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Synthesis, Structural, and Biological Studies of Some Bivalent Metal Ion Complexes with the Tridentate Schiff Base Ligand[1]

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Abstract—New complexes of a Schiff base derived from 2-hydroxy-5-chloroacetophenone and glycine with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and UO_2(VI) have been synthesized. The ligand and the complexes have been characterized on the basis of analytical data, electrical conductance, IR, ESR, and electronic spectra, magnetic susceptibility measurements and thermogravimetric analysis. The ligand acts as a dibasic tridentate (ONO) donor molecule in all the complexes except the Zn(II) complex, where it acts as a monobasic bidentate (OO) donor. Antibacterial activities of the ligand and its metal complexes have been determined by screening the compounds against various Gram(+) and Gram(–) bacterial strains. The solid state d.c. electrical conductivity of the ligand and its complexes has been measured over 313–398 K and the complexes were found to be of semiconducting nature.

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INTRODUCTION

Transition and nontransition metal complexes with Schiff Base ligands played a vital role in the development of coordination chemistry [1, 2]. Interest in the Schiff base and their metal complexes is enhanced by proteins and enzymes requiring metal ions for activity, catalytic activity in the hydrogenation of olefins [3], complexing ability toward toxic metals [4], and so on. All kinds of natural amino acids that have been used to synthesize Schiff bases are found to be very effective metal chelators. Several amino acid-Schiff base complexes [5, 6] are potential models for a number of important biological systems. Various applications of these complexes contributed to the field of metallopeptide chemistry [7]. The present article describes the synthesis and structural, thermal, and antibacterial studies of the Schiff base derived from 2-hydroxy-5-chloroacetophenone and glycine (**HCAGLY**) and its metal complexes with bivalent metal ions.

EXPERIMENTAL

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

Synthesis of the ligand HCAGLY. A homogenous mixture (25 ml) of an aqueous solution of glycine and an ethanolic solution of KOH (0.02 mol) was added with constant stirring to an ethanolic solution (25 ml) of 2-hydroxy-5-chloroacetophenone (0.02 mol). The mixture was refluxed for ~3 h. Excess solvent was then removed by slow evaporation. The yellow crystalline product obtained was dried under vacuum over P_2O_5. The yield was 79%, mp was 265°C. ^{1}H NMR (δ, ppm): 11.8 (1H, s., –NH); 2.85 (3H, s., methyl); 4.82 (2H, s., $–CH_2$); 7.82, 7.7, and 7.67 (3H, m., phenyl). The schematic representation of the synthesis of HCAGLY and its tautomeric forms are shown below.

The ^{1}H NMR spectrum of the ligand showed the value for –NH proton instead of –OH proton suggesting that the ligand exist predominantly in ketoenamine form (c).

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. In the case of the Fe(II) complex, 5–6 drops of acetic acid was added to 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, a solid product was obtained. The colored product obtained was filtered off, washed with an aqueous ethanolic solution, and finally dried over fused calcium chloride. The yield was 70–75%.

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. Excess

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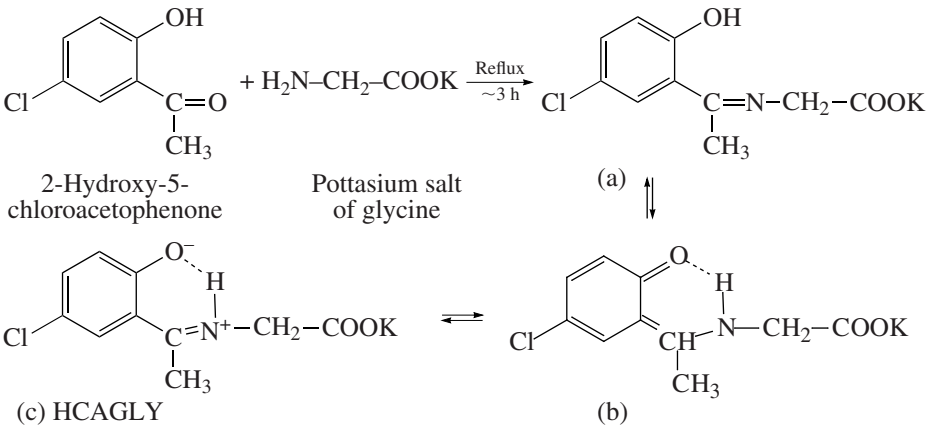


solvent was removed by slow evaporation. The colored product obtained was filtered off, washed with an aqueous ethanolic solution, and finally dried over fused calcium chloride. The yield was 70–75%.

