

PREPARATION, ELEMENTAL ANALYSIS, IR, ¹H NMR, UV-VISIBLE CHARACTERIZATION AND MICROBIAL EVALUATION OF Cu(II), Co(II), Ni(II), Mn(II), Cd(II) AND Hg(II) COMPLEXES DERIVED FROM SCHIFF'S BASE

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ABSTRACT

A chiral Mannich base, [1-((2-hydroxyphenyl)(piperidin-1-yl)methyl)thiourea] was prepared by treating with 2-hydroxy benzaldehyde, piperidine and thiourea. Using the above Schiff's base ligand, the metal complexes of Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Hg(II) were prepared. Schiff's base ligand and its metal complexes were characterized by physical methods such as elemental analysis, melting point, TLC, and spectral method such as IR, ¹H NMR, UV-Visible, ESR studies. For the complexes, molar conductivity and Magnetic susceptibility were also been carried out. The electronic spectra, elemental analysis and magnetic moment results proved that the complexes adopted octahedral geometry. The conductance

measurement showed that the complexes are non electrolytes proving their nonionic nature. The synthesized Schiff's base and its metal complexes were tested for their antifungal and antibacterial activity.

KEYWORDS: Piperidine, Thiourea, IR, ¹H NMR, UV-Visible and Microbial activity.

INTRODUCTION

Interest in the study of Schiff base thiourea has been growing because of their antimicrobial, anti-tuberculosis and anti-tumor activity.^[1,2] Schiff bases play an important role in inorganic chemistry, as they easily form stable complexes with most transition metal ions. The development in the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models

for biologically important species.^[3,4] Coordination compounds derived from aryl hydrazones have been reported to act as enzyme inhibitors and are useful due to their pharmacological applications.^[5,6] Schiff bases are organic compounds possessing the azomethine functional group. The hydrazones belong to this huge class of azomethines, characterized by the grouping $>C=N-N<$, they are distinguished from the other members of this class *viz.* imines, oximes etc., by the presence of inter linked nitrogen atoms. Hydrazones are usually obtained by condensing hydrazides with aldehydes or ketones.^[7,8] In view of the importance of such hydrazones, the present study is concerned with the synthesis and characterization of ligand and their Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Hg(II) metal complexes derived from the reaction of piperidine (0.1mole), 2-hydroxybenzaldehyde (0.1mole) and thiourea (0.1mole). The synthesized compounds were screened for their antifungal and antibacterial activity using standard drugs.

EXPERIMENTAL

Physical measurements

The used chemicals are analytical grade reagents and no need of further purification. The elemental analyses (CHN) were obtained from Thermo finnigam Italy, FLASH EA 1112 series. Magnetic susceptibilities were measured on a Guoy balance at room temperature using Hg[Co(SCN)₄] as calibrant. The molar conductance of the complexes was measured on ELICO CM-82 Conductivity Bridge in DMF solution at a concentration of 10^{-3} M. Infrared spectra of the ligand and its metal(II) complexes in KBr pellets were recorded in the spectral range $4000-350\text{ cm}^{-1}$ with Perkin Elmer Spectrum one FT-IR spectrometer. ¹H NMR spectra were recorded on AMX-400 NMR spectrometer, using TMS as internal standard and DMSO as a solvent. Electronic spectra were recorded on an Elico SL-164 DOUBLE BEAM UV-Vis Spectrophotometer in the range of 200-1200 nm. ESR spectra of Cu(II) complex were recorded as polycrystalline sample at room temperature, on X band of 9.1 GHz under the magnetic-field strength of 3200G.

Preparation of Schiff's base

The Schiff base was prepared by the reaction of 7.6 gm (0.1mole) thiourea was taken in a round bottom flask and 10 ml of water was added. To this solution 9.8 ml (0.1mole) of piperidine was added and stirred well for 15 minute by keeping the reaction mixture on a magnetic stirrer. 12.2 ml (0.1mole) of 2-hydroxybenzaldehyde was added to the above mixture and stirring was

continued under ice cold condition. The compound formed was filtered, washed and recrystallised using ethanol. The purity of the Schiff's base was checked by TLC.

