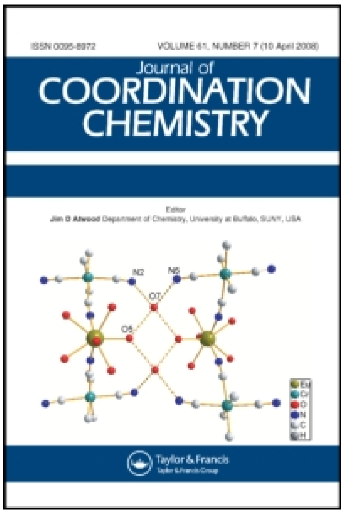

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Transition metal complexes of a Schiff base: synthesis, characterization, and antibacterial studies

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Transition metal complexes of a Schiff base: synthesis, characterization, and antibacterial studies

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Synthesis of a new Schiff base derived from 2-hydroxy-5-methylacetophenone and glycine and its coordination with compounds Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and UO_2(VI) are described. The ligand and complexes have been characterized on the basis of analytical, electrical conductance, infrared, ESR and electronic spectra, magnetic susceptibility measurements, and thermogravimetric analysis. The ligand is a dibasic tridentate (ONO) donor in all the complexes except Zn(II), where it is a monobasic bidentate (OO) donor. The solid state DC electrical conductivity of ligand and its complexes have been measured over 313–398 K, and the complexes were semiconducting. Antibacterial activities of ligand and its metal complexes have been determined by screening the compounds against various Gram (+) and Gram (−) bacterial strains.

Keywords: Schiff base; Transition metal complexes; Glycine; 2-Hydroxy-5-methylacetophenone; Antibacterial studies

1. Introduction

Schiff bases have often been used as chelating ligands in coordination chemistry [1, 2], useful in catalysis, medicine as antibiotics and anti-inflammatory agents, and industry for anticorrosion properties [3–5]. Amino acid-based Schiff bases are very effective metal chelators and their metal complexes are models for a number of important biological systems [6]. The variety of possible Schiff-base metal complexes with wide choice of ligands and coordination environments has prompted us to undertake research in this area [7]. In the present article, we report the synthesis and characterization of a Schiff base derived from 2-hydroxy-5-methylacetophenone and glycine, and its metal complexes to gain more information about related structural and spectral properties as well as their antimicrobial properties.

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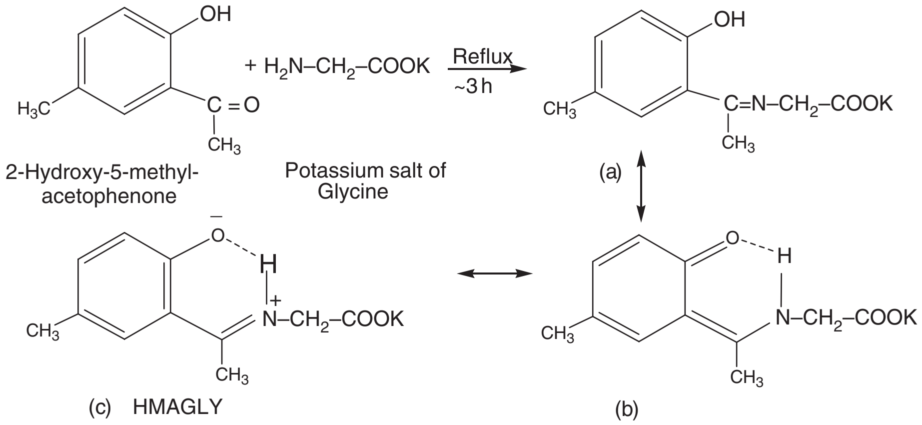

Figure 1. The schematic representation of synthesis of HMAGLY.

2. Experimental

The acetates of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II), ferrous ammonium sulfate hexahydrate, cadmium chloride monohydrate, and uranyl nitrate hexahydrate (S.D.'s fine chemicals) were used for synthesis of complexes. 2-Hydroxy-5-methylacetophenone was synthesized according to the published procedure [8].

