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Research Article

SYNTHESIS, SPECTRAL, THERMAL AND ANTIMICROBIAL ACTIVITIES OF Mn (II) AND Fe (III) SCHIFF BASE METAL COMPLEXES

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Abstract

A new transition metal complexes of Mn(II) and Fe(III) were prepared from bidentate Schiff base. The Schiff base ligand synthesized from the condensation of P-chlorobenzaldehyde and 2-amino-4-hydroxy-6-methylpyrimidine (L_5) in alcohol medium. These metal complexes were characterized on the basis of their micro analytical data, molar conductance, magnetic susceptibility, IR, UV-Vis, ^{1}H NMR, X-ray diffraction, thermogravimetric analysis. The ligand and their metal complexes were screened for fungicidal activity against various fungi like *Aspergillus niger, Penicillium chrysogenum, Fusarium moneliforme* and *Aspergllus flavus*. The antibacterial activity against various bacteria like *Escherichia coli, Salmonellatyphi, Staphylococcus aureus, B.subtilis*. The result indicated that the complexes exhibited good antifungal and antibacterial activities.

Keywords: Schiff bases, Transition metal complexes, Thermal analysis, Powder X-ray diffraction, Antimicrobial activity.

Introduction

The Schiff bases and their metal complexes have more importance recently [1-5] because of their application as biological, biochemical, analytical, antimicrobial, anticancer, antibacterial, antifungal and anti tumor activity. They have been studied as a class of ligands [6-8] and are known to coordinate with metal ions through the azomethine nitrogen atom. The synthesis of transition metal complexes with Schiff base ligands are studied due to sensitivity, selectivity and synthetic flexibility towards metal atoms [9]. They used as catalyst, in medicine like antibioticsand anti-inflammatory agents and in the industry as anticorrosion [10-16]. A search of literature revels that no work has been done on the transition metal complexes of the Schiff bases derived from 2-amino-4-hydroxy-6-methylpyrimidine and P-chlorobenzaldehyde. In this communication we report the synthesis of bidentate Schiff bases formed by the condensation of 2-amino-4-hydroxy-6-methylpyrimidine and P-chlorobenzaldehyde (Fig.5). The solid complexes of Mn(II) and Fe(III)

with these ligands have been prepared and characterized by different physico-chemical methods.

Materials and Methods

Reagents and solvents

2-amino-4-hydroxy-6-methylpyrimidine (Aldrich sigma), P-chlorobenzaldehyde, metal nitrate of (AR grade) was used for synthesis of ligand and metal complex.

Synthesis of ligand

The ligand was prepared by a modification of the reported methods [17-19]. The Schiff base ligand has been synthesized by refluxing a mixture of 0.01 mol (1.4057g) of P- chlorobenzaldehyde and 0.01 mol (1.2513 g) of 2-amino-4-hydroxy-6-methylpyrimidine in 50 ml super dry ethanol refluxed for about 4h. Schiff base thus formed was cooled to room temperature and collected by filtration, followed by recrystallization in

ethanol and dried *in vacuo* over anhydrous calcium chloride (Yield:75%).

Synthesis of metal complexes

To a hot ethanol solution (25ml) of the ligand (2 mol) and (25ml) of metal Nitrate (1mol) was added with constant stirring. The pH of reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 3 h. The precipitated solid metal complex was filtered off in hot condition and washed with hot ethanol and dried over calcium chloride in vacuum desiccators. (Yield: 70%)

Physical Measurement

IR spectra were recorded on FTIR (ATR)-BRUKER - TENSOR37 spectrometer using KBr pellets in the range of 4000-400 cm^{-1}. ^{1}H- NMR Varian mercury 300MHZ spectra of ligand were measured in $CDCl_3$ using TMS as internal standard. X-RD was recorded on BRUKER D8 Advance. TGA- DTA was recorded on Shimadzu. The carbon, hydrogen and nitrogen contents were determined on Elemental model vario EL-III. The UV-visible spectra of the complexes were recorded on model UV-1800, SHIMADZU spectrometer. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10^{-4} M solution in DMSO. Magnetic susceptibility measurements of the metal chelates were done on a Guoy balance at room temperature using $Hg[Co(SCN)_4]$ as a calibrate.