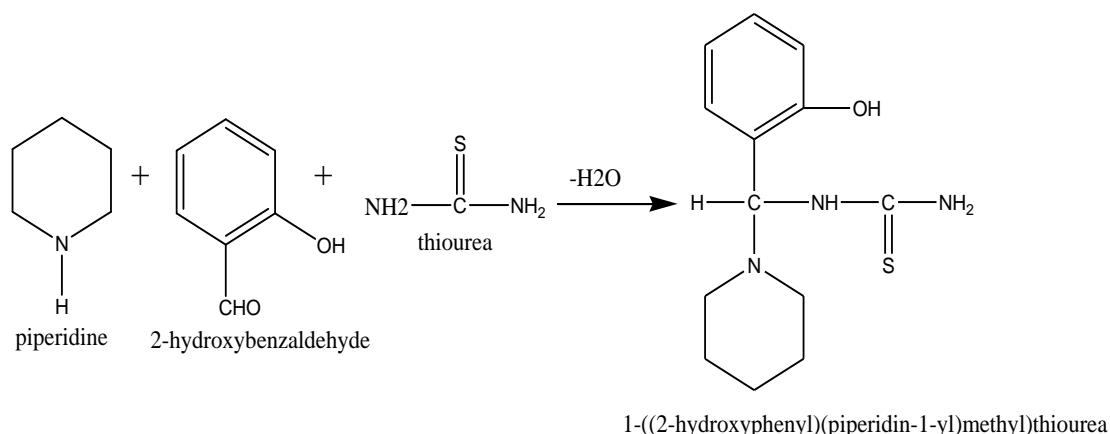


Figure 1: Preparation of ligand.

Preparation of complexes

The complexes were prepared by mixing the methanolic solution of the corresponding metal chlorides [Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Hg(II)] (0.1M) to the methanolic solution of the ligand in the mole ratio 1:2 respectively. The reaction mixture was refluxed on a water bath for 3 hours. On cooling solid was filtered, washed with methanol and chloroform mixture and dried over anhydrous CaCl₂ in desiccators.

RESULTS AND DISCUSSION

The analytical data of the ligand and its metal complexes are presented in table 1. The elemental analysis data indicates that the stoichiometry of the complexes are 1:2 (metal to ligand ratio) for Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Hg(II) complex. The prepared complexes were sparingly soluble in common organic solvents but soluble in DMSO and DMF. The observed molar conductance values measured in DMF solution fall in the range 15-20 Ohm⁻¹ cm² mol⁻¹ indicating that the complexes are non-electrolytic in nature.^[9,10] The Ni(II) complex shows magnetic moment of 2.93BM. The octahedral Ni(II) complex are reported to exhibit magnetic moment in the range of 2.80-3.40BM.,^[11,12] including spin orbital coupling contribution from ³A_{2g} and higher ³T_{2g} states. Hence the observed magnetic moment for the Ni(II) complex suggest that it may have octahedral geometry.^[13] The magnetic moment value of Mn(II) complex exhibits 5.73BM. Indicating it to be high spin type paramagnetic, it lies within the octahedral range which is very close to spin only value of 5.90BM. as the ground term is ³A_{2g} and thus supports the octahedral stereochemistry.^[14]

Table 1: Analytical, magnetic moment and molar conductance data of the ligand and its metal complexes.

Ligand / Complex	Mol. wt.	M. P. (°C)	Yield (%)	Elemental analysis (%): Found (Calc.)						μ_{ef} B.M	λ_M $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
				M	C	H	N	O	S		
$\text{C}_{13}\text{H}_{19}\text{N}_3\text{OS}$	265.4	210	70	--	58.84 (58.72)	7.22 (7.02)	15.83 (15.72)	6.03 (5.95)	12.08 (12.02)		
$\text{Cu}(\text{C}_{26}\text{H}_{36}\text{N}_6\text{O}_2\text{S}_2) \cdot 2\text{H}_2\text{O}$	628.3	275	75	10.11 (10.0)	49.70 (48.30)	6.42 (6.21)	13.38 (13.00)	10.19 (10.2)	10.21 (10.06)	1.94	15.20
$\text{Co}(\text{C}_{26}\text{H}_{36}\text{N}_6\text{O}_2\text{S}_2) \cdot 2\text{H}_2\text{O}$	623.7	275	75	9.45 (9.02)	50.07 (50.30)	6.46 (6.21)	13.47 (13.00)	10.26 (10.2)	10.28 (10.04)	4.84	19.85
$\text{Ni}(\text{C}_{26}\text{H}_{36}\text{N}_6\text{O}_2\text{S}_2) \cdot 2\text{H}_2\text{O}$	623.5	275	75	9.41 (9.02)	50.09 (49.30)	6.47 (6.13)	13.48 (13.00)	10.26 (10.1)	10.29 (10.06)	2.93	19.80
$\text{Mn}(\text{C}_{26}\text{H}_{36}\text{N}_6\text{O}_2\text{S}_2) \cdot 2\text{H}_2\text{O}$	619.7	275	75	8.87 (9.02)	50.39 (50.10)	6.51 (6.20)	13.56 (13.00)	10.33 (9.92)	10.35 (10.09)	5.73	18.76
$\text{Cd}(\text{C}_{26}\text{H}_{36}\text{N}_6\text{O}_2\text{S}_2) \cdot 2\text{H}_2\text{O}$	677.2	275	75	16.60 (16.1)	46.11 (45.30)	5.95 (5.61)	12.41 (12.00)	9.45 (9.22)	9.47 (9.26)	Dia	17.64
$\text{Hg}(\text{C}_{26}\text{H}_{36}\text{N}_6\text{O}_2\text{S}_2) \cdot 2\text{H}_2\text{O}$	765.4	275	75	26.21 (26.1)	40.80 (40.30)	5.27 (5.10)	10.98 (10.60)	8.36 (8.12)	8.38 (8.16)	Dia	16.15