2.1. *Synthesis of HMAGLY*

A homogenous mixture (25 mL) of an aqueous solution of glycine and ethanolic solution of KOH (0.02 mol) was added with constant stirring to an ethanolic solution (25 mL) of 2-hydroxy-5-methylacetophenone (0.02 mol). The mixture was refluxed for ~3 h. Excess solvent was removed by slow evaporation and the yellow crystalline product obtained was dried under vacuum over P_2O_5, yield 82%, m.p. 242°C. ^{1}H NMR (δ, ppm); 11.43 (1H, s, –NH); 2.7 (3H, s, methyl); 4.63 (2H, s, –CH_2); 2.4 (3H, s, Ar-methyl); 7.5, 7.1, and 6.9 (3H, m, phenyl). The schematic representation of synthesis of HMAGLY and its tautomeric forms are shown in figure 1. The ligand exists predominantly in ketoenamine form (c). Hence, the NH proton was seen in ^{1}H NMR spectrum instead of an OH proton.

2.2. *Preparation of metal complexes*

2.2.1. Synthesis of Fe(II), Ni(II), Zn(II), and Cd(II) complexes. Equimolar quantities of the Schiff base and appropriate metal acetate/metal sulfate/metal chloride were dissolved separately in aqueous ethanol and mixed with constant stirring. For the Fe(II) complex, 5–6 drops of acetic acid was added into the resultant solution to avoid oxidation. The mixture was stirred magnetically for 10–15 h using a $CaCl_2$ guard tube. On cooling to room temperature, solid product was obtained, filtered, washed with aqueous ethanolic solution and finally dried over fused calcium chloride. Yield 70–75%.

2.2.2. Synthesis of Mn(II), Co(II), Cu(II), and UO_2(VI) complexes. Equimolar quantities of the Schiff base and appropriate metal acetate/metal nitrate were dissolved separately in aqueous ethanol and mixed with constant stirring. The mixture was refluxed for 2–4 h and then excess solvent removed by slow evaporation. The colored product obtained was filtered, washed with aqueous ethanolic solution and finally dried over fused calcium chloride. Yield 70–75%. The formation of complexes may be represented by the following equations:

$$\mathrm{Zn(CH_3COO)_2 \cdot 2H_2O + 2LHK \xrightarrow[\text{Reflux 12 h}]{\text{Aq.ethanol}} [Zn(LH)_2] + 2CH_3COOK + 2H_2O}$$

$$\mathrm{Ni(CH_3COO)_2 \cdot 4H_2O + LHK \xrightarrow[\text{Reflux 13 h}]{\text{Aq.ethanol}} [Ni(L)(H_2O)_3]}$$
$$\mathrm{+ CH_3COOK + CH_3COOH + H_2O}$$

$$\mathrm{UO_2(NO_3)_2 \cdot 6H_2O + LHK \xrightarrow[\text{Reflux 2 h}]{\text{Aq.ethanol}} [UO_2(L)(H_2O)] \cdot H_2O}$$
$$\mathrm{+ HNO_3 + KNO_3 + 4H_2O}$$

$$\mathrm{Co(CH_3COO)_2 \cdot 4H_2O + LHK \xrightarrow[\text{Reflux 6 h}]{\text{Aq.ethanol}} [Co(L)(H_2O)] \cdot H_2O}$$
$$\mathrm{+ CH_3COOK + CH_3COOH + 2H_2O}$$

$$\mathrm{Cu(CH_3COO)_2 \cdot H_2O + LHK + H_2O \xrightarrow[\text{Reflux 4 h}]{\text{Aq.ethanol}} [Cu(L)(H_2O)] \cdot H_2O}$$
$$\mathrm{+ CH_3COOK + CH_3COOH}$$

$$\mathrm{2Mn(CH_3COO)_2 \cdot 3H_2O + 2LHK \xrightarrow[\text{Reflux 3 h}]{\text{Aq.ethanol}} [Mn(L)(H_2O)_2]_2 \cdot H_2O}$$
$$\mathrm{+ 2CH_3COOK + 2CH_3COOH + 4H_2O}$$

$$\mathrm{2(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O + 2LHK \xrightarrow[\text{Reflux 10 h}]{\text{Aq.ethanol}} [Fe(L)(H_2O)_2]_2H_2O}$$
$$\mathrm{+ 2(NH_4)_2SO_4 + H_2SO_4 + K_2SO_4 + 7H_2O}$$

$$\mathrm{2CdCl_2 \cdot H_2O + 2LHK + 2H_2O \xrightarrow[\text{Reflux 13 h}]{\text{Aq.ethanol}} [Cd(L)(H_2O)_2]_2 + 2HCl + 2KCl}$$

where LHK = HMAGLY ($C_{11}H_{12}NO_3K$), L = $C_{11}H_{11}NO_3$.

