

Spectral, Thermal, X-Ray and Antimicrobial Studies of Newer Tetradentate N₂O₂ Schiff Base Complexes of First Transition Series

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ABSTRACT

Asymmetrical tetradentate complexes of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) of Schiff bases which are synthesized from o-phenylenediamine, 3-Acetyl-6-methyl-pyran-2, 4-dione and 5-bromo salicylaldehyde have been synthesized. The structures of ligands and complexes are characterized by elemental analysis, magnetic susceptibility, thermal analysis, X-ray diffraction, ¹H-NMR, mass, IR, UV-visible spectra, and conductometry. TGA/DSC spectral and kinetic parameter of the complexes was observed keenly. The ligand field parameters have been characterized for Mn(II), Fe(III), Co(II), complexes, which recommend octahedral geometry, and square planar geometry for Ni(II) and Cu(II). The X-ray diffraction data proposes monoclinic crystal system for all five complexes. The ligand and their metal complexes were subjected for antibacterial activity against Escherichia coli and Staphylococcus aureus and fungicidal activity against Trichoderma and Aspergillus Niger.

Keywords: Dehydroacetic acid, Tetradentate Schiff base, Thermal analysis, Powder X-ray diffraction, Antimicrobial activity

INTRODUCTION

The contribution of Schiff Bases and its complexes with metal in the ocean of coordination chemistry [1], medicinal, analytical, supramolecular chemistry is due to their capability of chelation with variety of metal ions. So researcher and chemist infatuated with the idea of use it in Catalysis [2] or use it as potential antibacterial [3], antifungal [4-6], antitumor [7,8] anti-tuberculosis [9], antioxidant [10], DNA cleavage [11] agents. It is well known fact that asymmetrical Schiff bases with N₂O₂ donor atoms are Igo toco-ordinate with various metal ions forming stable compound with aliphatic as well as aromatic compound i.e. 1,2-diamines and 3-Acetyl-4-hydroxy-6-methyl-2H-pyran-2-one. Dehydroacetic acid serves as a precursor for the synthesis of large number of heterocyclic derivatives [12]. In addition the derivatives of DHA are well known to possess potential anti-fungal and anti-microbial properties [13]. After going through literature it was revealed that it is more challenging to prepare asymmetrical Schiff bases of this type [14].

In this paper we are proclaiming our earlier work of tetradentate Schiff bases formed by the reaction of o-phenylenediamine, DHA, and 5-bromo Salicylaldehyde (**Figure 1**). The complexes of various color of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with this tetradentate ligands were synthesized and characterized.

MATERIALS AND METHODS

Merck was the supplier for all reagents and solvents. DHA, o-phenylenediamine, and 5-bromoSalicylaldehyde of AR grade were used for synthesis of ligand. AR grade metal chlorides were also used for the formation of the complexes.

Synthesis of ligand

There are several methods to prepare Schiff bases as, beginning from Hugo Schiff. L was prepared by using reported methods with some alteration [15]. It's a two-step synthesis; in the first step mono-Schiff base compound was prepared

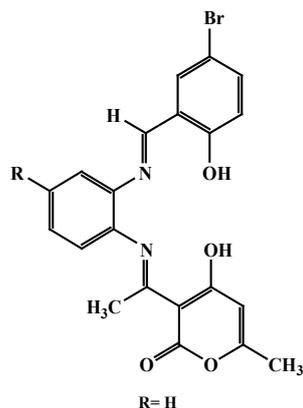


Figure 1: Structure of Ligand.

by refluxing 50 ml solution of (10 mmol) of DHA and (10 mmol) *o*-phenylenediamine in absolute ethanol for about 3 hours. The progress of reaction was monitored via thin layer chromatography. The resulting mono Schiff base thus formed was then refluxed with 10 mmol of 5-bromo Salicylaldehyde to synthesis final product. Product was then cooled at room temperature and collected by filtration, followed by recrystallization in super dry ethanol. (Yield: 75%).

Synthesis of metal complexes

Metal complexes were prepared by mixing a stoichiometric ratio (1:1) by dissolving in methanol. The ligand (0.01 mol) and metal chloride (0.01 mol) are mixed in hot condition with continuous stirring [16]. The mixture was heated at reflux for about 3 to 4 hours. On cooling, the volume of reaction mixture is reduced to half, then colored solid metal complex is appeared. Thus obtained solid metal complex was purified by petroleum ether and dried over vacuum desiccator (yield: 75%).