Infrared spectral data of the Schiff's base and its complexes

The significant IR bands for the ligand [1-((2-hydroxyphenyl)(piperidin-1-yl)methyl)thiourea] as well as for its metal(II) complexes and their tentative assignments are compiled and represented in table 2. The broad band observed at 3412 cm^{-1} in the IR spectra of the ligand assigned to $\nu(\text{OH})$, which was found to have disappeared in all its Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Hg(II) respective complexes, There by indicating the involvement of Phenolic oxygen in bonding with metal ions through deprotonation.^[15,16] The new broad band appeared in all metal(II) complexes in the rang of $3335\text{-}3352 \text{ cm}^{-1}$ due to the presence of co-ordinated water molecules. The $\nu(\text{C}=\text{N})$ mode of the ligand appeared at 1640 cm^{-1} in the spectrum of the ligand has been found shifted to lower wave numbers in the spectra of the complexes indicates the involvement of nitrogen atom of the azomethine in binding with the metal ion. The band observed at 1235 cm^{-1} of the ligand is attributed to $\nu(\text{C}=\text{S})$ and it is shifted to higher wave numbers ($40\text{-}20 \text{ cm}^{-1}$) in all respective metal(II) complexes due to the formation of $\nu(\text{SH})$ band, it indicate the non-involvement in the complexation. The low frequency skeletal vibration due to M-O and M-N stretching provide direct evidence for complexation. In the present investigation the bands in the $520\text{-}529 \text{ cm}^{-1}$ and $416\text{-}452 \text{ cm}^{-1}$ region are due to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ vibration respectively.^[17,18]

Table 2: Characteristic IR frequencies of the ligand and its complexes (cm⁻¹).

Ligand/ complex	$\nu_{\text{H}_2\text{O}}$	ν_{OH}	ν_{NH}	$\nu_{\text{C}=\text{N}}$	$\nu_{\text{C}-\text{S}}$	$\nu_{\text{M}-\text{O}}$	$\nu_{\text{M}-\text{N}}$
C ₁₃ H ₁₉ N ₃ OS	--	3412	3112	1640	1235	--	--
Cu(C ₂₆ H ₃₆ N ₆ O ₂ S ₂) 2H ₂ O	3350	--	3109	1618	1270	525	425
Co(C ₂₆ H ₃₆ N ₆ O ₂ S ₂) 2H ₂ O	3335	--	3110	1620	1261	521	430
Ni(C ₂₆ H ₃₆ N ₆ O ₂ S ₂) 2H ₂ O	3340	--	3115	1623	1255	520	437
Mn(C ₂₆ H ₃₆ N ₆ O ₂ S ₂) 2H ₂ O	3352	--	3110	1620	1258	524	416
Cd(C ₂₆ H ₃₆ N ₆ O ₂ S ₂) 2H ₂ O	3340	--	3105	1615	1265	528	452
Hg(C ₂₆ H ₃₆ N ₆ O ₂ S ₂) 2H ₂ O	3345	--	3110	1610	1267	529	426

