	414	3426	----

Table No 1.4 Infrared spectral data of the ligand (PMDP) and their La(III), Pr (III), Nd(III), Tb(III) and Sm(III) metal complexes

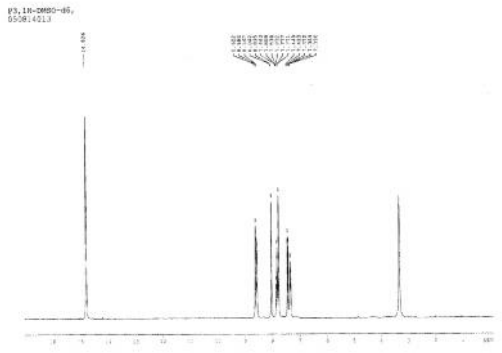


Figure 1.1: NMR ligand PMDP

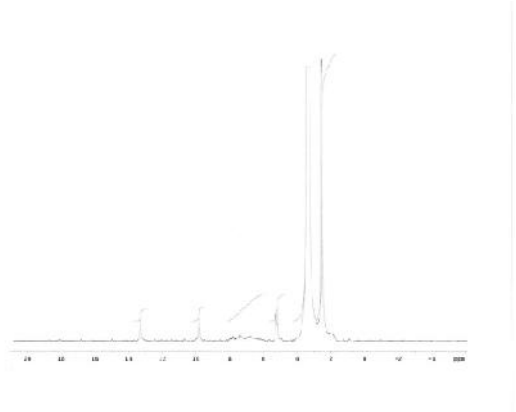


Figure 1.2: : NMR Nd$(L)_2$]Cl2H_2O

Complex	Decomposition Temp°C	Lost fragment	Weight loss %	
			Experimental	Theoretical
[Nd$(L)_2$]Cl2H_2O	25 - 210 ^{O}C	Two lattice water molecule,one lattice chloride	6.35	6.35
	210 - 450 ^{O}C	Two diiodo benzene ring	57.38	56.87
	450 - 680 ^{O}C	Organic moiety	23.79	24.57
	680 - 1000 ^{O}C	Metal oxide	14.71	13.35
[Pr$(L)_2$] Cl2H_2O	25 - 80 ^{O}C	Two lattice water molecule	3.028	3.15
	80 - 225^{O}C	One lattice chloride,Four iodide molecule	46.34	46.54
	225 - 800 ^{O}C	Organic moiety	42.19	41.17
	800 - 1000 ^{O}C	Metal Oxide	13.71	14.30
[Tb$(L)_2$] Cl 2H_2O	25-110 ^{O}C	Two lattice water molecule	3.215	3.10
	110 - 390 ^{O}C	One lattice chloride and two diiodio benzene ring	55.87	56.62
	390 - 800 ^{O}C	Organic moiety	19.4	20.5
	800 - 1000 ^{O}C	Metal oxide	15.37	15.78