Physical measurements. Elemental analysis was carried out at the microanalytical laboratory (CDRI, Lucknow). Chloride was estimated by Volhard's method. Metal contents of the complexes were analyzed using the classical oxide method. IR spectra were recorded on a Perkin-Elmer-RX-1 spectrophotometer using KBr pellets. ^{1}H NMR spectrum of the ligand was recorded in a mixed solvent ($CDCl_3$–DMSO) on a Bruker AC-300 F spectrometer using TMS as an internal standard. The diffuse reflectance spectra of the complexes were recorded on Varian Cary-2390 spectrophotometer using MgO as reference. ESR spectra were recorded at room temperature on a VE112-ESR spectrometer. Magnetic susceptibility was measured at room temperature by Gouy's method using $Hg[Co(SCN)_4]$as a calibrant, and diamagnetic corrections were made using Pascal's constants. Molar conductance was measured on an EQ-660 equiptronic digital conductivity meter with a cell constant of 1.00 cm^{-1}. Solid state d.c. electrical conductivity of the compounds was measured by the two probe method in their compressed pellet form over the 313–398 K temperature range. Thermogravimetric analysis of the complexes was carried out on a Perkin-Elmer TG-2 thermobalance in ambient air with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

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

The infrared spectrum of the ligand exhibits a strong band due to ν(C=N) (azomethine) at 1620 cm^{-1}, shifted to a lower frequency by 10–45 cm^{-1} in the spectra of complexes, indicating the coordination through azomethine nitrogen [9]. The ν(C–O) (phenolic) frequency of the Schiff base ligand at 1255 cm^{-1} is shifted to a higher frequency and appeared in the region 1297–1310 cm^{-1} on complexation suggesting the involvement of the O···H group in complex formation via deprotonation [10]. The absence of the NH stretching band (which is overlapped with the O–H band of the ligand at 3385 cm^{-1}) in all the complexes, except the Zn(II) complex confirms, the coordination of the ligand through nitrogen and phenolic oxygen [11]. Thus, HCAGLY behaves as a tridentate ONO donor dibasic ligand.

The IR spectra of all the complexes display two bands at 1575–1623 and 1385–1404 cm^{-1} assignable to the ν_{as}(OCO) and ν_s(OCO) modes, respectively. The separation of these peaks by ~200 cm^{-1} indicates the monodentate coordination of the acetato group to the metal ion [12]. The presence of coordinated water in the complexes except Zn(II) is indicated by a broad band at 3212–3388 assignable to OH group of water molecules. These complexes also exhibit weak but sharp bands at 1521–1533 and 823–854 cm^{-1} assigned as the OH rocking and wagging vibrations, respectively [13]. The IR spectrum of the Zn(II) complex is somewhat different as compared to other complexes. The band at 3385 cm^{-1}, which is due to NH stretching vibration in the spectrum of potassium salt of HCAGLY, did not change its position in the spectrum of the Zn(II) complex, which rules out the possible coordination through the nitrogen atom [14].

In addition to the above mentioned bands, all the complexes display a band in the regions 515–548 and 460–480 cm^{-1} assignable to ν(M–N) and ν(M–O) stretching vibrations, respectively [15].