Physical measurement

The CHN analysis was carried out on Thermo Scientific (FLASH 2000) CHN elemental analyser. ¹H-NMR spectra of ligand were recorded on FT NMR spectrometer (400 MHz₂) model Advance-II (Bruker) in CDCl₃ as a solvent using tetramethylsilane as internal standard. IR study has been carried out on Perkin Elmer-Spectrum RX-I FTIR spectrometer using KBr pellets. These three facilities are availed by SAIF, Punjab University Chandigarh. The TGA/DSC and XRD were recorded on TA Inc. SDT-2790 and Pan analytical X'Pert Pro respectively. All electronic absorption spectra of the complexes and ligand were chronicled on Shimadzu 1800 spectrometer. Molar conductance of complexes was probed on Elico CM 180 conductivity meter using 10⁻³ M solution in DMF. Magnetic susceptibility of the metal complexes is investigated on a Guoybalance at room temperature using Hg[Co(SCN)₄] as a calibrator.

RESULTS AND DISCUSSION

Table 1 indicates physical characteristics, as CHN, mp, color and molar conductance data of ligand and metal complexes. The data shows equimolar stoichiometry (metal:ligand) and satisfying general formula [ML(H₂O)₂], where M=Mn(II), Fe(III), Co(II) and [ML], where M=Ni(II) and Cu(II). The study of magnetic properties reveal those two types of geometry for the complexes. One octahedral for Mn(II), Fe(III) and Co(II) at room temperature with two water molecules coordinated to metal ion. Existence of two coordinated water molecules was further confirmed by weight loss before 270°C in TGA-DSC analysis. Second square-planar geometry for Ni(II), Cu(II) complexes at room temperature.

Table 1: Physical characterization, analytical and molar conductance data of compounds.

Compound Molecular formula	Mol.Wt.	M.P/Decomp Temp. °C	Color	Molar conduc. Mho cm ² mol ⁻¹	Found (calculated)			
					C	H	N	M
(H ₂ L) C ₂₁ H ₁₇ N ₂ O ₄ Br	442.10	189	Dark Yellow	-----	56.71 (57.16)	3.69 (3.88)	6.87 (6.35)	-----
[LMn(H ₂ O) ₂]	496.21	234	Brown	19.20	50.22 (50.83)	2.65 (2.45)	5.85 (5.65)	11.55 (11.07)
[LFe(H ₂ O) ₂]	497.12	260	Reddish Brown	42.21	50.23 (50.74)	2.63 (2.55)	5.98 (5.64)	11.86 (11.23)
[LCo(H ₂ O) ₂]	500.21	223	Faint Red	12.40	50.75 (50.42)	2.95 (2.55)	5.85 (5.60)	12.11 (11.78)
[LNi]	499.97	220	Faint Red	21.20	50.89 (50.45)	3.12 (2.60)	5.88 (5.60)	12.10 (11.74)
[LCu]	504.82	237	Green Brown	18.10	50.22 (49.96)	2.85 (2.55)	5.43 (5.55)	12.45 (12.59)

¹H-NMR spectra of ligand

The ¹H NMR spectra of free ligand in CDCl₃ at room temperature shows the following signals. 2.07 δ (s, 3H, C₆-CH₃), 2.13 δ (s, 3H, N=C-CH₃), 5.83 δ (s, ¹H, C₅-H), 6.73-7.04 δ (m, aromatic protons), 8.96 δ (s, ¹H, N=C-H), 9.98 δ (phenolic (-OH) hydrogen of phenyl ring) and 15.89 δ (s, ¹H, enolic OH of DHA moiety) [12,17,18].

FTIR spectra

The IR data of ligand (H₂L) and its metal complexes are listed in **Table 2**. It depicts prominent bands at 3296, 1689, 1656, 1360 and 1212 cm⁻¹ assignable to ν OH, ν C=O (lactone carbonyl), ν C=N (azomethine), ν C-N (aryl azomethine) and ν C-O (phenolic) stretching modes respectively [19,20]. The presence of a strong broad band in the 3296 cm⁻¹ region, in the spectra of the ligand, which is not observed in complexes elucidates coordination of phenolic oxygen to the metal ion by deprotonation [21]. Resulting up swing to an extent of 40 cm⁻¹ to 60 cm⁻¹ in the ν C-O (phenolic) band [22]. This shift further confirms the involvement of the enolic oxygen in C-O-M bond [23]. Chelation by nitrogen of azomethine (C=N) is confirmed by observing band at 1656 cm⁻¹ in the spectra of ligand, which shifts to lower frequency 1603 cm⁻¹ to 1632 cm⁻¹ when complex is formed [24]. This change can be supported by transfer of electrons from nitrogen to the vacant d-orbitals of the metal [25]. Finding new bands in the 447-565 and 410-480 cm⁻¹ regions confirms the M-O and M-N bonding respectively [26]. No change in skeletal vibrations (C=C) upon complexation. The presence of coordinated water is confirmed by the appearance of strong band in the 3027 cm⁻¹ to 3096 cm⁻¹ region in case of Mn(II), Fe(III) and Co(II), which is also supported by appearance of non-ligand band in 825 cm⁻¹ to 846 cm⁻¹ region, quoted for rocking mode of water [21,27].

