Synthesis and Characterization of Mn (II), Co (II) and Ni (II) Metal Complexes of Tetradentate N, O Donor Schiff Bases

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Abstract **Transition metal complexes of Symmetrical and Asymmetrical Schiff base ligands with benzene 1,3 diamine, pyridine 2,6 diamine and substituted aromatic aldehyde &ketone was prepared by condensation reaction at room temperature. The complexes are 1:1 (metal: ligand) stoichiometry non electrolytes in solution. Schiff's base and Metal complexes was characterized by elemental analysis, FTIR, SEM, TGA, magnetic susceptibly and antimicrobials. The surface morphology of complex carried curved of Schiff Base and complex carried out 300 C to 6000 C by TGA. The thermal carried in solid complexes.**

Keyword: TGA, SEM, Magnetic susceptibly, Schiff base.

INTRODUCTION

Schiff bases are compounds formed through the condensation of primary amines with carbonyl compounds. They were first described by the German chemist and Nobel Prize winner Hugo Schiff. Let me know if you'd like it to sound more technical, formal, or simplified further. The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R. Where R is aromatic ring. These compounds are also known as anils, imines or azomethines [1].Imine or azomethine groups are present in various natural, naturally derived and non- natural compounds (Figure 1). The imine group present in such compounds has been shown to be significant to their biological activities [2-3].

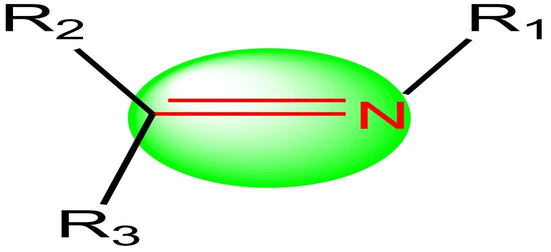


Figure 1 Imine or azomethine groups

Schiff base played a fundamental role as Ligands even a century after their discovery in coordination chemistry [4]. Schiff base are derived from the condensation reaction of aromatic aldehydes and aromatic ketones with aromatic amines. They are an important class of organic Ligands being widely studied [5]. Schiff base complexes of transition metals are at rest applicable to be of great concern in inorganic chemistry, although this topic has been extensively studied [6-7]. Schiff base have been used as chelating agents in the field coordination. While transition metals are known to from complexes with Schiff base Ligands. It is well known that N and O atoms play a key part in the coordination of metals at the active sites of numerous metallobiomolecules. Schiff base complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer, anti viral and herbicidal application. They serve as models for biologically significant species and find application on biometric catalytic reaction (Adeola,2009). Global scientist expand their limit of research in search for these complexes that will be of biological importance[8]. Schiff bases derived from aromatic diamines such as o-phenylene diamine have usual attention due to their synthetic flexibility[9], application in catalysis and coordination chemistry [10], in understanding the process of metal binding in metalloproteins and metalloenzymes in the body [11]. The metal complexes have a variety of application including biological, clinical and analytical [12]. Earlier work has shown that some drugs showed increased activity when administered as metal chalets rather than as organic compounds and that coordinating possibility of o-phenylene diamine has been improved by condensing with variety of carbonyl compounds [13].

Current research has greater interest in the medicinal use of metal compounds containing technetium and platinum. Which as lead to the development of compounds like cis-platin containing platinum along with technetium in addition to Manganese, Cobalt, Nickel and Copper used for diagnostic medicinal purpose. Metal with magnetic properties, has access to their use in pharmaceuticals. It is used of gold drugs to treat rheumatoid arthritis, platinum to treat certain type of cancer, Nickel to treat stomach ulcers, vanadium to treat some cases of diabetes, iron and its compounds to treat anaemia, and to control blood pressure, cobalt in vitamin B_{12} to treat pernicious anaemia and certain radioactive metals to alleviate the pain of bone cancer.

In this paper keeping the above requirements in mind, we describe the synthesis and characterized by elemental theoretical analysis, FT-IR, Thermal analysis, SEM, ^{1}H-NMR and antibacterial screening of transition metal complexes of Mn(II), Co(II), and Ni(II) with Schiff base derived namely HBMPD, HBDAP, and ABDAPby condensation of aromatic aldehyde / ketones with diamines (2:1) and its complexes with Mn(II), Co(II), and Ni(II) in ratio (1:1) (M:L) was prepared.. The obtained results are helpful for conducting further research in developing newer and effective antimicrobials.