The room temperature ESR spectrum of a powdered sample of Cu(II) showed normal features with $g_\parallel > g_\perp > 2$ indicating that an unpaired electron lies in the $d_{x^2-y^2}$ orbital [16] characteristic of square planar geometry around the Cu^{2+} ion. The exchange interaction parame-

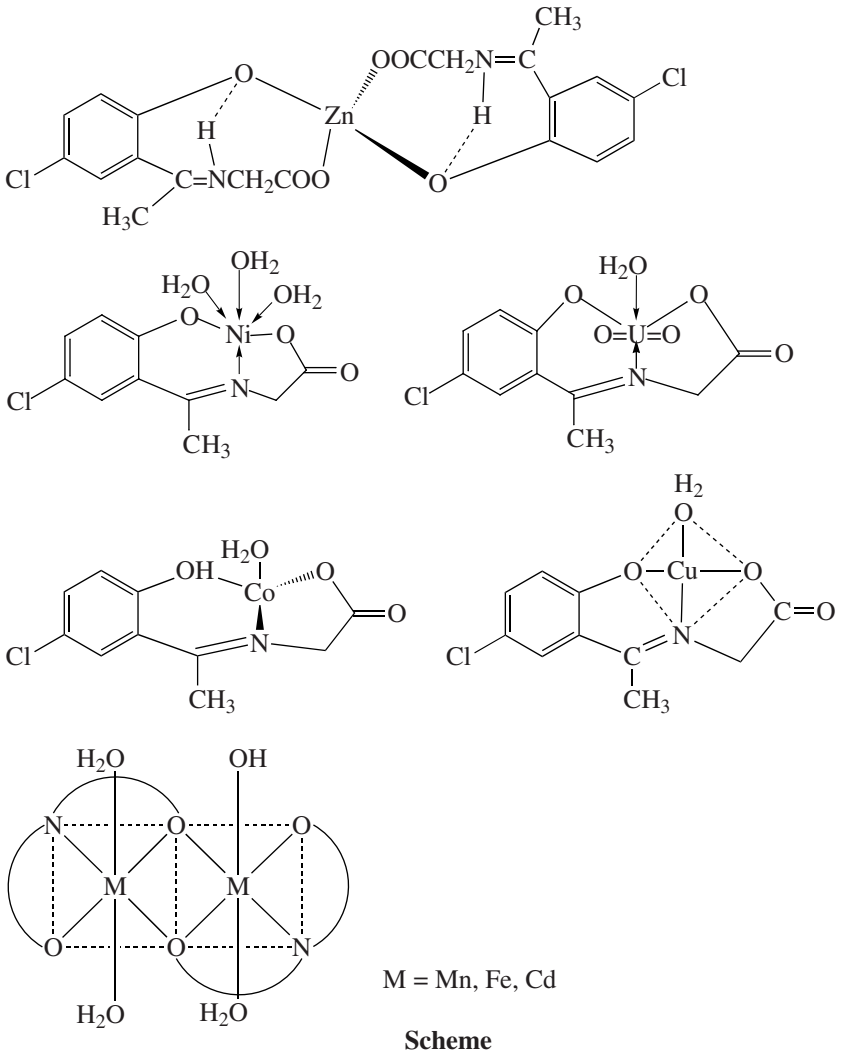
Table 1. Analytical and physical data of HCAGLY and its complexes