2.3. *Physical measurements*

Elemental analyses were carried out in the microanalytical laboratory, CDRI, Lucknow. Metal contents of the complexes were analyzed using classical oxide method. Infrared (IR) spectra were recorded on a Perkin–Elmer-RX-1 spectrophotometer using KBr pellets. ^{1}H NMR spectrum of ligand was recorded in a mixed solvent ($CDCl_3 + DMSO$) on a Bruker AC-300 F spectrometer using TMS as internal standard. The diffuse reflectance spectra of the complexes were recorded on a Varian Cary-2390 spectrophotometer using MgO as reference. The ESR spectra were recorded at room temperature on a VE112 – ESR spectrometer. Magnetic susceptibilities were measured at room temperature by Gouy's method using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were made using Pascal's constants. Solid state DC electrical conductivities of the compounds were measured by the two probe method in their compressed pellet form from 313 to 398 K. Thermogravimetric analysis of the complexes was carried out on a Perkin–Elmer TG-2 thermobalance in ambient air with a heating rate of $10^{\circ}C\,min^{-1}$.

3. Results and discussion

All the complexes are colored solids, air stable for an extended period of time, but decomposing at higher temperature. They are insoluble in common organic solvents and soluble in DMSO. The complexes are monomeric [except Mn(II), Fe(II), and Cd(II) which are dimeric] as indicated by their analytical data along with the magnetic, thermal, and spectral studies. The analytical data indicate 1 : 1 metal : ligand stoichiometry in all complexes except 1 : 2 in Zn(II) complex (table 1).

3.1. *IR spectra*

The IR spectrum of the ligand shows a broad band of medium intensity at $3386\,cm^{-1}$ due to ν(NH) (that may be overlapping with hydrogen bonded $O \cdots H$ stretching vibrations [9]. The other bands at 1688, 1621, 1422, and $1271\,cm^{-1}$ are assignable to ν(COO) asymmetric, ν(C=N)/ν(C=C) ring, ν(COO) symmetric, and ν(C–O) (phenolic), respectively [9, 10]. The band due to N–H disappeared in the spectra of complexes (except Zn(II) complex) and ν(C–O) (phenolic) band shifted to higher frequency by $11–60\,cm^{-1}$, indicating that nitrogen and phenolic oxygen are directly linked to metal [11]. The band due to azomethine shifts to lower wavenumber by $15–45\,cm^{-1}$, indicating coordination of azomethine nitrogen. The medium intensity bands in the region 1575–1626 and $1360–1411\,cm^{-1}$ may be assigned to –COO antisymmetric and symmetric vibrations, respectively [12]. In Mn(II), Fe(II), Ni(II), Cu(II), Cd(II), and UO_2(VI) complexes the band due to $\nu(COO)_{asy}$ may be overlapped with the strong band due to (C=N) group. The separation between antisymmetric and symmetric stretching is $\sim 200\,cm^{-1}$, indicating the covalent nature of metal oxygen bond in complexes and monodenticity of carboxylate [13, 14].

The position of the N–H band did not change in the spectrum of Zn(II) complex, indicating that nitrogen of NH group is not involved in coordination [9]. Except Zn(II) complex, the others show characteristic absorption bands for water. A broad band centered at $3230–3371\,cm^{-1}$ may be due to ν(OH) of water [15, 16] and a sharp shoulder from 1520 to $1536\,cm^{-1}$ may be assigned to $\delta(H_2O)$. Water molecules are coordinated, confirmed by occurrence of an additional strong and sharp band at $820–860\,cm^{-1}$ arising due to OH rocking vibrations [17, 18]. A band at $912\,cm^{-1}$ in the spectrum of the UO_2(VI) complex is assignable to ν_{asy}(O=U=O) [19]. Nonligand bands at 505–531 and

Table 1. Analytical and physical data of HMAGLY and its complexes.