2. EXPERIMENTAL

2.1Materials and reagents

Chemical m-phenyldiamine 98% 250gm (LOBA), Ortho hydroxyl acetophenol 100ml (SD), 0- hydroxyl benaldehyde 100ml (SD). We are purchase from AMI chemical Borivali (E), Mumbai. The metal acetate are Mn Acetate, Co Acetate, while metal salt are used as $NiCl_2$ $6H_2O$ all solvents and chemicals was of commercially reagents grade. The Ligands and metals of the complexes was determined as per standard method [14].

2.2Methods

The InfraRed spectra (KBr Disc) was recorded on FT-IR spectrophotometer in range of 400 to 4000 cm^{-1}. Thermogravimetric analyses (TGA-50) of Schiff base Ligands and their chelates for thermal stability. SEM images was recorded in a SEM analyze.^{1}H-NMR spectra was recorded on a BRUKER AVANCE II 400MHz NMR Spectromter (SAIF) for ^{1}H spectra. Antimicrobical test report for metal complexes are Bio-active.

2.3Synthesis of Schiff base

The symmetric Schiff base ligand (HBMPD, ABDAP), asymmetric Schiff base ligand (HBDAP) was synthesized by condensation of 2,6 diamine with o-hydroxyl acetophenol and o- hydroxyl benaldehyde. The 2,6 diamine (1 mmol) dissolved in absolute ethanol 20 ml was added drop wise to a constant stirring solution in (2 mmole) of o-hydroxyl acetophenol or o- hydroxyl benaldehyde in 30 ml ethanol with 2 ml a catalytic amount of dil. NaOH and the mix for 4-5 hours at 100–150°C, during which a yellowish solid compound was separated. It was filtered, washed, recrystallized from diethyl ether and dried in vacuum. The structure of Schiff base shows in Figure 2

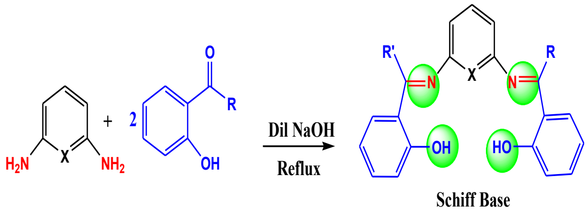


Figure 2- Synthesis of symmetric Schiff base ligand.

Schiff Base I HBMPD(L_1) X = CH, R = H and R' = H

Schiff Base II HBDAP(L_2) X = N, R = H and R' = H

Schiff Base III ABDAP(L_3) X = N, R = H and R' = CH_3

2.4Synthesis of Schiff base complexes

All metal complexes was prepared in 1:1 molar ratio (metal: Ligand) ethanol solution 20 ml of transition metal (2 mmol) was taken in two nicked round bottom flask and kept on magnetic stirrer respect to metal acetate & salt (2 mmol). The reaction mixture refluxed on water bath for 4-5 hours then reaction mixture cooled to room temperature precipitates was found which is filtered, washing ethanol, acetone, dried in vaccum decitator over unhydrous $CaCl_2$ the purity of each complexes was tested by TLC plate using different solvent. The structure of metal complexes shows in Figure 3.

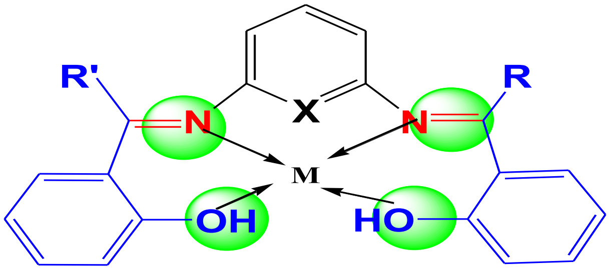


Figure 3 Schiff base of Transition metal complexes.

3.RESULT AND DISCUSSION

3.1Physical measurements:

The metal complexes are intensive color, amorphous solid. Complexes are non – hydroscopic and thermally stable having decomposition temperature more than 300 ^{0}C demonstrating a strong metal ligand bonding. Elemental analysis data of ligand and metal complex. The physical properties of the synthesized Schiff base ligand and metal complex shown in Table 1.