¹H NMR spectral data of the Schiff's base and complexes

The ¹H NMR spectra of the ligand showed a sharp peak at δ 12.2 (s, 1H) due to OH at 2-position of phenyl ring of 2-hydroxybenzaldehyde moiety has resonated, but in the spectra of metal complexes which has been disappeared indicating the involvement of phenolic oxygen in the coordination via deprotonation.^[19,20] The sharp peak at δ 10.08 (s, 2H, NH₂) appeared in ligand and it appeared in complex at δ 10.07. The sharp singlet peak at δ 10.20 (s, 1H, NH) appeared in ligand but in complexes disappeared and new peak is formed due to formation of C-SH. The fourteen aromatic protons of the ligand have resonated as multiplet in the region δ 7.00-7.85(m, 14H, Ar-H).^[21,22]

Electronic spectral analysis data

The electronic spectral data of Cu(II), Co(II), Ni(II) and Mn(II) complexes of the Schiff's base were recorded in DMF solution at 10⁻³ M concentration and are given in table 3. They have been studied with a view to obtaining more information on the stereochemistry of the complexes and to procure more support for the conclusion deduced with the help of magnetic data. The Cu(II) complex exhibits a broad asymmetric band in the region 12660-16790 cm⁻¹ with a maxima at 14480 cm⁻¹ in an distorted octahedral geometry.^[23] The crystal field splitting energy (Dq) and LFSE value of Cu(II) complex is obtained as 1445 cm⁻¹ and 24.74 kcalmol⁻¹ respectively.^[24] The electronic spectra of the Co(II) complex gave two absorption bands at 9475 cm⁻¹ and 24390 cm⁻¹, due to ⁴T_{1g}(F)→⁴A_{2g}(F)(ν_1) and ⁴T_{1g}(F)→⁴T_{1g}(P)(ν_3) transitions.^[25] The bands due to the ⁴T_{1g}(F)→⁴A_{2g}(F)(ν_2) transitions could not be observed because of its very low intensity. The position of ν_2 band has been calculated (19380 cm⁻¹) by using the equation $\nu_2 = \nu_1 + 10Dq$. These transitions suggest octahedral geometry for Co(II) complex.^[26] The ligand field parameters such as Dq, B', β and $\beta\%$ have been calculated by using band-fitting equation given by Billing and Underhill.^[27] The crystal field splitting energy (Dq) value of 1028 cm⁻¹, is well within the range reported for most of the octahedral

Co(II) complexes.^[28] The Co(II) complex under present investigation possess Racha parameter B' 770 cm^{-1} . The Racha parameter B' is less than free ion value 971 cm^{-1} , suggesting a considerable orbital overlap and delocalization of electrons on the metal ion. The nephelauxetic ratio (β) for the present Co(II) complex is 0.74 cm^{-1} . This is less than one, suggesting partial covalency in the metal ligand bond. The values Dq , $\beta\%$, LFSE and v_2/v_1 suggest the octahedral geometry for Co(II) complex.^[29,30] The electronic spectrum of Ni(II) complexes shows three bands at 9650 cm^{-1} , 14410 cm^{-1} and 25450 cm^{-1} assignable to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(v_1)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(v_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(v_3)$ transitions respectively, in an octahedral environment.^[31,32] The lowest band v_2 (10Dq) was not observed due to limited range of instrument used. However, it is calculated by using equation suggested by Billing and Underhill. Racha parameter B' is less than the free ion value of 1040 cm^{-1} indicating the covalent character of the complex. The ratio v_2/v_1 and $\beta\%$ value further support the octahedral geometry around the Ni(II) ion.^[33,34] The observed bands for Mn(II) complex are at 10524 cm^{-1} , 16450 cm^{-1} and 24245 cm^{-1} due to the transition ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(v_1)$, ${}^3A_{2g}(F) \rightarrow {}^3A_{1g}(F)(v_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(v_3)$ respectively. The position of bands indicates that the complex has six coordinated octahedral geometry.^[35,36]

Table 3: Electronic spectral data of Cu(II), Co(II), Ni(II) and Mn(II) complexes (cm^{-1}).