Table No.1.5: Thermal analysis data of metal complexes

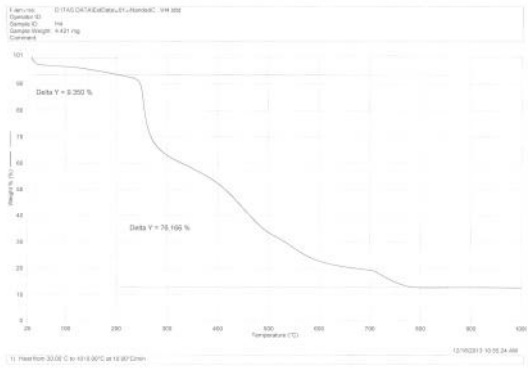


Figure 1.3: TG/DSC $[Nd(L)_2]Cl2H_2O$

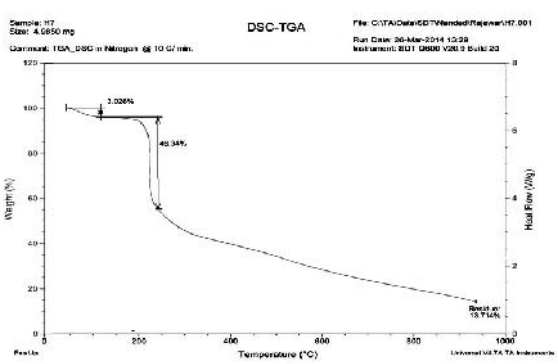


Figure 1.4: TG/DSC $[Pr(L)_2]$ $Cl2H_2O$

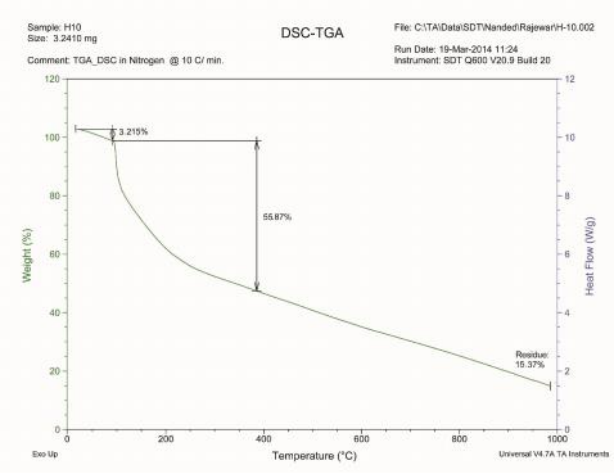


Figure 1.5: TG/DSC $[Tb(L)_2]$ Cl $2H_2O$

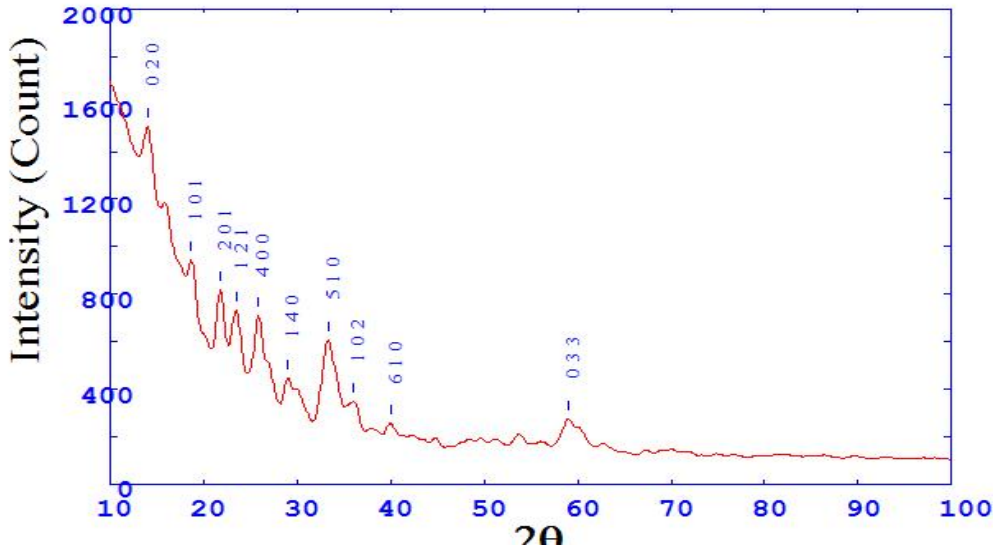
$[Nd(L)_2]Cl2H_2O$

Crystal system: **Orthorhombic** Lattice Type**: P**

Lattice Parameter: a= 16.28383 b= 8.60044 c= 3.80777 A^0

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

h	k	l	2θ (cal)	2θ (Obs)	d(cal)	d (obs)
0	2	0	7.01963	7.00478	6.30311	6.31186
1	0	1	9.34675	9.34605	4.74296	4.74077
2	0	1	10.90719	10.89982	4.07095	4.07179
1	2	1	11.72726	11.74426	3.78985	3.78283
4	0	0	12.95736	12.94174	3.43537	3.43812
1	4	0	14.52277	14.51571	3.07180	3.07221
5	1	0	16.67041	16.66909	2.68522	2.68464
1	0	2	18.05727	18.04392	2.48510	2.48620
6	1	0	19.98929	19.98761	2.25336	2.25299
0	3	3	29.51554	29.50984	1.56355	1.56358