Compound	Molecular Formula	Molecular Weight	M.P	Cal. Elemental Analysis Calculated					BM	Yield %
				M	C	H	N	O		
HBMPD (L$_1$)	$C_{20}H_{16}N_2O_2$	316.35	280	----	75.93	5.10	8.86	10.11	--	90.50
MnL$_1$	$C_{20}H_{16}MnN_2O_2$	371.29	>360	14.80	65.70	4.34	7.54	8.62	4.66	75.74
CoL$_1$	$C_{20}H_{16}CoN_2O_2$	375.05	>360	15.70	64.01	4.30	7.46	8.53	3.75	67.46
NiL$_1$	$C_{20}H_{16}NiN_2O_2$	375.06	204	15.65	64.05	4.30	7.47	8.53	3.59	63.73
HBDAP (L$_2$)	$C_{19}H_{15}N_3O_2$	317.35	258	----	71.91	4.76	13.24	10.08	--	81.38
MnL$_2$	$C_{19}H_{15}MnN_3O_2$	372.29`	>360	14.76	61.30	4.06	11.29	8.60	4.82	73.11
CoL$_2$	$C_{19}H_{15}CoN_3O_2$	376.05	244	15.66	60.65	4.02	11.17	8.50	3.48	64.09
NiL$_2$	$C_{19}H_{15}NiN_3O_2$	376.06	208	15.61	60.69	4.02	11.17	8.51	3.36	52.65
ABDAP (L$_3$)	$C_{20}H_{17}N_3O_2$	331.37	256	----	72.49	5.17	12.68	9.66	--	80.16
MnL$_3$	$C_{20}H_{17}MnN_3O_2$	386.31	>360	14.22	62.18	4.44	10.88	8.28	4.75	73.31
CoL$_3$	$C_{20}H_{17}CoN_3O_2$	390.30	240	15.10	61.55	4.39	10.77	8.20	3.50	65.64
NiL$_3$	$C_{20}H_{17}NiN_3O_2$	390.06	214	15.05	61.58	4.39	10.77	8.20	2.98	64.35

3.2 Magnetic moment

The experimental values of magnetic moment for complexes was lie in the range 2.98– 4.75 B.M. respectively. [15-16] Magnetic moment values of Mn(II), Co(II) and Ni(II) complexes indicated the presence of five, three and two unpaired electrons, respectively as shown in Table 1.

3.3FT-IR

The FT-IR spectrum of 2,6-diaminopyridine shows a pair of medium intensity bands present at 3200–3400 cm^{-1} which correspond to ν(NH2) stretching vibration. These bands are absent in the spectrum of the Schiff base ligand. This indicates that the condensation of carbonyl groups of aldehyde or ketone and amino groups of 2,6- diaminopyridine has taken place[17-19]. The comparison of the IR spectra of the Schiff base ligands and their mixed ligand complexes revealed out the way of complexation of ligands to the metal ion. The bands observed at 1616, 1629 and 1650 cm^{-1} in the free L$_1$, L$_2$ and L$_3$ respectively. Schiff base ligands was assigned to the azomethine group υ (CH=N)) stretching vibration was recorded due to this condensation reaction respectively. In the mixed ligand complexes, these bands was shifted to higher or lower wave numbers which may indicate the participation of the azomethine group in coordination. The stretching vibration band due to υ(C=N) of the pyridine group of L$_2$ and L$_3$ ligand was found at 1151 cm^{-1}. The FT-IR spectra of the mixed ligand complexes was characterized by the appearance of bands at 3400-3600 cm^{-1} for υ(OH) band [20-22]. The acetato complexes showed the IR bands in the range 1408-1483 cm−1 due to νs(OAc) stretching vibrations[23]. The IR spectra of the Schiff base and its meta complexes along with their tentative assignments are reported in table 2.

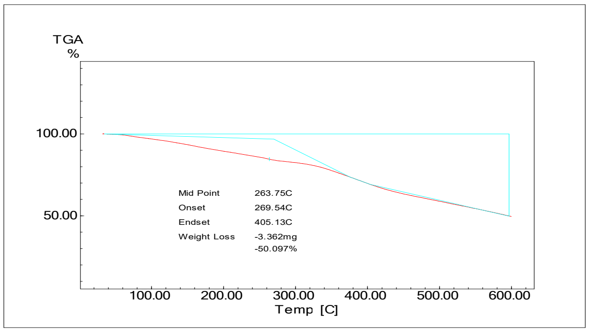
Table 2 –The FT-IR of the Ligands and the complexes.