Table 2: IR data of ligand and metal complexes.

Compound	IR band frequency (cm ⁻¹)							
	ν (OH)	ν (C=O)	ν (C=N)	C=C	C-N	C-O	M-O	M-N
L	3296	1689.3	1656.7	1566.8	1360	1212	-	-
M _n -L	3027	1687.2	1626	1517.7	1330	1256	526	480
F _e -L	3096	1682.1	1632	1567.1	1325	1257	565.2	478.2
CO-L	3088	1679.0	1624	1566.0	1321	1285	550.8	447.1
Ni-L	3025	1684.0	1620	1566.0	1327	1260	447.3	410
Cu-L	3284	1681.2	1603	1566.0	1321	1267	525.1	477.1

Magnetic susceptibility and electronic absorption spectra

The electronic absorption spectrum of Mn(II) complex contains three bands at 14727, 24691 and 26455 cm⁻¹ assignable to the transitions 6A_{1g} → 4T_{1g}, 6A_{1g} → 4T_{2g} and charge transfer respectively. Magnetic moment value 5.84 BM matches with standard value (5.92 BM) corresponding to octahedral geometry for Mn(II) complex [28,29]. The electronic absorption spectra of Fe(III) complex show three strong bands at 12787, 18621 and 34364 cm⁻¹ which may be assigned to the transitions 6A_{1g} → 4T_{1g}(4D), 6A_{1g} → 4T_{1g} and charge transfer respectively. Electronic transitions together with magnetic moment value 5.83 BM indicate high spin octahedral geometry for Fe(III) complex [30]. Co(II) complex shows three bands at 10660, 18796 and 26881 cm⁻¹ which may be attributed to the transitions 4T_{1g} → T_{2g}(F), 4T_{1g} → 4A_{2g}(F) and charge transfer respectively. Electronic transitions along with magnetic moment value 4.55 B.M. suggest high spin octahedral geometry for Co(II) complex [30,31]. The octahedral geometry is further supported by ratio ν₂/ν₁=1.750 which is close to the value expected for octahedral geometry. The electronic absorption spectra of Ni(II) complex consist of two bands at about 17361 cm⁻¹ and 26385 cm⁻¹ assignable to 1A_{1g} → 1T_{2g} and charge transfer transitions respectively. Observed electronic transitions, the diamagnetic nature and red color of the complex suggest square planar geometry for Ni(II) complex [31,32]. Cu(II) shows three bands at 16366, 26385 and 37313 cm⁻¹ assignable to the transitions 2B_{1g} → 2A_{1g} and two intra ligand charge transfer bands. These electronic transitions and observed 1.80 BM magnetic moment value suggest square-planar geometry around Cu(II) [13,33].

Thermal analysis

The TG/DSC analysis of all Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes was done from ambient temperature to 1000°C in nitrogen atmosphere using α-Al₂O₃ as reference. The TG curve of Mn(II) complex shows first mass loss 6.39% (calcd. 6.40%) in the range 160-230°C and an endothermic peak in this region ΔT min=200°C, indicating removal of two coordinated water molecules. The second step is slow decomposition from 250°C to 1000°C with 14% mass loss. This can be further confirmed by observing broad exotherm in DSC with ΔT max=378°C, indicating that the complex is thermally quite stable. The thermal profile of Fe(III) complex shows mass loss 4.7% (calcd. 4.64%) in the range 160°C-230°C and an endothermic peak in this region ΔT min=217°C, indicating loss of two coordinated water