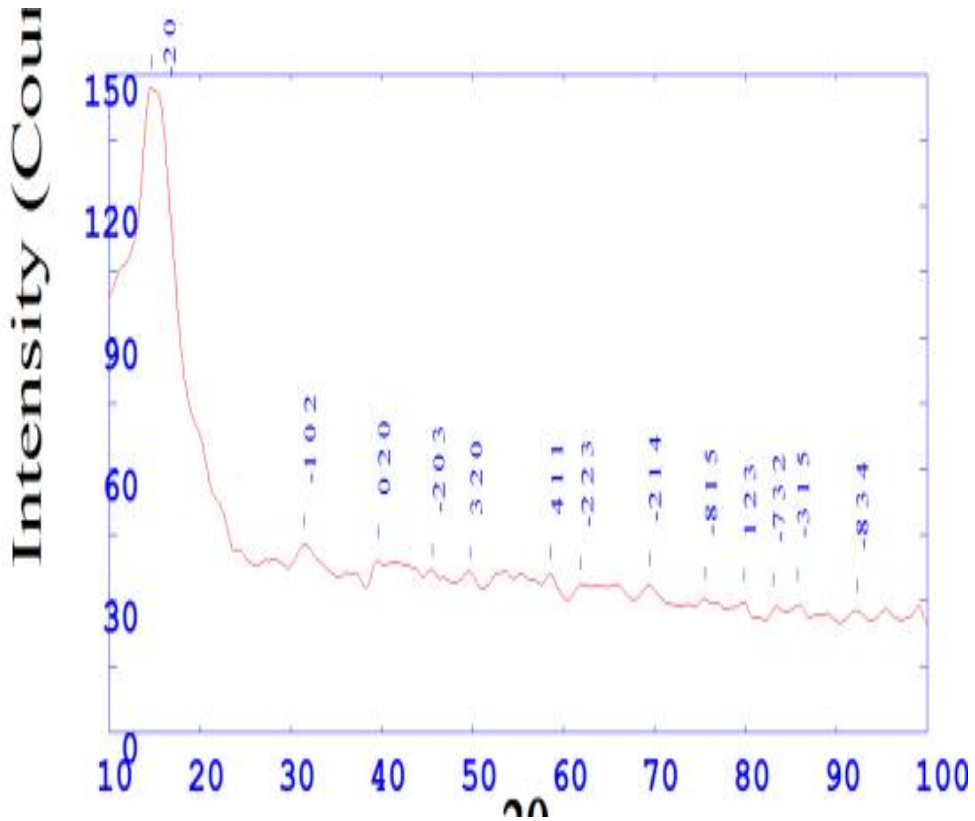


Cell data and crystal lattice parameter of Cd(II) complex indicates that it has orthorhombic crystal system[57] crystal system with lattice type-P.

$[Pr(L)_2]$ $Cl2H_2O$

Crystal system: **Monoclinic** Lattice Type**:** **P**
Lattice Parameter: a= 12.91538 b= 4.54932 c= 6.64278 A^0
Lattice Parameter: Alpha= 90.000 Beta= 134.080 Gama= 90.000

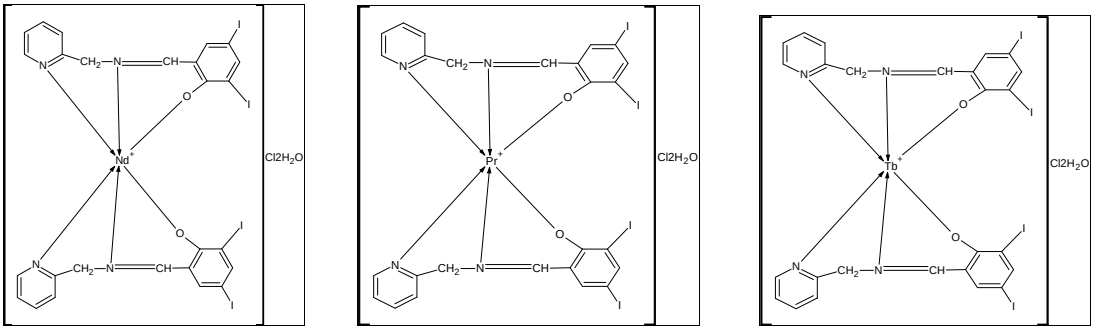
h	k	l	2θ (cal)	2θ (Obs)	d(cal)	d (obs)
-2	0	1	7.36092	7.34228	6.02754	6.02067
-1	0	2	15.75880	15.76158	2.83579	2.83807
0	2	0	19.79930	19.78922	2.27522	2.27523
-2	0	3	22.80986	22.79620	1.98810	1.98782
3	2	0	24.86972	24.85281	1.83279	1.83232
4	1	1	29.30634	29.30049	1.57400	1.57421
-2	2	3	30.97007	30.96626	1.49708	1.49736
-2	1	4	34.69366	34.68278	1.35370	1.35368
-8	1	5	37.78345	37.77603	1.25747	1.25755
1	2	3	39.92253	39.92025	1.20036	1.20056
-7	3	2	41.50704	41.48532	1.16284	1.16258
-3	1	5	42.85387	42.83059	1.13307	1.13279
-8	3	4	46.10211	46.10116	1.06902	1.06919



Cell data and crystal lattice parameter of Pr(III) complex indicates that complex have monoclinic[58] crystal system with lattice type-P.