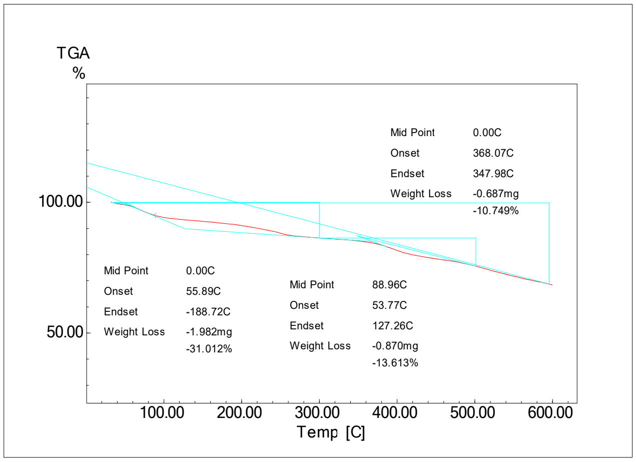
Compound	Free –OH	Azo methine υ (C=N)	Ar.Di substitued ring	Pyridine ring deformation	υ(C-O)	υ(M-O)	υ(M-N)	Ar.(C-H)	νs(OAc)
HBMPD (L$_1$)	3327	1616	752	--	1274	--	--	3061	--
MnL$_1$	--	1616	752	--	1274	908	852	3070	1452
CoL$_1$	3533	1612	754	--	1276	939	852	3026	1483
NiL$_1$	3535	1612	754	--	1276	939	846	2922	--
HBDAP (L$_2$)	3535	1629	756	1151	1228	--	--	3043	--
MnL$_2$	--	1570	756	1151	1230	956	--	3041	1408
CoL$_2$	--	1622	756	1151	1228	--	844	--	1452

NiL_2	3529	1612	754	1151	1230	945	--	--	--
ABDAP (L_3)	3298	1618	759	1149	1238	--	--	3026	--
MnL_3	--	1612	759	1149	1276	910	860	2924	1481
CoL_3	---	1612	748	1130	1240	925	846	3016	1491
NiL_3	3560	1608	742	1126	---	908	848	3014	--

3.4 TGA

In the present study, the weight loss for each mixed ligand complex was calculated within the corresponding temperature ranges. The TG curves of complexes showed three decomposition steps within the temperature range from 30 to 599 °C. The thermal decomposition of [MnL_1], [CoL_2] and [NiL_3] complex with proceeds with three main degradation steps. The first step occurs within the temperature range 305 – 518 , 304 -400 and 306 – 372K with an estimated mass loss 13.85%, 6.88% and 16.28% (calculated mass loss = 12.06%, 12.04% and 15.73%) respectively which is reasonably accounted for by the loss of the fragment acetate and chloride group. The second step occurs within the temperature range 518-690, 400-620 and 372-704 K with an estimated mass loss 32.29%, 14.86% and 51.55% (calculated mass loss = 42.94%,4.75% and 57.75%), which is reasonably accounted for by the loss of the fragment phenyl group. The Third step occurs within the temperature range 690-872, 620-872, and 704-872, K with an estimated mass loss 50.52%, 31.75% and 59.16% (calculated mass loss = 48.46%,47.75% and 63.14%), which is reasonably accounted for by the loss of rest of the ligand molecule, leaving MnO, CoO and NiO respectively as residue as table 3.





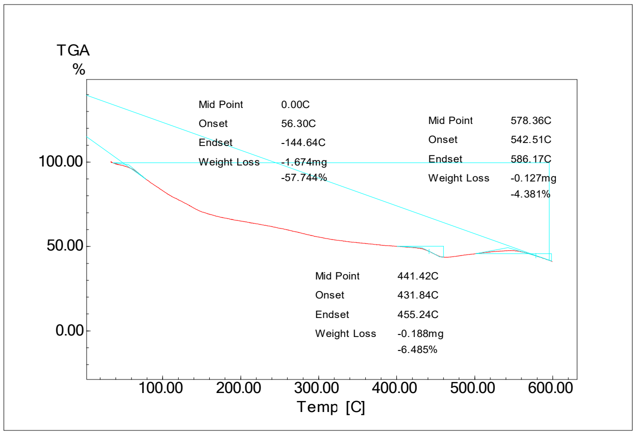


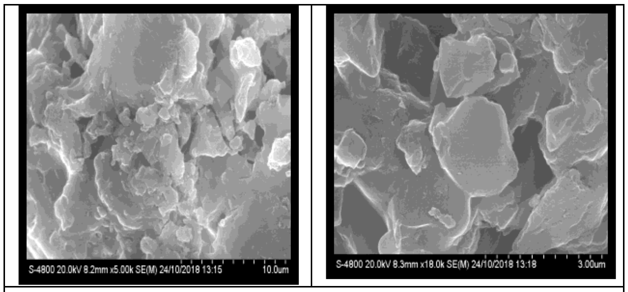
Figure 4 TGA of (5A) [MnL_1] (5B) [CoL_2] (5C) [NiL_3] complexes

Table 3 –The TGA of the Ligands and the complexes.