Proposed composition of the complexe	*M*, g/mol	Color	Contents (found/calcd), %					Electrical conductance		Λ_M Ohm^{-1} cm^2 mol^{-1}
			M	C	H	N	Cl	σ, Ohm^{-1} cm^{-1} (373 K)	E_a, eV	
HCAGLY (LH_2)	265.7	Dark yellow		44.83/ 45.20	3.35/ 3.41	5.15/ 5.27	13.29/ 13.34			
$[Mn(L)(H_2O)_2]_2$	633.19	Ivory	17.40/ 17.35	37.49/ 37.94	3.92/ 3.82	4.33/ 4.42	10.32/ 11.20	3.35×10^{-7}	0.996	10.18
$[Fe(L)(H_2O)_2]_2$	635.00	Volcano	17.50/ 17.59	37.61/ 37.83	3.74/ 3.81	4.18/ 4.41	10.98/ 11.17	2.06×10^{-8}	0.389	10.22
$[Co(L)(H_2O)]$	302.57	Brown	19.34/ 19.48	39.15/ 39.69	3.41/ 3.33	4.48/ 4.63	11.48/ 11.72	1.58×10^{-8}	0.400	8.00
$[Ni(L)(H_2O)_3]$	338.30	Ocean spray	17.17/ 17.35	35.71/ 35.50	4.09/ 4.17	4.18/ 4.14	10.31/ 10.48	5.62×10^{-7}	0.718	8.39
$[Cu(L)(H_2O)]H_2O$	325.20	Asian green	19.33/ 19.54	36.86/ 36.93	3.61/ 3.72	4.37/ 4.31	10.75/ 10.90	5.90×10^{-7}	0.228	10.30
$[Zn(LH)_2]$	518.66	Peace	12.53/ 12.61	46.01/ 46.31	3.38/ 3.50	5.33/ 5.40	13.36/ 13.67	6.68×10^{-8}	0.679	11.78
$[Cd(L)(H_2O)_2]_2$	748.13	Yellow	29.89/ 30.05	32.00/ 32.11	3.18/ 3.23	3.69/ 3.74	9.32/ 9.48	1.50×10^{-8}	0.252	13.23
$[UO_2(L)(H_2O)]$	513.67	Dark yellow	46.00/ 46.34	23.24/ 23.38	1.85/ 1.96	2.69/ 2.73	6.82/ 6.90	1.26×10^{-7}	0.601	16.01

ter term G, estimated from the expression $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$, is found to be 1.80, indicating that the ligands are strong-field ligands [10]. Also, the value of G is less than 4, indicating a considerable exchange interaction between the metal ions. The value of $A_{\parallel}$ (157), nuclear hyperfine constant, and α^2 (0.69), degree of covalency, support the structure [17]. The μ_{eff} value, calculated using the equation $\mu_{eff}^2 = 3/4\ g_{av}^2$, was found to be 1.86 μ_B, which closely agreed with the observed magnetic moment.

The reflectance spectrum of the Mn(II) complex exhibited broad bands in the range 16949, 23255, and 26315 cm^{-1} due to $^6A_{1g} \longrightarrow {}^4T_{1g}\ (^4G)$, $^6A_{1g} \longrightarrow {}^4T_{2g}\ (^4G)$ and $^6A_{1g} \longrightarrow {}^4E_g$ transition in an octahedral symmetry. The Fe(II) complex exhibits three bands at 11628 cm^{-1} due to the $^5T_{2g} \longrightarrow {}^5E_g$, and the other two bands in a higher region 15385 and 24390 cm^{-1} are ascribed due to charge – transfer transitions, suggesting an octahedral geometry around the Fe^{2+} ion. The reflectance spectral parameters for Fe^{2+} are found to be Dq = 1162.8 cm^{-1}, B = 628 cm^{-1}, $\beta = 0.593$, $\beta° = 40.7$, and the ligand field stabilization energy (**LFSE**) = 139.1 kJ mol^{-1}. The reduction of the Racah parameter (B) from the free ion value of 1060 to 628 cm^{-1} and $\beta°$ value of 40.7% indicates the partial covalent character of the Fe–L bond [18]. The reflectance spectrum of the Co(II) complex shows bands at 7353, 9091, 15873, and 25641 cm^{-1}, which may be assigned to $^4A_{2g} \longrightarrow {}^4T_{1g}$, $^4A_{2g} \longrightarrow {}^4T_{1g}(F)$, $^4A_{2g} \longrightarrow {}^4T_{1g}\ (P)$ and charge transfer (**CT**) transitions, respectively, toward tetrahedral structure around the Co^{2+} ion [19]. The Ni(II) complex exhibit three bands at 10526, 16950, and 25640 cm^{-1} due to $^3A_{2g}\ (F) \longrightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$, and $^3A_{2g}\ (F) \longrightarrow {}^3T_{1g}(P)$ transitions, respectively, in an octahedral symmetry. Three bands observed at 15625, 16949 and 20408 cm^{-1} in the Cu(II) complex may be assigned to $^2B_{1g} \longrightarrow {}^2A_{1g}$, $^2B_{1g} \longrightarrow {}^2E_g$ and spin-forbidden ligand-to-metal CT transitions, respectively, indicating square planar geometry [20].