Proposed structures of the complexes

Based on above result probable structure have been proposed.



$Nd(L)_2]Cl2H_2O$ **$[Pr(L)_2]\ Cl2H_2O$** **$[Tb(L)_2]Cl\ 2H_2O$**

Thermal study of $[Pr(L)_2]$ $Cl2H_2O$

TGA of Pr(III)complex shows weight loss corresponding to two mole of coordinated water in temperature range 80^0C corresponds to mass loss 3.028%. In the temperature range of 80-225^0C with the observed weight loss is 46.34% which is corresponds to removal of four iodide and one chloride molecule.

The complex decomposition beyond 225^0C continuous up to 800^0C which corresponding to loss of 42.19%organic moiety of the complex. Further at final temperature from 800-1000°C [54]. The percentage of residual metal oxide was found to 13.71% which is very close to theoretical value 14.30%.

Thermal study of $[Tb(L)_2]$ Cl $2H_2O$

2-(((Pyridin-2-Yl)Methylimino)Methyl)-4,6-Diiodophenol Tb(III) chloride complex shows decomposition in four steps. The thermogram of Tb(III) complex shows weight loss corresponding to water molecule [55] of the complex in the temperature range 110^0C which observed value percentage is 3.215.The decomposition of complex continuous up to 390°C and the loss corresponds to 55.87% indicating decomposition of chloride part and with two molecule of diiodobenzene. from 390-800^0C loss of 19.4 % pyridine containing organic moiety . At 1000^0C complex remains in the form of Tb_2O_3 as a stable residue[56] 15.37%.

Powder X-Ray analysis

Powder XRD diffractrograms of the selected complexes as recorded in 2θ range from 10 to 90^0 using Cu Kα radiation source at a wave length of 1.540 A° at room temperature.

Major refluxes were used to determine corresponding inter planar distances. Diffractogram was then indexed independently, miller indices were calculated and lattice parameter a , b, c and interfacial angles α, β, γ were determined by determined by computer based powder X programmer. Data has been summarized in the following tables.