Complexes	Transition in cm^{-1}			Dq (cm^{-1})	B' (cm^{-1})	β	$\beta\%$	v_2/v_1	LFSE (Kcalmol^{-1})
	v_1	v_2	v_3						
Cu($\text{C}_{26}\text{H}_{36}\text{N}_6\text{O}_2\text{S}_2$) 2H ₂ O	12660-16790			1445					24.74
Co($\text{C}_{26}\text{H}_{36}\text{N}_6\text{O}_2\text{S}_2$) 2H ₂ O	9475	19380	24390	1028	770	0.74	21.28	2.05	23.80
Ni($\text{C}_{26}\text{H}_{36}\text{N}_6\text{O}_2\text{S}_2$) 2H ₂ O	9650	14410	25450	1018	637	0.698	29.80	1.47	32.20
Mn($\text{C}_{26}\text{H}_{36}\text{N}_6\text{O}_2\text{S}_2$) 2H ₂ O	10524	16450	24245	940	862	0.642	23.42	1.45	16.82

ESR spectral analysis

ESR spectra of Cu(II) complex were recorded as polycrystalline sample at room temperature, on X band of 9.1 GHz under the magnetic-field strength of 3200G. The analysis of spectra gives the data $g_{\parallel}=2.260$ and $g_{\perp}=2.047$, $g_{av}=2.151$, $g_{iso}=2.204$ and $G=5.588$ and are shown in table 4. The observed g_{\parallel} value for the Cu(II) complex was less than 2.3 is in agreement with covalent character of the metal ligand bond. The observed value of $g_{\parallel} > g_{\perp} > g_{av}$ which suggest that the presence of unpaired electron dx^2-y^2 orbital giving octahedral geometry.^[37,38] The Cu(II) complex reported in this paper has the G value greater than 4, indicating the

exchange interaction is negligible in solid complex. It concludes that the reported complex is mononuclear in nature.

Table 4: ESR data of the Cu(II) complex of Schiff's base ligand.

Complexes	g_{\parallel}	g_{\perp}	g_{av}	g_{iso}	G
Cu(C ₂₆ H ₃₆ N ₆ O ₂ S ₂) 2H ₂ O	2.260	2.047	2.151	2.204	5.588

Microbial activity

Antifungal activity of zone of inhibition (in mm) (conc. mg/ml)

The antifungal activity of synthesized ligand and its Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Hg(II) metal complexes were carried out by standard cup-plate method.^[39,40] The antifungal activity results of the tested compounds are given in the table 5. Antifungal activity against *C. albicans* and *A. niger* at 100mg/ml concentration were carried out. The some factors such as solubility, conductivity, dipole moment, size of metal ions, stability constants of the complexes and their magnetic moments are also reported to affect the microbial activity of the complexes.^[41] The enhanced activity of the Schiff base and its complexes were explained based on chelation theory. On chelation the positive charge of metal is partially shared with the donor atoms present in the ligand, there may be π - electron delocalization over the whole chelating. This increases the lipophilic character of the metal chelate and favors its penetration through the lipid layer of the bacterial membranes. Chelation is not only the criterion for antibacterial activity it is expected to be a function of steric, electronic and pharmacokinetic factors along with mechanistic Pathway.^[42] The obtained results of the synthesized compounds were compared with standard drugs. The Schiff's base show very low activity compared to both antibacterial and antifungal activity of standard drugs. The standard drug Amphotericin shows the good activity against *C. albicans* (13mm) and *A. niger* (14mm) using variable concentration (0.2 to 1.0mg/ml) as shown in table. The prepared ligand and its Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Hg(II) metal complexes are carried out at same variable concentration (0.2 to 1.0mg/ml) as shown in table. The results of antifungal activity of ligand (08 to 10 in mm) are shows low compared with metal complexes (10 to 12 in mm). It indicates that prepared metal complexes are better activity than the ligand.

Table 5: Antifungal activity of Zone of inhibition (in mm) (Conc. mg/ml).

	<i>E. coli</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>S. aureus</i>
Conc. mg/ml	0.2	0.2	0.4	0.4	0.6	0.6	0.8	0.8	1.0	1.0
Ligand	08	09	09	09	10	10	10	10	10	10
Cu(II)	10	10	10	11	11	12	12	12	12	12
Co(II)	10	10	10	11	11	12	12	12	12	12
Ni(II)	10	10	10	11	11	12	12	12	12	12
Mn(II)	10	10	10	11	11	12	12	12	12	12
Cd(II)	10	10	10	11	11	12	12	12	12	12
Hg(II)	10	10	10	11	11	12	12	12	12	12
Std Streptomycin	13	14	13	14	13	14	13	14	13	14

Antibacterial activity of zone of inhibition (in mm) (conc. mg/ml)