Results and Discussion

Schiff bases of 2-amino-4-hydroxy-6-methylpyrimidine and its complexes have a variety of applications including biological, clinical and analytical. The coordinating possibility of 2-amino-4-hydroxy-6-methylpyrimidine has been improved by condensing with a variety of carbonyl compounds. An attempt has been made to synthesize Schiff bases 2-amino-4-hydroxy-6-methylpyrimidine with P-chlorobenzaldehyde. Physical characteristics, micro analytical, and molar conductance data of ligand and metal complexes are given in (Table 1 and 2).The analytical data of complexes revels 2:1 molar ratio (ligand: metal) and corresponds well with the general formula $[ML(H_2O)_2]$ (where M= Mn(II) and Fe(III). The magnetic susceptibilities of Mn(II) and Fe(III) complexes at room temperature are consistent with high spin octahedral structure with two water molecules coordinated to metal ion. The presence of two coordinated water molecules was confirmed by TG-DTA analysis. The metal chelate solutions in DMSO show low conductance and supports their non-electrolyte nature.(Table 1)

1H-NMR spectra of ligand

The ^{1}H-NMR. Spectra of free ligand at room temperature show the following signals. 2.48 (s, 3H, Methyl hydrogen bonded to pyrimidine ring), 3.79 (s, 2H, Phenolic (OH) hydrogen of pyrimidine ring), 5.76 (s, 1H, Hydrogen bonded to pyrimidine ring), 7.95 (s, 1H, hydrogen bonded to azomethine carbon), 7.3-7.6 (D,4H, Aromatic H_a, H_b, protons of phenyl ring).

IR Spectra

The IR spectra of the complexes are compared with that of the ligand to determine the changes that might have taken place during the complexation.The bands at 3473, 1656, 1597, 1356, and 1230 cm^{-1} assignable to ν OH (intramolecular hydrogen bonded), ν C=C(aromatic), ν C=N (azomethine), ν C-N (aryl azomethine) and ν C-O (phenolic) stretching modes respectively[18-20] The absence of a weak broad band in the 3200-3400 cm^{-1} region, in the spectra of the metal complexes suggests deprotonation of the intramolecular hydrogen bonded OH group on complexation and subsequent coordination of phenolic oxygen to the metal ion. This is further supported by downward shift in C-O (phenolic) [21] with respect to free ligand. On complexation, the ν (C=N)[22] band is shifted to lower wave number with respect to free ligand, denoting that the nitrogen of azomethine group is coordinated to the metal ion. The ν C-N band is shifted to lower wave number with respect to free ligand, The IR spectra of metal chelates showed new bands in between the 500-800 and 400-500 cm^{-1} regions which can be assigned to ν M-O and M-N [23] vibrations respectively The IR spectra of Mn(II) and Fe(III) show a strong band in the 3050-3600 cm^{-1} region, suggesting the presence of coordinated water in these metal complexes. The presence of coordinated water is further confirmed by the appearance of non-ligand band in 830-840 cm^{-1} region, assignable to the rocking mode of water. The presence of coordinated water is also established and supported by TGA/DTA analysis of these complexes. Hence it is concluded that the coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule.