References

1. H. K. Shapiro. Carbonyl-trapping therapeutic strategies, *Am. J. Ther.*, **5**, 323–353(1998).
2. H. Chen; J. Rhodes. Schiff base forming drugs: Mechanisms of immune potentiation and therapeutic potential, *J. Mol. Med.*, **74**, 497–504(1996).
3. V. Ambike; S. Adsule; F. Ahmed; Z. Wang; Z. Afrasiabi; E. Sinn; F. Sarkar; S. Padhye. Copper conjugates of nimesulide Schiff bases targeting VEGF, COX and Bcl-2 in pancreatic cancer cells, *J. Inorg. Biochem.*, **101**, 1517–1524(2007).
4. M. Singh. Transferrin as a targeting ligand for liposomes and anticancer drugs, *Curr. Pharm. Des.*, **5**, 443–451(1999).
5. O. P. Anderson; A. la Cour; M. Findeisen; L. Hennig; O. Simonsen; L. F. Taylor; H. Toftlund. Zinc(II) N2S2 Schiff-base complexes incorporating pyrazole: syntheses, characterization, tautomeric equilibria and racemization kinetics, *J. Chem. Soc., Dalton Trans.*, 111–120(1997).
6. S. Uhlenbrock; R. Wegner; B. Krebs. Syntheses and characterization of novel tri- and hexa-nuclear zinc complexes with biomimetic chelate ligands, *J. Chem. Soc., Dalton Trans.*, 3731–3736(1996).
7. Selbin. J. *Coord. Chem. Rev*., **1**, 293(1966).
8. Vasin. S.-V.; Cetralla, J.; Genogel, R.-A.; Bernal, J. *Inorg. Chem*., **29**, 885(1990).
9. Maki,M.; Hashimato, H. *Bull. Chem. Soc. (Japan)*, **25**, 411(1952); **27**, 602(1954).
10. Papie, S.; Kaprivanae, N.; Grabarie, Z.; Paracosterman, D. *Dyes Pigments*, **25**, 229(1994).
11. Khedr, A.-M.; Gaber, M.; Issa, R.-M.; Erten, H. *Dyes Pigments*, **67**, 117(2005).
12. Vleck, Coord. Chem., Rev.(2002) 225.
13. M. Liu, R. G. Xiong and K. K. Cheung. Polyhedron, 15 (1996) 4565.
14. (a). C.M.Liu, R.G.Xiong and K.K.Cheung. Polyhedron, 6 (1978) 713. (b). C.M.Liu, R.G.Xiong and K.K.Cheung. Polyhedron, 7 (1996) 4565.
15. S.A.Abdel-Latif, H.B.Hassib and Y.M.Issa Spectrochim. Acta, Part A, 2007,67,950.
16. R.Ramesh and S.Maheswaran, J.Inorg. Biochem, 2003,96,457.
17. Z.Cimerman, N. Galic and B.Bosner, Anal. Chim.Acta, 1997,343,145'
18. Z.Cimerman, S. Miljanic and N.Galic, Croat. Chem. Acta, 2000,73,81.
19. IssacSobanaRaj, M.Christudhas and G.AllenGnanaRaj., *J.chem pharm. Res.* **2011**, 3(6), 127-135.
20. G.G.Mohamed, M.M.Omar., *Spectrochim,Actapart A,* **2005,** 62,1140.
21. A.Scozzafava, L.Menabuoni, F.Minicone, G.Mincione, C.T.Supran., *Biorg.Med.Chem.Lett.11* **2001**, 575.