			Elemental analysis				Electrical conductance	
Proposed composition of the complexes	Formula weight	Color	Metal	C	H	N	σ (at 373 K) ($\Omega^{-1}\,cm^{-1}$)	E_a (eV)
HMAGLY (LHK)	245.30	Yellow crystalline	–	53.52 (53.86)	5.02 (4.93)	5.65 (5.71)	–	–
$[Mn(L)(H_2O)_2]_2H_2O$	610.37	Mid buff	18.18 (18.00)	42.82 (43.29)	4.75 (5.26)	3.92 (4.59)	9.84×10^{-7}	0.942
$[Fe(L)(H_2O)_2]_2H_2O$	315.10	Volcano	18.37 (18.20)	42.77 (43.16)	4.98 (5.27)	4.42 (4.58)	1.24×10^{-7}	0.345
$[Co(L)(H_2O)]H_2O$	300.17	Golden brown	19.70 (19.63)	43.90 (44.01)	4.88 (5.04)	4.14 (4.67)	3.07×10^{-7}	0.323
$[Ni(L)(H_2O)_3]$	317.90	Ocean green	18.59 (18.46)	44.05 (41.55)	5.27 (5.39)	3.38 (4.41)	2.48×10^{-6}	0.534
$[Cu(L)(H_2O)]H_2O$	304.80	Surf green	21.07 (20.85)	43.72 (43.35)	4.82 (4.96)	4.32 (4.60)	1.41×10^{-6}	0.559
$[Zn(LH)_2]$	477.80	Lime light	14.02 (13.68)	55.07 (55.30)	4.95 (5.06)	5.39 (5.86)	2.90×10^{-7}	0.609
$[Cd(L)(H_2O)_2]_2$	707.30	White	31.98 (31.79)	37.18 (37.36)	4.19 (4.28)	3.82 (3.96)	1.67×10^{-7}	0.306
$[UO_2(L)(H_2O)]H_2O$	511.26	Dark yellow	46.72 (46.56)	25.36 (25.84)	2.80 (2.96)	2.27 (2.74)	7.45×10^{-7}	0.625
							4.16×10^{-11}	

470–493 cm^{-1} in spectra of all complexes are assignable to ν(M–N) and ν(M–O) [17], respectively.

The above discussion indicates that HMAGLY in Zn(II) complex is monobasic bidentate coordinating through O $\cdots$ H and COO. In the other complexes, it is dibasic tridentate coordinating through azomethine nitrogen, deprotonated phenolic oxygen, and carboxylic group.

3.2. *ESR spectra*

The ESR spectrum of powdered sample of Cu(II) complex measured at room temperature showed normal features with $g_{\parallel} > g_{\perp} > 2$ indicating that the unpaired electron lies in the $\mathrm{d}_{x^2-y^2}$ orbital [20], characteristic of square planar geometry around Cu(II) ion. The exchange interaction parameter term G, estimated from the expression $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ is 1.813, indicating that the ligands are strong field ligands [21]. The value of G is less than 4 indicating considerable exchange coupling and the misalignment is appreciable. The value of $A_{\parallel}$(158), nuclear hyperfine constant and α^2 (0.69) degree of covalency support the structure [22]. The μ_{eff} value, calculated using the equation $\mu_{\mathrm{eff}}^2 = 3/4\, g_{\mathrm{av}}^2$, was 1.86 B.M., which closely agreed with the observed magnetic moment.