Thermogravimetric analysis

The dynamic TGA with the percentage mass loss at different steps have been recorded. The simultaneous TGA/DTA analysis of Mn(II) and Fe(III) was studied from ambient temperature to 1000 ^{0}C in nitrogen atmosphere using -Al$_2$O$_3$ as reference. An analysis of the thermogram of the complexes indicated that Mn(II) complexes of ligand L_5 (Fig.1) shows two step decomposition. The first weight loss 5.66%, in

between temp. 60-130^{0}C could be correlated with the loss of two lattice water (calcd 6.14 %). The anhydrous compound does not remain stable at higher temperature, it undergoes rapid decomposition in the range 130-650°C, with 80.89 % mass loss corresponds to decomposition of the complex (calcd. 81.75%) in second step. The decomposition is completed leading to the formation of stable residue of metal oxide MnO obs. 11.32 % (calcd. 12.09 %). In TG curve of Fe(III) complex of ligand L$_5$ (Fig.2) shows two step decomposition. The first weight loss 5.78 %, in between temp. 75-180^{0}C could be correlated with the loss of two lattice water (calcd 6.13 %). The anhydrous compound does not remain stable at higher temperature, it undergoes rapid decomposition in the range 180-585°C, with 65.51 % mass loss corresponds to decomposition of the complex (calcd. 66.67%) in second step. The decomposition is completed leading to the formation of stable residue of metal oxide Fe$_2$O$_3$ obs. 26.97 % (calcd. 27.19 %). The kinetic and thermodynamic viz the energy of activation (Ea), frequency factor (Z), entropy change (-ΔS) and free energy change (ΔG) for the non-isothermal decomposition of complexes have been determined by employing Horowitz-Metzger method [24] values are given in Table 3. The Calculated values of the given activation energy of the complexes are relatively low, indicating the autocatalysis effect of metal ion on the thermal decomposition of the complex. The negative value of

activation entropy indicates that the activated complexes were more ordered than the reaction was slow. The more ordered nature may be due to the polarization of bonds in the activated state, which might occur through charge transfer transitions [25].

Magnetic measurements and electronic absorption spectra

The electronic absorption spectrum of the L$_5$ Mn(II) complexes shows bands at 13477 cm-^{1} and 24875 cm-1 are assigned to ^{6}A$_1$g ^{4}T$_2$g and charge transfer transitions. The Mn(II) complexes were paramagnetic in nature indicates octahedral geometry[26,27]. The electronic absorption spectrum of the L$_5$ Fe(III) complexes shows bands at 29239 cm-1. These transitions may be assigned to charge transfer transitions. The Fe(III) complexes were paramagnetic in nature indicates octahedral geometry[28-30]. All the Mn (II) and Fe (III) complexes were paramagnetic in nature.

Molar Conductivity Measurements

The metal Mn(II) and Fe(III) complexes were dissolved in DMSO and the molar conductivity of 10^{-4}M of their solution at room temperature was measured. The lower conductance values of the complexes support their non-electrolytic nature of the compounds.

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

Compound	Mol.Wt.	M.P. Decomp temp. ^{0}C	Colour	μ_{eff} B.M.	Molar Conduc. Mho. Cm^{2}mol^{-1}
L$_5$	247.68	142	White	--	----
Mn-L$_5$	586.33	>300	Brown	4.57	61.82
Fe-L$_5$	587.24	>300	Brown	7.70	51.30

Table 2. Elemental Analysis of Mn(II) and Fe(III) Complex:-

Compound	Found (Calculated)			
	C	H	N	M
L$_5$	58.18 (58.18)	4.07 (4.07)	16.97 (16.97)	-
Mn-L$_5$	49.16 (49.10)	4.12 (4.00)	14.33 (14.20)	9.36 (9.25)
Fe-L$_5$	49.08 (49.00)	4.11 (4.04)	14.31 (14.10)	9.51 (9.40)

Powder x-ray diffraction

The x-ray diffractogram of Mn(II) and Fe(III) complexes of L$_5$ was scanned in the range 20-80° at wavelength 1.540 Å(Fig.3,4). The diffractogram and associated data depict the 2 value for each peak, relative intensity and inter-planar spacing (d-values). The diffractogram of Mn(II) complex of L$_5$ had ten

reflections with maxima at 2 = 6.63° corresponding to d value 6.65Å. The diffractogram of Fe(III) complex of L$_5$ had thirteen reflections with maxima at 2 = 6.60° corresponding to d value 6.69Å. The x-ray diffraction pattern of these complexes with respect to major peaks of relative intensity greater than 10% has been indexed by using computer programmed [31]. The above indexing method also yields Miller indices (hkl),