The complexes of Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) exhibit magnetic moments of 6.18, 5.18, 4.08, 3.80, and 1.87 μ_B, respectively. These data are close to the reported values for these complexes [21]. The complexes of Zn(II), Cd(II), and UO_2(VI) are diamagnetic as expected from their electronic configuration. The magnetic measurements, infrared and electronic spectral data provided evidence for the structures of the isolated complexes. On the basis of these studies, probable structures for the complexes under study have been proposed (Scheme).



Scheme

Thermal analyses of the complexes were carried out up to 700°C. All the complexes show a gradual mass loss indicating decomposition by fragmentation with an increase in temperature. The Cd(II) and UO_2(VI) complexes decompose in three steps, the ligand and Mn(II), Fe(II), Co(II), and Ni(II) complexes decompose in two steps, while the complexes of Cu(II) and Zn(II) decompose in one step. The Mn(II) complex is stable up to 80°C, the ligand, Cu(II) and Co(II) complexes are stable up to 60°C, whereas the complexes of Fe(II), Cd(II), Ni(II), and Zn(II) are stable to ~105°C. The presence of a water molecules in all the complexes, except the Zn(II) complex, suggested from the IR spectra, is confirmed by the weight loss observed in the first decomposition step of these complexes. The Cu(II) complex lose its weight up to 130°C corresponding to one lattice water molecule (weight loss, %: obs./calcd 5.60/5.54) and further up to 250°C corresponding to one coordinated water molecule. The weight loss at different temperatures in the range 190–250°C corresponds to the loss of two coordinated water molecules in the Mn(II), Fe(II), and Cd(II) complexes, one in the Co(II) and UO_2(VI) complexes and three coordinated water molecules in the Ni(II) complex [22] (weight loss, %: obs./calcd for Mn(II) 11.45/11.38; Fe(II) 11.40/11.34; Cd(II) 11.0/10.4; Co(II) 6.0/5.95; UO_2(VI) 3.5/3.5; Ni(II) 16.25/15.97).

The Zn(II) complex does not show significant weight loss up to 200°C indicating the absence of any water molecule. The organic moiety decomposed further with increasing temperature. Although the decomposed fragment of the ligand could not be approximated owing to continuous weight loss, the complete decomposition of the ligand occurs at ~620°C. At the end of the final step, stable metal oxides are formed corresponding to Mn_3O_4, Fe_2O_3, Co_3O_4, NiO, CuO, ZnO, CdO, and U_3O_8, respectively. From the half decomposition temperature, the relative thermal stability of the complexes is found to be

$$\text{Cu(II)} < \text{Fe(II)} < \text{Ni(II)} < \text{Co(II)} < \text{Mn(II)} < \text{Zn(II)} \approx \text{Cd(II)} < \text{UO}_2\text{(VI)}.$$

Table 2. Thermal decomposition data of HCAGLY and its complexes

Compound	Mp*/half decomposition temperature, °C	Activation energy (E_a), kJ mol^{-1}		Frequency factor (Z), s^{-1}	Entropy change ($-\Delta S$), J mol^{-1} K^{-1}	Free energy change (ΔG), kJ mol^{-1}
		B*	HM*			
HCAGLY (LH_2)	265*	26.80	23.69	30.68	269.50	43.69
$[Mn(L)(H_2O)_2]_2$	341	21.96	19.61	33.96	268.47	39.51
$[Fe(L)(H_2O)_2]_2$	294	27.05	24.13	42.61	264.95	41.45
$[Co(L)(H_2O)]$	330	25.65	24.55	41.57	266.30	43.99
$[Ni(L)(H_2O)_3]$	305	26.29	32.77	65.93	261.34	51.19
$[Cu(L)(H_2O)]H_2O$	270	25.02	30.93	43.08	264.15	47.05
$[Zn(LH)_2]$	364	32.39	46.69	72.81	261.66	67.72
$[Cd(L)(H_2O)_2]_2$	365	23.63	26.97	64.19	262.94	48.17
$[UO_2(L)(H_2O)]$	435	25.30	26.15	72.28	263.24	50.77

* Method: B = Broido and HM = Horowitz–Metzger.