3.3. *Electronic spectra and magnetic measurements*

The reflectance spectrum of Mn(II) complex exhibited broad bands in the range 17241, 23809, and 27027 cm^{-1} due ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}({}^4G)$ and ${}^6A_{1g} \rightarrow {}^4E_g$ transitions in octahedral symmetry. Fe(II) complex exhibit bands at 11,765 cm^{-1} due to the ${}^5T_{2g} \rightarrow {}^5E_g$ and two bands at higher region 16,949 and 22,727 cm^{-1} ascribed to charge transfer transitions, suggesting an octahedral geometry around Fe(II). The reflectance spectral parameters for Fe(II) are $Dq = 1176.5\ \mathrm{cm}^{-1}$, $B = 636\ \mathrm{cm}^{-1}$, $\beta = 0.600$, $\beta^{\circ} = 40.0$, and $\mathrm{LFSE} = 140.7\ \mathrm{kJ\,mol}^{-1}$. The reduction of Racah parameter (B) from the free ion value of 1060–636 cm^{-1} and β value of 40.0% indicates partial covalent character of Fe–L [23]. The reflectance spectrum of Co(II) complex shows bands at 7407, 9346, 16,667, and 25,641 cm^{-1}, assigned to ${}^4A_2 \rightarrow {}^4T_1$, ${}^4A_2 \rightarrow {}^4T_1(F)$, ${}^4A_2 \rightarrow {}^4T_1(P)$ and CT transitions, respectively, for tetrahedral Co(II) [24]. Ni(II) complex exhibit three bands at 10,526, 16,950, and 25,000 cm^{-1} due to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively, in octahedral symmetry. Three bands observed at 14,995, 16,949, and 17,857 cm^{-1} in Cu(II) complex may be assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ and spin forbidden ligand to metal charge transfer transitions, respectively, indicating square planar geometry [25].

The complexes of Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) have magnetic moments of 6.12, 5.16, 4.05, 3.25, and 1.85 B.M., respectively, close to reported values for these complexes [26]. Complexes of Zn(II), Cd(II), and $\mathrm{UO_2}$(VI) are diamagnetic. The magnetic measurements, infrared and electronic spectral data provide evidence for the structures of the isolated complexes.

3.4. *Thermogravimetric analysis*

Thermal analysis of the complexes were carried out up to 700°C. The thermogram of HMAGLY and its complexes show a gradual weight loss, indicating decomposition by fragmentation with increase in temperature. The thermogram of the complexes shows nearly the same pattern of decomposition reflecting their isostructural characteristics. A careful analysis of thermogram of the UO_2(VI) complex and the ligand shows that they undergo two-step decomposition after dehydration. All the other complexes undergo one-step decomposition. The Zn(II) complex is stable up to 200°C, suggesting the absence of both lattice and coordinated water [27]. Complexes of Mn(II), Fe(II), Cu(II), and UO_2(VI) with weight loss at ~140°C indicate the presence of one lattice water [28]. [% Weight loss observed/Calcd Mn(II): 5.83/5.73; Fe(II): 5.77/5.72; Cu(II): 5.95/5.91; UO_2(VI): 3.62/3.52]. In these complexes, there is further loss in weight up to ~240°C indicating the presence of two coordinated waters [29] in Mn(II) and Fe(II) complexes and one coordinated water in Cu(II) and UO_2 complexes. [% Weight loss observed/Calcd Mn(II): 12.00/11.46; Fe(II): 11.72/11.42; Cu(II): 5.93/5.91; and UO_2(VI): 3.5/3.52]. Co(II) and Ni(II) complexes are stable up to 100°C indicating the absence of lattice water but continuous weight loss up to 220°C corresponding to one and three waters, respectively, indicate the presence of coordinated water. [% Weight loss observed/Calcd Co(II): 6.62/6.38; Ni(II): 17.13/17.00]. In all the complexes rapid weight loss was observed around 300°C, indicative of decomposition of coordinated ligand. Finally, the horizontal nature of the thermogram beyond ~600°C suggests the formation of final decomposition products corresponding to Mn_3O_4, Fe_2O_3, Co_3O_4, NiO, CuO, ZnO, CdO, and U_3O_8, respectively. The relative thermal stability of the compounds is found to be Mn(II) < Fe(II) < Cu(II) < HMAGLY < Ni(II) < Cd(II) < Co(II) < Zn(II) < UO_2(VI). From the thermal decomposition data various kinetic parameters have been calculated by using two methods, namely Broido [30] (B) and Horowitz–Metzger [31] (HM), and comparable values obtained are given in the supplementary table S1.