42

unit cell parameters and unit cell volume. The unit cell of Mn(II) complex of L_3 yielded values of lattice constants, a= 9.45Å, b=10.32 Å, c = 17.44 Å and unit cell volume V=1700.81853 Å^3. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β = γ =90^0 required for sample to be orthorhombic were tested and found to be satisfactory. Hence it can be concluded that Mn(II) complex has orthorhombic crystal system. The unit cell of Fe(III) complex of L_5 yielded values of lattice constants, a=10.21 Å, b=9.99Å, c = 19.21Å and unit cell volume V=1959.37953 Å^3. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β = γ =90^0 required for sample to be orthorhombic. Hence it can be concluded Mn(II) and Fe(III) complex

of L_5 has orthorhombic crystal system. The experimental density values of the complexes were determined by using specific gravity method [32,33] and found to be 1.0758 and 1.0392 gcm^{-3} for Mn(II) and Fe(III) complexes respectively. By using experimental density values, molecular weight of complexes, Avogadro's number and volume of the unit cell were calculated. Number of molecules per unit cell were calculated by using equation ρ = nM/NV and was found Mn(II) and Fe(III) complexes respectively. With these values, theoretical density were computed and found to be 1.0648 and 1.0282 gcm^{-3} for respective complexes. Comparison of experimental and theoretical density shows good agreement within the limits of experimental error [34].

Table: 3 The kinetic and thermodynamic parameters for decomposition of metal complexes

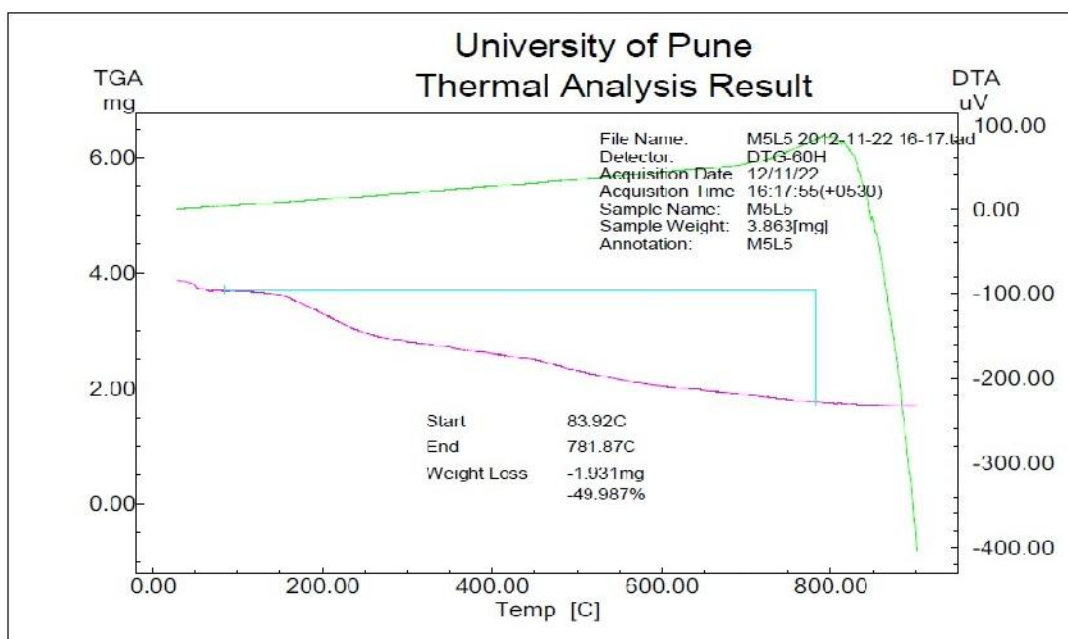| Complex	Step	Decomp. Temp. (^{0}C)	n	Ea (kJmole^{-1})	Z (S^{-1})	ΔS (JK^{-1}mole^{-1})	ΔG (kJmole^{-1})	Correl - ation coeffici- ent
Mn-L_5	I	330	0.6	10.44	1.99 ×10^4	-168.50	22.66	0.939
Fe-L_5	I	170	0.4	3.76	1.89 ×10^3	-185.49	13.64	0.948
	II	450	0.8	15.01	2.86 ×10^4	-167.00	29.53	0.981