molecules [34]. The anhydrous complex first show slow decomposition from 230°C to 645°C with mass 32.66% (calcd.32.44%) loss and a broad exotherm $\Delta T_{\max}=360^\circ\text{C}$ in DSC may be attributed to removal of non-coordinated part of ligand. The second step decomposition is sharp from 645°C to 675°C with mass loss of 14.50% (calcd. 14.85%) a sharp endotherm in DTA at 650°C is observed for this step. The third step decomposition is from 675°C to 820°C with 19% mass loss. The mass of the final residue 8.2% does not corresponds to any stoichiometry of end product. The thermogram of Co(II) complex show mass loss 6.6% (calcd.6.8%) in the range 160°C to 240°C and an endothermic peak in this region $\Delta T_{\min}=230^\circ\text{C}$, indicates loss of two coordinated water molecules [13,30]. The anhydrous complex first show slow decomposition in 240°C to 500°C range with 27% mass loss (calcd.27.01%) and a broad exotherm $\Delta T_{\max}=316^\circ\text{C}$ in DSC may be attributed to removal of non-coordinated part of ligand. The second step decomposition at 500°C to 850°C, with mass loss of 53.30% (calcd.53.08%) corresponds to decomposition of coordinated part of ligand. A broad endotherm in DSC is observed for this step. The mass of the final residue corresponds to stable CoO with mass 13.36% (calcd.13.85%).

The TG curve of Ni(II) complex, show three step decomposition. No mass loss up to 230°C indicates absence of coordinated water in these complexes. The first step from 230°C to 350°C, with a mass loss 11.57% (calcd. 11.60%), an endothermic peak $\Delta T_{\min}=244.62^\circ\text{C}$ in DSC may be attributed to the decomposition of non-coordinated part of ligand. The sudden decomposition in second step from 350°C to 400°C with mass loss 10.51% (calcd.10.65%), an endothermic peak $\Delta T_{\min}=359.29^\circ\text{C}$ in DSC. Third decomposition slow and starts from 400°C to 800°C with mass loss 52.99%, an exothermic peak in DSC at $\Delta T_{\max}=423.73^\circ\text{C}$ may corresponds to removal of coordinated part of ligand. The mass of the final residue 11% does not corresponds to any stoichiometry of end product.

In the TG curve of Cu(II) complexes no mass loss up to 250°C indicates absence of coordinated water in these complexes [35]. In the TG curve of Cu(II) complex, the first step of decomposition from 250°C to 350°C, with a mass loss 26.70% (calcd. 25.25%), an exothermic peak $\Delta T_{\max}=265.47^\circ\text{C}$ in DSC may be attributed to the removal of non-coordinated part of ligand. The second slow step from 350°C to 650°C with mass loss 21.50% (calcd.21.46%), an exothermic peak $\Delta T_{\max}=438.90^\circ\text{C}$. The third step starts from 650°C to 850°C with mass loss 39.43% (calcd.40.46%) a broad endotherm is observed in same region in DSC corresponds to decomposition of coordinated part of ligand. The mass of the final residue corresponds to stable CuO, 10.5% (calcd.10.82%).

Kinetic calculations

The kinetic and thermodynamic parameters viz ΔG (free energy change), ΔS , z (pre-exponential factor), E_a and n (order of reaction), together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Horowitz-Metzger (HM) approximation method [36] and Coats-Redfern integral method [37] The data is arranged in **Table 3**. The results show that the values obtained by two methods are analogous. Low values of E_a of the complexes are indicating the autocatalytic effect of metal ion after thermal decomposition.

Table 3: The kinetic parameter of metal complexes calculated by the methods Horowitz-Metzger (HM) and Coats-Redfern (CR).

Complex	Step	n	Method	E_a (kJ)mol ⁻¹	Z S ⁻¹	ΔS JK ⁻¹ mol ⁻¹	ΔG kJ mol ⁻¹	Correlation coefficient (r)
Mn (II)	I	1.35	HM	35.14	58320	-159.28	41.63	0.9997
			CR	34.08	172113	-111.99	41.93	0.9986
	II	1.35	HM	24.08	61868	-132.69	36.73	0.9989
			CR	23.99	362280	-89.69	32.50	0.9980
Fe (III)	I	0.55	HM	33.99	44568	-103.76	42.20	0.9999
			CR	31.54	47183215	-104.61	39.81	0.9987
	II	0.55	HM	40.47	73267	-120.17	55.32	0.9999
			CR	38.83	35088264	-91.63	50.16	0.9999
CO (II)	I	0.51	HM	32.42	53248	-129.69	47.98	0.9980
			CR	31.88	75580	-85.00	42.08	0.9989
Ni (II)	I	0.51	HM	53.89	66843	-159.16	66.48	0.9990
			CR	51.72	2044177	-130.71	62.06	0.9979
	II	0.39	HM	28.03	42848	-132.92	42.86	0.9999
			CR	27.65	625548707	-85.97	37.24	0.9999
Cu (II)	I	1.13	HM	62.07	124015	-152.34	70.37	0.9981
			CR	59.74	112875	-153.12	69.73	0.9952
	II	0.35	HM	17.25	29812	-142.44	29.72	0.9992
			CR	17.56	425170645	-87.17	25.19	0.9995