From the thermal decomposition data various kinetic parameters have been calculated by using two methods, viz., Broido [23] and Horowitz–Metzger [24], and comparable values obtained are given in Table 2.

The solid state d.c. electrical conductivity of the synthesized ligand and its complexes in a compressed pellet form (5 ton cm^{-2}) was measured in the temperature range 313–398 K and a linear dependence of $\log\sigma = f(10^3/T)$, indicating the semiconducting behavior of these compounds [25]. 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 is the absolute temperature, and K is the Boltzmann constant. The d.c. electrical conductivity value of the complexes at 373 K lies in the range 1.50×10^{-8} to 5.90×10^{-7} Ohm^{-1} cm^{-1} and decreases in the order Cu > Ni > Mn > UO_2 > Zn > Fe > Co > Cd. The observed low value of electrical conductivity may be attributed to a low molecular weight due to which the extent of conjugation becomes low or undesirable morphology is observed due to pressing of the sample into the hard brittle pellet form [26].

The antibacterial activity was evaluated by the single disc method [27]. The compounds were dissolved in dimethyl sulfoxide at a concentration of 10.0 mg/ml. The 10-mm diameter Whatmann no. 1 paper discs were soaked in different solutions of the compounds, dried, and then placed on the lawn of cultures on neutrient agar plates. 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 the Cappuceino and Sherman method [28] (Table 3).

The ligand HCAGLY was found bactericidal against *S. epidermidis, S. flexneri, S. typhi*, and *S. typhimurium* and bacteriostatic against other strains. The Cu(II) complex shows either good or fairly good activity against all the tested bacterial strains. The Cd(II) and UO_2 complexes have pronounced sensitivity to *S. epidermidis* and *B. coagulans*, respectively. The Ni(II) complex showed low bactericidal activity against *B. coagulans* and bacteriostatic against other organisms. The Co(II) complex evidences moderate zone of inhibition against *S. epidermidis*, *S. flexneri*, and *S. typhi*. The Fe(II) complex shows maximum zone of inhibition against *P. vulgaris*, and *S. epidermidis*, whereas against *S. typhimurium*, *B. coagulans*, and *E. aerogenes*, it is shown by the Zn(II) complex. The Mn(II) complex exhibits fairly good bactericidal nature against *B. coagulans* and *E. faecalis*.

It has been observed that the metal complexes have a higher activity than the free ligand against the same organism under identical experimental conditions [29]. This can be attributed to Tweedy's chelation theory [30], according to which the chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with donor groups and possible π-electron delocalization over the whole ring. This increases the lipophilic character of the metal chelate, which favors its permeating through the lipid layer of bacterial membranes. The toxicity increases with an increase in the concentration of the complexes.

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Table 3. Antibacterial activity of the ligand and its complexes (diameter of inhibition zone in mm)

Compound	*E. coli*	*S. flexneri*	*S. typhi*	*P. vulgaris*	*B. coagulans*	*P. aeruginosa*	*S. aureus*	*K. pneumoniae*	*S. typhimurium*	*E. faecalis*	*S. epidermidis*	*E. aerogenes*
$HCAGLY(LH_2)$	R	13	14	R	R	R	R	R	15	R	13	R
$[Mn\ (L)(H_2O)_2]_2$	R	R	18	R	28	16	13	17	R	22	R	R
$[Fe(L)(H_2O)_2]_2$	R	R	R	21	R	R	R	R	17	18	25	R
$[Co(L)(H_2O)]$	R	18	19	R	R	R	R	R	R	R	17	R
$[Ni(L)(H_2O)_3]$	R	R	R	R	13	R	R	R	R	R	R	R
$[Cu(L)(H_2O)]H_2O$	13	R	13	14	13	14	13	13	R	R	21	13
$[Zn(LH)_2]$	R	R	18	R	28	16	13	17	R	22	R	R
$[Cd(L)(H_2O)_2]_2$	R	14	R	R	29	26	28	R	13	15	R	R
$[UO_2(L)(H_2O)]$	R	13	15	R	18	13	15	R	14	R	15	R

R = resistant.

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