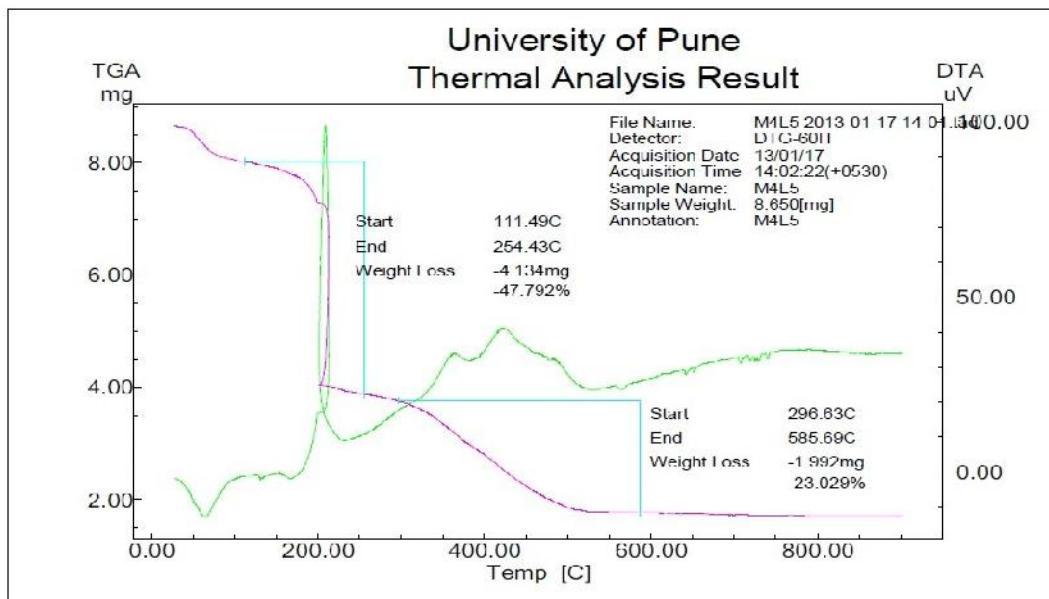**Fig. 1 TGA-DTA Curve of Mn (II) Complex of Ligand L_5**
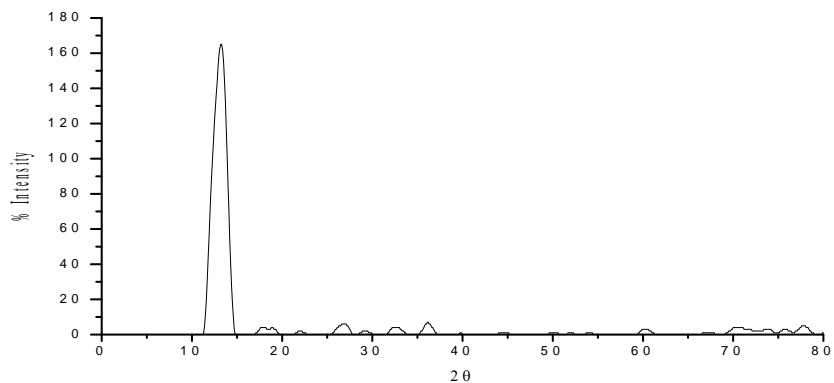
43