Powder X-ray diffraction

Scanning of X-ray diffractogram of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) metal complexes of L is done at wavelength 1.543 Å in the range 5° to 100°. The X-ray diffraction pattern of these complexes compared with major peaks of relative intensity greater than 10% has been indexed to their hkl value by using computer program [38]. The diffractogram of Mn(II) complex of L had nine reflections with maxima at $2\theta=8.123^\circ$ corresponding to d value 10.87616 Å. The unit cell of Mn(II) complex of L yielded values of lattice constants, $a=14.69362$ Å, $b=5.101341$ Å, $c=12.86531$ Å and unit cell volume $V=929.98359$ Å³. The diffractogram of Fe(III) complex of L shows eight reflections with maxima at $2\theta=10.673^\circ$ corresponding to d value 8.28255 Å. The unit cell of Fe(II) complex of L yielded values of lattice constants, $a=7.874721$ Å, $b=16.62674$ Å, $c=4.850123$ Å and unit cell volume $V=625.59328$ Å³. The diffractogram of CO(II) complex of L had eight reflections with maxima at $2\theta=5.924^\circ$ corresponding to d value 14.90744 Å. The unit cell parameters of Co(II) complex of L yielded values of lattice constants, $a=15.90439$ Å, $b=7.102246$ Å, $c=8.499650$ Å and unit cell volume $V=897.70014$ Å³. The diffractogram of Ni(II) complex of L had ten reflections with maxima at $2\theta=10.533^\circ$ corresponding to d value 8.39194 Å. The unit cell of Ni(II) complex of L yielded values of lattice constants, $a=14.44839$ Å, $b=8.387201$ Å, $c=7.482108$ Å and unit cell volume $V=897.24919$ Å³. The diffractogram of Cu(II) complex of L had Fourteen reflections with maxima at $2\theta=10.598^\circ$ corresponding to d value 8.35818 Å. The unit cell of Cu(II) complex of L yielded values of lattice constants, $a=11.67385$ Å, $b=9.076698$ Å, $c=8.643076$ Å and unit cell volume $V=885.63313$ Å³. In respect of these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \gamma = 90^\circ \neq \beta$ required for sample to be monoclinic were tested and found to be satisfactory. Hence it can be concluded that Mn(II), Fe (III), Co(II), Ni(II) and Cu(II) complex of L has monoclinic crystal system. Density values of the complexes were determined practically by using specific gravity method [39] and found to be 2.5002, 2.3560, 2.8890, 2.9568 and 3.2345 gcm⁻³ for Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes respectively. Where theoretical density found to be 2.5174, 2.3346, 2.8965, 2.9789 and 3.2378 gcm⁻³ for respective complexes, and find near to experimental value. By using experimental density values, molecular weight of complexes, Avogadro's number and volume of the unit cell were computed.

Antimicrobial activity

Ligand and metal complexes are subjected for antimicrobial activity against bacteria such as *Escherichia coli* and *Staphylococcus aureus* by paper disc plate method [36]. The compounds were tested at the concentration 500 ppm and 1000 ppm in DMF, considering Ciproflaxin as standard (Table 4). Mycelial dry weight method is used for fungicidal activity, compounds were tested against *Trichoderma* and *Aspergillus Niger* [40]. The activity is tested at 250 and 500 ppm in DMF and depicted in (Table 5) with comparison with standard.

Table 4: Antibacterial activity of compounds.

Test Compound	Inhibition Zone (mm)			
	<i>E.Coli</i>		<i>Staphylococcus</i>	
	500 ppm	1000 ppm	500 ppm	1000 ppm
Ciproflaxin	29	32	31	35
(H ₂ L)	11	14	11	14
[LMn(H ₂ O) ₂]	11	15	11	16
[LFe(H ₂ O) ₂]	11	15	11	16
[LCO(H ₂ O) ₂]	13	17	11	16
[LNi]	15	18	12	16
[LCu]	19	21	16	19

Table 5: Yield of Mycelial dry weight in mg (% inhibition).