22. M.S.Sastry, R.Ghose, A.K.Ghose., *Bull.Chem.Soc.Ethiop* , **1990,** 4, 61.
23. N.Raman, S.Thalamuthu, J.Dhaveethuraja, M.A.Neelakandan, S.J.Banerjee., *Chil.Chem.Soc* **2008,** 53, 21.
24. V.Mishra, D.K.Sena, M.C.Jain., *Synth React Inorg Met Org Chem.* **1987,** 17, 987-1002.
25. S.R.Bhusare, V.G.Pawer, S.B.Shinde, R.P.Pawer and Y.B.Vibhute., *Int.J.Chem.Sci*. **2003,**1, 31-36.*Chem.Abstr*, **2004,** 140, 357246.
26. Feng Shi, SSNing Ma. Green chemoselective synthesis of thiazolo[3,2-a]pyridine derivatives and evaluation of their antioxidant and cytotoxic activities, Bioorg. & Med. Chem., Letters 2009;19:5565 5568.
27. Alice Maria Rolim Bernardino, Helena Carla Castro, et.al. Design, synthesis, SAR, and biological evaluation of new 4-(phenylamino)thieno[2,3-b]pyridine derivatives, Bioorg. & Med. Chem 2006;14:5765 5770.
28. Adel M. Attia and Hanaa A. Mansour. synthesis of some pyfudine ribosides and their biological activity, Nucleosides & Nucleotides, 1999**;**18(l0): 2301-2306**.**
29. Jean-Michel Chezal. synthesis and antiviral activity of an imidazo[1,2- a]pyrrolo[2,3-c]pyridine series against the bovine viral diarrhea virus, E. J. of Med. Chem 2010; 45:2044 2047.
30. KC Nicolaou. Chemical synthesis and biological properties of pyridine epothilones, Chemistry & Biology 2000; 7:593-599.
31. Jong-Keun Son , Eung-Seok Lee. Synthesis of 2,6-diaryl-substituted pyridines and their antitumor activities, E. J. of Med. Chem 2008;43:675-682.
32. Alexandre V Ivachtchenko, Sergiy M Kovalenko. Synthesis and antimicrobial activity of 5-hydroxymethyl-8-methyl-2-(N-arylimino)-pyrano[2,3-c]pyridine-3- (N-aryl) carboxamides, Bioorganic & Medicinal Chemistry Letters 15 (2005) 5483 5487.
33. T. Suksrichavalit, E. J. of Med. Chem 2009;44:3259 3265.
34. Rajesh H Bahekar, Mukul R. Jain et al. Synthesis and antidiabetic activity of 2,5-disubstituted- 3-imidazol-2-yl-pyrrolo[2,3-b]pyridines and thieno[2,3- b]pyridines, Bioorg. & Med. Chem 2007;15:6782 6795.
35. Luiza R. S. Dias. Synthesis, in vitro evaluation, and SAR studies of a potential antichagasic 1H-pyrazolo[3,4-b]pyridine series , Bioorg. & Med. Chem 2007;15:211 219.
36. Ahmet Ozdemir, Fatih Demirci. synthesis and the selective antifungal activity of 5,6,7,8-tetrahydroimidazo[1,2-a]pyridine derivatives. E. j. of med. Chem 2010;45:2080-2084.
37. Kasabe Amit J, Kasabe Prasant J. Synthesis, antitubercular and analgesic activity evaluation of new 3-pyrazoline derivatives, Int. Journal of pharmacy andpharmaceutical sciences 2010;2:132-135.
38. Siddapa, K., Reddy, T., Mallikarjun , M. and Reddy, C.V., E-Journal of Chemistry, Vol.5(1), 2008,p.162.
39. Mishra, A.P. and Sharma, N., J. Ind. Council Chem., Vol. 26, 2009, p. 125.
40. Derebe, M .G., Raju, V.J.T. and Retta,N., Bull. Chem. Soc. Ethiop., 16(1), 2002, p.53.
41. Yadav, R. S., J. Ind. Council. Chem., Vol. 25, 2008, p.87.
42. Niazi,S., Javali,C., Paramesh, M. and Shivraja, S.,Int. J. Pharmacy Pharm. Sci .,Vol.2(3),2010,p.108.
43. Sharma, S.S., Ramani, J.V., Dalwadi, D.P., Bhalodia, J.J., Patel, N.K., Patel, D.D. and Patel, R.K., E-Journal of Chemistry, 8(1), 2011, p.361.
44. Datta, A., GolzarHossain, G.M., Karan, N.K., Abdul Malik, K.M. and Mitra, S., Inorganic Chemistry Communication, Vol. 6(3), 2003, p. 266.
45. Canpolat, E., Polish J. Chem., 79, 2005, p. 619.
46. Redha I, H., AL-Bayati, Mandi, F., Radi and Ahmed, A.H., Al-Amiery, 14th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-14) ,1-30 Nov., 2010.
47. Calinescu, M., Ion, E., Georgescu, R. and Negreanu-Pirjol, T., Revue Roumaine de Chimie, 53(10), 2008,p.911.
48. Balakrishna, A., Reddy, C.S., Naik, S.K., Manjunath, M. and Naga Raju, C.N., Bull. Chem. Soc. Ethiop., 23(1), 2009, p.69.
49. Turan,N. And Sekerci,M., J. Chem. Soc. Pak., Vol.31(4),2009 ,p.564.
50. De, R.L., Mandal, M., Roy, L., Mukherjee, J., Bhawal, R. and Maiti, K., Indian Journal of Chemistry. Vo1.47A, 2008, p.1480.
51. Pingalkar, S.R., and Deshpande, M.N., Orient. J. Chem., Vol.23 (1), 2007. P.265.
52. Prashanthii, Y. and Shiva Raj, J. Sci. Res., 2(1), 2010, p.1 14.
53. Aly, A.A.M., Osman, A.H., El-Mottaleb, M. and Gouda, G.H., J. Chil. Chem. Soc., 54, No4, 2004, p.349.
54. Lascalea, G.E., Lamas, D.G. Perez, Ai., Canbanillas, E.D. and WalsoeReca, N.E., Material Letters, Vol.58 (20), 2004, p. 2456.
55. Arish, D. and Nair, M.S., A Journal of Molecular Structure, Vol. 983(1-3), 2010, p.112.

56. Xiangru Meng, Xiaoging Zhu, Yongfang Qi, Hongwei Hou, and Yaoting Fan, Journal of Molecular structure, Vol.934(1-3), 2009, p. 28.
57. Fang Yu Xuan, Wei-Min Zhu, Cheng-Feng Yuan, Guo-Zan Cui Yong, Chinese J. Struct. Chem., 30(8), 2011, p.1147.
58. Onwudiwe, D.C. and Ajibade, P. A., Int. J. Mol. Sci., 12, 2011,p. 1964.