Fig. 2 TGA-DTA Curve of Fe (III) Complex of Ligand L$_5$
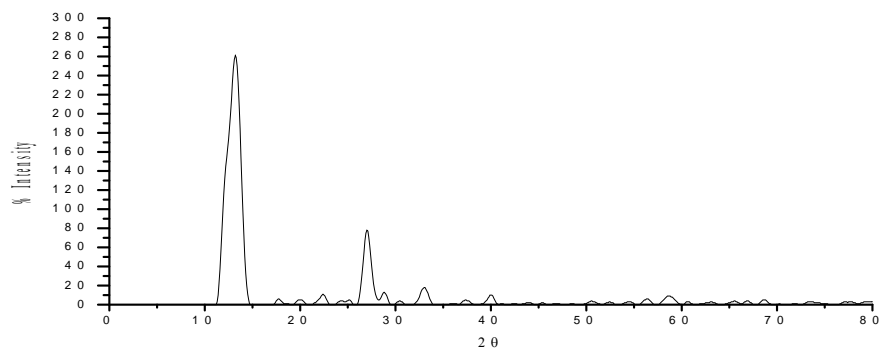

Fig.3 X-ray Diffractogram of Mn (II) complex of L$_5$

Fig.4 X-ray Diffractogram of Fe (III) complex of L$_5$

44

Table 4 Antifungal activity of ligands

Test Compound	Antigungal growth							
	Aspergillus niger		*Penicillium chrysogenum*		*Fusarium moneliforme*		*Aspergillus flavus*	
	1%	2%	1%	2%	1%	2%	1%	2%
L₅	RG	+ve	-ve	-ve	-ve	-ve	RG	+ve
Mn- L₅	+ve	-ve	-ve	-ve	-ve	-ve	+ve	RG
Fe- L₅	-ve	RG	-ve	-ve	-ve	RG	+ve	-ve
+ve control	+ve	+ve	+ve	+ve	+ve	+ve	+ve	+ve
-ve control (Griseofulvin)	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve

Ligand& Metal : +ve – Growth (Antifungal Activity absent)

 -ve - Growth (Antifungal Activity present)

 RG - Reduced Growth (More than 50% reduction in growth observed)

Table 5 Antibacterial activity of ligands and their metal complexes

Test Compound	Diameter of inhibition zone (mm)							
	E. coli		*Salmonella typhi*		*Staphylococcus aureus*		*Bacillus subtlis*	
	1%	2%	1%	2%	1%	2%	1%	2%
L₅	15mm	16mm	14mm	18mm	21mm	29mm	18mm	23mm
Mn- L₅	11mm	15mm	13mm	14mm	17mm	18mm	14mm	18mm
Fe- L₅	10mm	14mm	-ve	12mm	-ve	17mm	10mm	13mm
DMSO	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve
Penicillin	14mm	14mm	17mm	17mm	30mm	30mm	19mm	19mm

Ligand & Metal: - ve   - No Antibacterial Activity

Zone of inhibition   -   --mm

Antibacterial activity

Antifungal activity and Antibacterial activity of ligand and metal complexes were tested *in vitro* against fungal such as *Aspergillus niger ,Penicillium chrysogenum,Fusarium moneliforme, Aspergillus flavus* and bacteria such as *E. Coli, B.Subtilis*, *S. aureus* And *Bacillus subtlis* by paper disc plate method