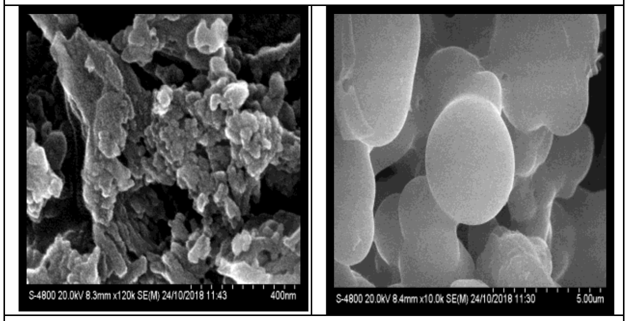
Compound	TGA range (^{0}C)	Weight loss %			Residues
		Obs.	Cal.		
MnL_1	32 – 245	13.85	(12.06)	Loss due to two acetate groups.	
	245 – 417	32.29	(42.94)	Loss due to a phenyl group.	MnO
	417 – 599	50.52	(48.46)	Loss due to remaining organic moieties.	
CoL_2	31 -127	6.88	(12.04)	Loss due to two acetate groups	
	127 – 347	14.86	(24.10)	Loss due to a phenyl group.	CoO

	347 – 599	31.75 (47.75)	Loss due to remaining organic moieties.	
NiL_3	33 – 99	16.28 (15.73)	Loss due to two chloride groups.	
	99- 431	51.55 (57.75)	Loss due to a phenyl group and azomethine	NiO
	431 - 599	59.16 (63.14)	Loss due to remaining organic moieties.	

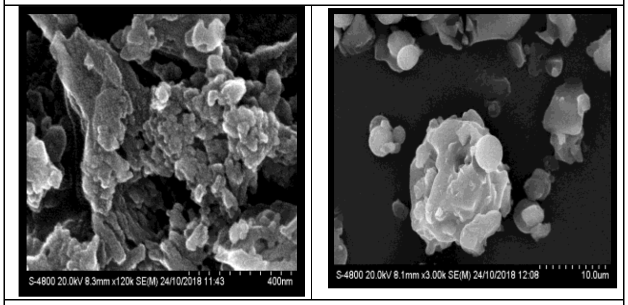
2.5 SEM:



(5A) L_1 and $[MnL_1]$



(5B) L_2 and[CoL_2]



(5C) L_3 and $[NiL_3]$

Figure 5- SEM micrographs of (6A) L_1 and $[MnL_1]$, (6B) L_2 and [CoL_2], (6C) L_3 and $[NiL_3]$ complexes

The morphology and grain size of the metal complexes was observed by scanning electron micrography (SEM). The SEM micrographs of all the metal complexes are shown in Figure 4(a)–(c). For all the complexes, the SEM micrographs was taken in the frequent scale of 3-10 µm and 400 or 500nm. From the SEM micrographs, it is noted that there is a uniform matrix in all the metal complexes. The micrograph of the Mn(II) complex shows a plate-like morphology, and the Co(II) complex shows small spherical -like morphology. The Ni(II) complexes show oval-like morphology as shown in figure 5.

4.CONCLUSION

The study of the reaction between the transition metal and the derived Schiff base indicates its high stability. This encourages the synthesis and careful investigation of the nature of bonding between the Schiff base and the transition metal cation of important biological role, using physicochemical method of analyses. It is clear from above discussion that the spectral studies of the complex confirm and illustrate the proposed geometry obtained by elemental analysis, IR, TGA, SEM and microbial study. Hence, the proposed tentative structure of the metal complex is given as in Figure 3. Schiff base ligands (L_1), (L_2) and (L_3) and their mixed ligand transition metal complexes with 2,6- pyridine diamine) with molar ratio 2:1 was synthesized and characterized by elemental analysis and spectroscopic studies. The metal complexes showed electrolytic nature. The complexes showed higher antibacterial and antifungal activities than free Schiff base ligands.

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