The antibacterial activity of synthesized ligand and its Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Hg(II) metal complexes were carried out by standard cup-plate method.^[43,44] The antibacterial activity results of the tested compounds are given in the table 6. Antibacterial activity against *E. coli* and *S. aureus* at 100mg/ml concentration were carried out. The enhanced activity of the Schiff base and its complexes were explained based on chelation theory. On chelation the positive charge of metal is partially shared with the donor atoms present in the ligand, there may be π - electron delocalization over the whole chelating. The obtained results of the synthesized compounds were compared with standard drugs. The Schiff's base show very low activity compared to both antibacterial and antifungal activity of standard drugs. The standard drug Streptomycin shows the good activity against *E. coli* (13mm) and *S. aureus* (14mm) using variable concentration (0.2 to 1.0mg/ml) as shown in table. The prepared ligand and its Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Hg(II) metal complexes are carried out at same variable concentration (0.2 to 1.0mg/ml) as shown in table. The results of antibacterial activity of ligand (08 to 10 in mm) are shows low compared with metal complexes (10 to 12 in mm). It indicates that prepared metal complexes are better activity than the ligand.

Table 6: Antibacterial activity of Zone of inhibition (in mm) (Conc. mg/ml).

	<i>C. Albicans</i>	<i>A. niger</i>	<i>C. Albicans</i>	<i>A. niger</i>	<i>C. Albicans</i>	<i>A. niger</i>	<i>C. Albicans</i>	<i>A. niger</i>	<i>C. Albicans</i>	<i>A. niger</i>
Conc. mg/ml	0.2	0.2	0.4	0.4	0.6	0.6	0.8	0.8	1.0	1.0
Ligand	08	09	09	09	10	10	10	10	10	10
Cu(II)	10	10	10	11	11	12	12	12	12	12
Co(II)	09	09	10	11	11	11	11	12	12	12
Ni(II)	09	10	09	11	10	11	12	12	12	12
Mn(II)	09	09	09	10	10	11	12	12	12	12
Cd(II)	09	10	10	10	11	12	12	12	12	12
Hg(II)	09	09	09	10	10	11	11	12	12	12
Std Amphotericin	13	14	13	14	13	14	13	14	13	14

CONCLUSION

The elemental analysis, conductivity data, magnetic susceptibility, IR, ^1H NMR spectral observations, ESR, electronic spectral data reveals the mononuclear nature of all the synthesized complexes. From the elemental and IR spectral analysis it is clear that the complexes contain two coordinated water molecules. The Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Hg(II) metal complexes exhibit octahedral geometry (figure 2). All the complexes show higher microbial activity than the ligand. The metal complexes of Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Hg(II) show moderate antifungal activity compared with amphotericin standard drug and antibacterial activity compared with streptomycin standard drugs.

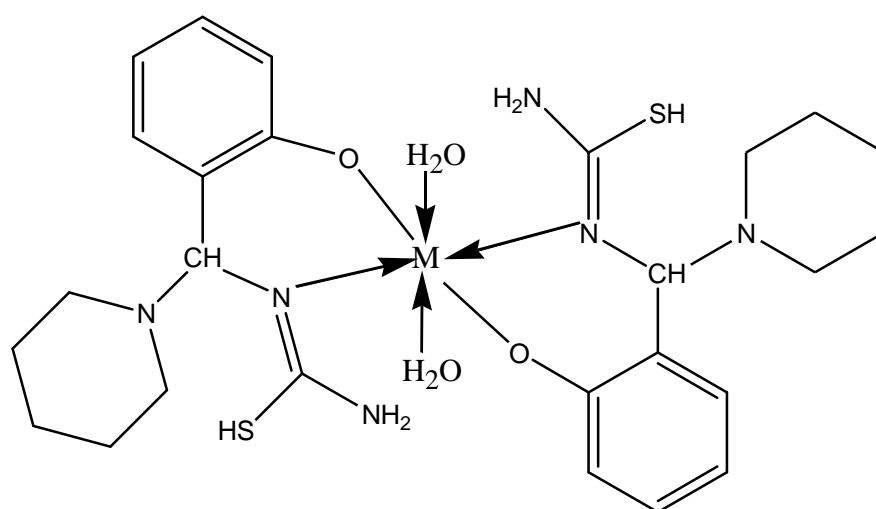


Figure 2: Proposed structure of the complexes.

[Where M = Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Hg(II)]

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