3.5. *Solid state conductivity*

The solid state DC electrical conductivity of the synthesized ligand and its complexes in compressed pellet form (5 ton cm^{-2}) was measured in the temperature range 313–398 K and a linear dependence of $\log\sigma = f(10^3/T)$ from Arrhenius plot of electrical conductivity, indicates the semiconducting behavior of these compounds [32]. The electrical conductivity (σ) varies exponentially with the absolute temperature according to the relation $\sigma = \sigma_o \exp(-E_a/KT)$, where σ_o is constant, E_a is the activation energy of electrical conduction, T the absolute temperature and K the Boltzman constant. The DC electrical conductivity of the complexes at 373 K follows the order Ni > Cu > Mn > UO_2 > Co > Zn > Cd > Fe and lies in the range 1.24×10^{-7}–$2.48 \times 10^{-6}\ \Omega^{-1}\,cm^{-1}$. The low-electrical conductivity may be attributed to the extent of conjugation becoming low or undesirable morphology due to pressing of the sample into hard brittle pellet [33]. The activation energy of electrical conduction of the complexes has been found to increase in the order – Cd < Co < Fe < Ni < Cu < Zn < UO_2 < Mn.

3.6. *Antibacterial activity*

The *in vitro* evaluation of antibacterial activity was performed by the Single Disc method [34]. Compounds were dissolved in DMSO at 10.0 mg mL^{-1}. The 10 mm

Table 2. Antibacterial activity of the ligand and its complexes (diameter of inhibition zone in mm).

Compounds	*E. coli*	*S. flexneri*	*S. typhi*	*P. vulgaris*	*B. coagulans*	*P. aeruginosa*	*S. aureus*	*K. pneumoniae*	*S. typhimurium*	*E. faecalis*	*S. epidermidis*	*E. aerogenes*
HMAGLY (LHK)	R	14	R	13	13	R	R	R	R	R	R	R
$[Mn(L)(H_2O)_2]_2H_2O$	R	R	14	R	R	R	13	R	R	18	R	13
$[Fe(L)(H_2O)_2]_2H_2O$	18	19	23	R	20	R	16	13	22	R	18	R
$[Co(L)(H_2O)]H_2O$	R	R	25	R	18	13	17	R	23	15	20	R
$[Ni(L)(H_2O)_3]$	R	R	R	14	R	22	25	R	R	18	R	29
$[Cu(L)(H_2O)]H_2O$	15	13	R	14	20	13	19	14	13	R	25	14
$[Zn(LH)_2]$	R	29	R	R	R	R	19	R	13	25	25	22
$[Cd(L)(H_2O)_2]$	R	25	R	15	R	18	17	13	28	R	14	30
$[UO_2(L)(H_2O)]H_2O$	13	28	R	13	R	14	17	R	17	25	23	23
Streptomycin	28	32	29	26	25	25	30	22	30	29	28	33

Note: R = resistant.