[35-38] The compounds were tested at the concentrations 1% and 2% in DMSO and compared with known antibiotics *viz Griseofulvin* and *Penicilin*. (Table 4 and 5)., it is found that the inhibition by metal chelates is higher than that of a ligand and results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes [39]
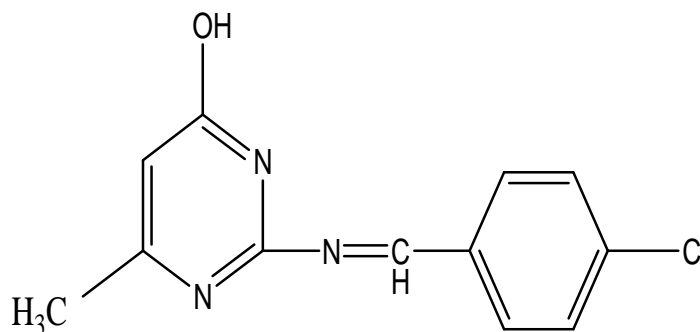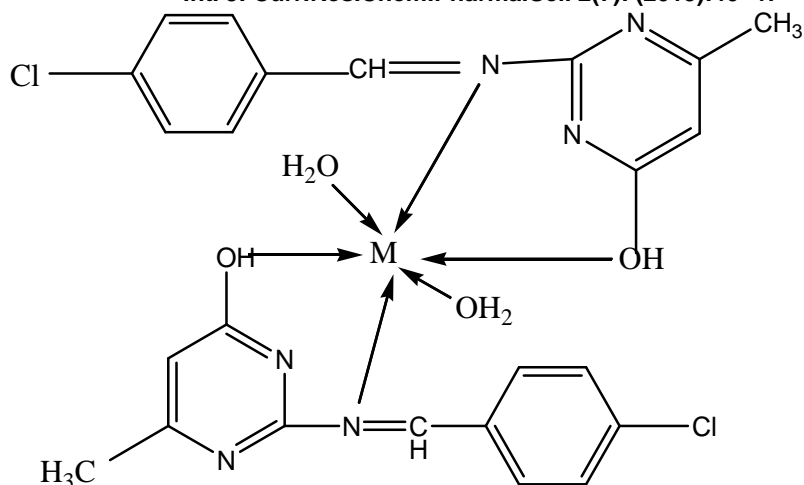

Figure 5. Structure of ligand

Figure 6. The proposed Structure of the complexes
When M= Mn(II) and Fe(III).

Conclusion

In the light of above discussion we have proposed octahedral geometry for Mn(II) and Fe(III) complexes. On the basis of the physico-chemical and spectral data discussed above, one can assume that the ligand behave as dibasic, NO bidentate, coordinating via phenolic oxygen and imino nitrogen as illustrated in Fig.6. The complexes are biologically active and show enhanced antimicrobial activities compared to free ligand. Thermal study reveals thermal stability of complexes. The X-ray study suggests monoclinic crystal system for Mn(II) and Fe(III) complexes.

Acknowledgments

References

[1] Mishra, Lallan and Sinha Ragini, *Indian J. Chem., Sect. A*, **29**, 1131(2000).
[2] Mukhopadhyay, Uday and Ray, Debashis, *Indian J.Chem., Sect. A*, **40**, 228(2001).
[3] K. Krishnankutty and Ummathur, Mohammed Basheer, *J. Indian Chem Soc.* **83**, 663(2006).

[4] Raj Debey, Kumar, *J. Indian Chem. Soc.*,**83**, 1087 (2006).
[5] P.Saritha, B. Reddy, Satyanarayan and Jayatyagaraju, *J. Indian Chem. Soc.*, **83**, 1204(2006).
[6] K. Arora, K.P. Sharma, *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 913(2003).
[7] P. A.Vigato, *S.* Tamburini, *Coord. Chem. Rev.*, **248**, 1717(2004).
[8 *T.*] Katsuki, *Coord. Chem. Rev.*, **140**, 189(1995)
[9] C. Spinu and A Kriza, *Acta Chim. Slov.*,**47**, 179(2000).
[10] B. Sun J. Chen, J.Y. Hu and Lix*, J Chin Chem. Lett.*, **12(II)**, 1043(2001).
[11] D.M. Boghaei and S. Mohebi, *Tetrahedron.*, **58 (26)**, 5357(2002).
[12] J. Liu, B. Wu, B. Zhang and Y. Liu, *Turk. J. Chem.*, **30**, 41(2006).
[13] G. J. P. Britovsek, V. V. Gibson, S. Mastroianni, D. C. H. Oakes, C. Red Shaw, Solan G. A., White A. J. P. and D. J. Williams, *Eur. J. Inorg. Chem.,* **(2)**, 431(2001).
[14] A. Budakoti, M. Abid and A. Azam *, Eur. J. Med. Chem.*, **41(I)**, 63(2006).
[15] V.X. Jin, S.I. Tan and J.D. Ranford, *Inorg. Chim. Acta.*, **358(3)**, 677(2005).
[16] N.K. Mehta and V.S. Agarwala, *Int. Corros. Cong. Proc.*, **13 (319)**, 1(1996).
[17] A. A. Osowole1, R. Kempe , R Schobert and S. A. Balogun, *Candian journal of pure and applied sciences,* **4(2)** ,1169-1178(2010).
[18] A.A. Osowole, R. Kempe, R. Schobert and K. Effenberger,. *Synth. React. Inorg. Met. Org. Chem. and Nano-Met. Chem* ,**41**, 825-833(2011).
[19] A.A. Osowole and E.J. Akpan, *European Journal of Applied Sciences* **4 (1)**, 14-20(2012).