Test Compound	<i>Aspergillus Niger</i>		<i>Trichoderma</i>	
	250 ppm	500 ppm	250 ppm	500 ppm
Control	79	79	70	70
(H ₂ L)	47(41)	19(76)	29(59)	17(76)
[LMn(H ₂ O) ₂]	36(54)	14(82)	26(63)	05(93)
[LFe(H ₂ O) ₂]	37(53)	17(78)	27(61)	08(89)
[LCO(H ₂ O) ₂]	36(54)	13(84)	21(70)	02(97)
[LNi]	31(61)	10(87)	12(83)	02(97)
[LCu]	34(57)	08(90)	10(86)	01(99)

Observing Tables 4 and 5, conclusion made that the inhibition by metal complexes is more than a ligand [33,36,40]. Solubility of metal complexes in organic solvents increases its activity [36]. Hydrogen bonding with active center of cell may responsible for enhanced activity [41,42].

CONCLUSION

In present investigation we report synthesis of ligand and its transition metal complexes. Spectral study suggests that azomethine nitrogen and phenolic oxygen are involved in the coordination with metal ions (**Figure 2**). Proposing octahedral geometry for Mn(II), Fe(III) and Co(II), complexes, and square- planar geometry for Ni(II) and Cu(II) complexes. It is concluded that the ligand is dibasic in nature and ONNO tetradentate metal complexes are biologically active and show enhanced antimicrobial activities compared to its free ligand (**Figure 3**). The XRD reveals monoclinic crystal system for all Mn(II), Fe (III), Co(II), Ni(II) and Cu(II) complexes. Thermal study predicts thermal behaviour of complexes (**Figure 4**).

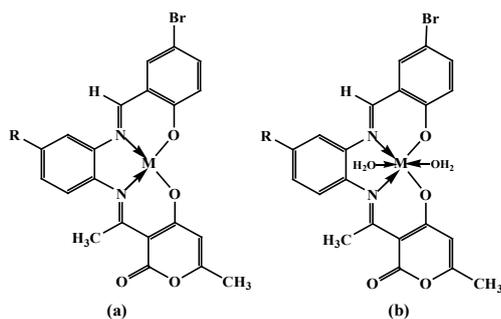


Figure 2: (a) The proposed structure of the complexes Where M= Ni(II),Cu(II); (b) The proposed structure of the complexes Where M=Mn(II),Fe(III),Co(II) and R=H.

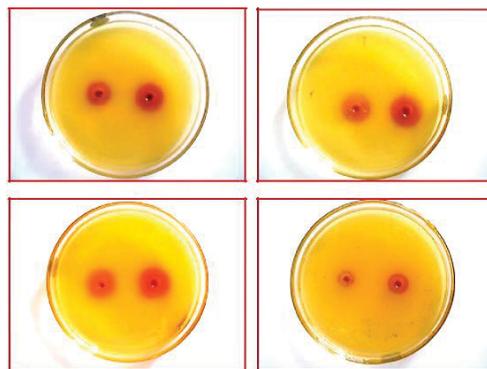


Figure 3: Antimicrobial Study of Ligands and Complexes at 500 ppm and 1000 ppm.

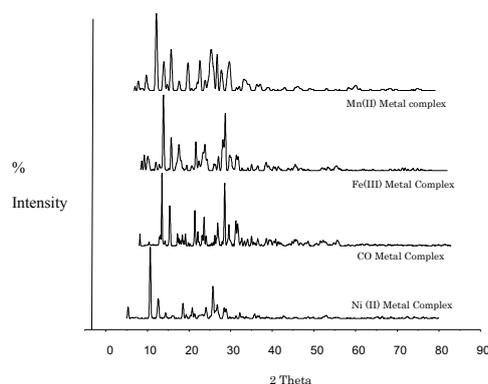


Figure 4: XRD of Four complexes.

ACKNOWLEDGEMENT

The Authors are thankful to Principal Milind College of Science, for providing laboratory facility, and SAIF Punjab University, Chandigarh for providing CHN, IR, ¹HNMR, Mass and XRD facility. Also grateful to USIC, Shivaji

University, Kolhapur for providing TGA-DSC facility, and Head Dept. of Biotechnology Milind college of science, Aurangabad, for biological activity.

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