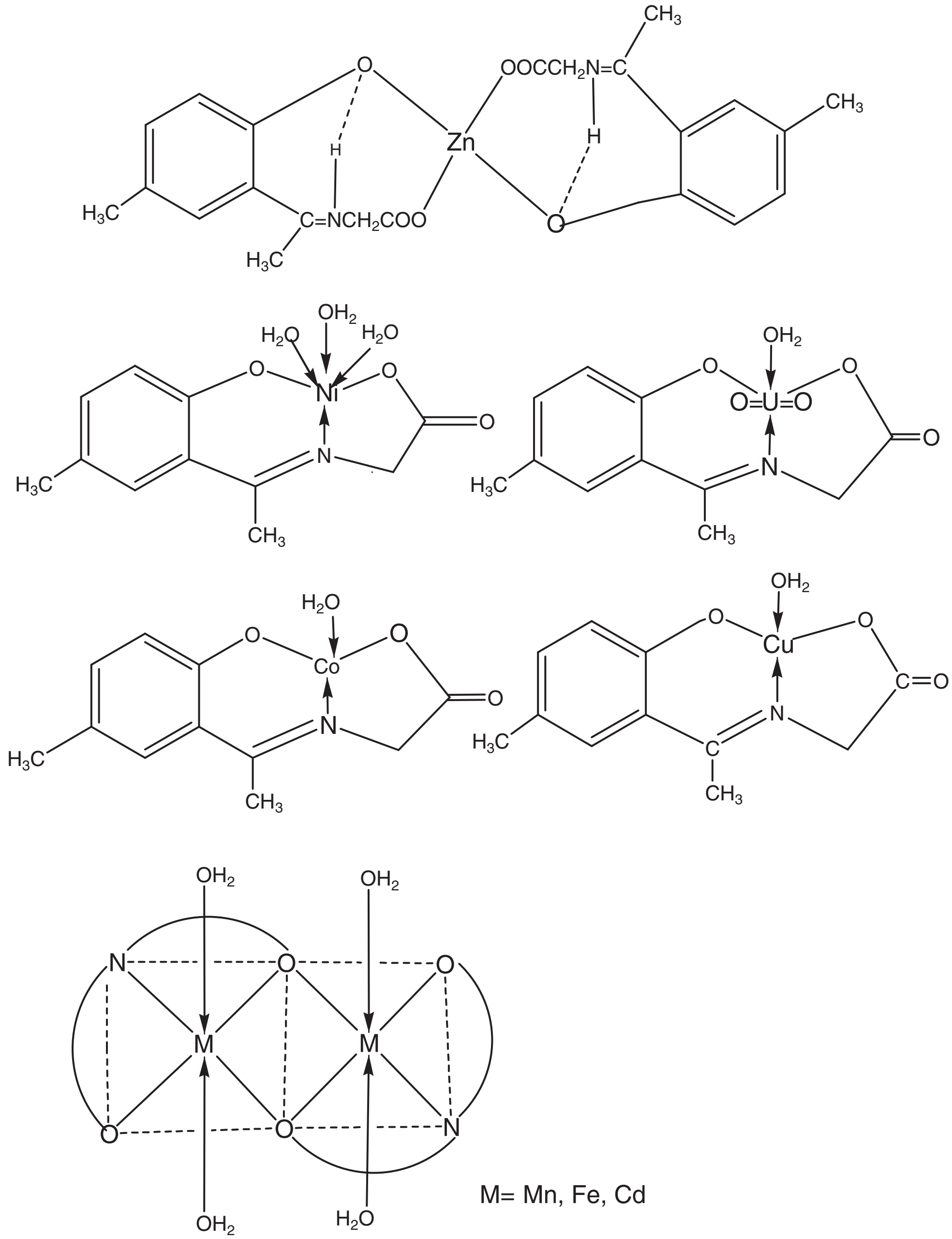

Figure 2. Probable structure of the complexes.

diameter Whatmann No. 1 paper discs were soaked in different solutions of the compounds, dried, and then placed on cultures on nutrient agar plates. Streptomycin was used as the standard antibiotic and DMSO as the negative control. The plates were incubated for 24 h at 37°C and the inhibition zone around each disc was measured. The results were interpreted according to Cappuccino and Sherman method [35]. The different bacterial stains and the zone of inhibition are reported in table 2.

The ligand was bacteriostatic against bacterial strains except *Proteus vulgaris*, *Shigella flexneri*, and *Bacillus coagulans*. All complexes are either resistant or less sensitive against *P. vulgaris*. However, compared to the antibacterial activity of the standard antibiotic streptomycin, the activity exhibited by the ligand and metal complexes was lower.

The metal complexes showed to exhibit higher activity than the free ligand against the same organism under identical experimental conditions [36]. Such increased activity of the metal chelates can be explained on the basis of chelation theory [37].

4. Conclusions

The ligand HMAGLY coordinates in 1 : 1 and 1 : 2 metal : ligand ratio as a dibasic tridentate (ONO) donor towards all the complexes except Zn(II), where it is a monobasic bidentate (OO) donor. The analytical, thermal, magnetic, IR, and electronic spectral study suggested the structures shown in figure 2. For the diamagnetic complexes, the geometry tetrahedral for Zn(II) and octahedral for Cd(II) and UO_2(VI) complexes have been assigned from various physicochemical methods. Thermogravimetric analysis showed that the complexes are thermally more stable than the ligand. Electrical conductance data indicated semiconducting complexes. The antimicrobial activity of the free ligand was enhanced upon complexation.

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