[20] M.L. Sonmez, A.event, M.Sekerci,. *Russian Journal of Coordination Chemistry,* **30(9)**,655-659(2004).

[21] A.A. Osowole and R. O. Yoade, *Scientific Journal Of Applied Research,* **4** 101-106(2013).

[22] Sakthilatha D.and Rajavel R., *J Chem Pharm Res*, 5(1) 57-63(2013).

[23] M. Usharani, E. Akila And R. Rajavel, *International Journal of Recent Scientific Research,* **4(9)** 1385- 1390**(**2013).

[24] K., Arora *Indian J. Chem.*, **74**,589(1997).

[25] P. G. Avaji, B. N. Reddy and S. A Patil., *Trans. Met. Chem*, **31**, 842(2006).

[26] N. Sharada and M. C. Ganorkar, *Indian J. Chem.* 1988 , **27A** 542.

[27] V. S. Shrivastav and G. C. Saxena, *J. Indian Chem. Soc.*, **63** 578(1986).

[28] S. K. Sen Gupta, S. K. Sahani and R.N. Kapoor, I*ndian J. Chem.* 1980**, 19A** (7) 703.

[29] Anand Kumar, S. Gupta and V.D. Barhate, *Research Journal of Pharmaceutical, Biological and Chemical Sciences,* **3(3)**,1013-1026(2012).

[30] Abbas Noor Al-Shareefi, SalihHadiKadhim and Waleed Abbas Jawad, *Journal of Applicable Chemistry*, **2(3) ,**438-446(2013).

[31] J. R. Carvajal, T. Roisnel, Winplotr, *A Graphic Tool for Powder Diffraction, Laboratories* Leon brillouin (ceal/enrs) 91191 gif suryvette cedex, France (2004).

[32] E. Akila, M. Usharani, S. Vimala and R. Rajavel, *Che.Sci.Rev.Lett.,* **1(4)**,181-194 (2012).

[33] H.H. Horowitz, G. Metzger, *Anal. Chem*, **35**, 1464(1963).

[34] M.B. Deshmukh, S. Dhongade, S. Dasai, S.S. Chavan, *Indian J.Chem* **44**, 1659(2005)**.**

[35] H.H. Thornberry, *Phytopathology*, **40**,419(1950).

[36] V.G. Despande, S. Shaha, M.M. Despande., S.I. Habib, P.A. Kulkarni, *Asian Journal of Biochemical Pharmaceutical Research,* **1(3)**,63-70(2013).

[37] M.V.Lokhande, *Asian Journal of Chemistry*, **18(4)**, 2662-2668(2006).

[38] Ranjana Shastri, *World Journal of Pharmacy and Pharmaceutical Sciences*,**3(7)**,1814-1823(2014).

[39] A. K. Madhure, A. S. Aswar*, Am.J.Pharm. Tech.* Res, **3(6)**, 462-484. (2013)**.**

47