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Research Article

SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITIES OF SCHIFF BASES DERIVED FROM HYDRAZIDE DERIVATIVE AND THEIR Cu(II) Ni(II), Co(II), Zn(II), Cd(II) AND Hg(II), COMPLEXES

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ABSTRACT

Schiff bases derived from 2-(2-(2,6-dichlorophenylamino)phenyl)acetylhydrazide and salicylaldehydes and their Cu(II) Ni(II), Co(II), Zn(II), Cd(II) and Hg(II)complexes have been synthesized and characterized by elemental analysis, conductance measurements, magnetic moment, infrared, NMR, ESR, XRD and electronic spectral studies. The Zn(II), Cd(II) and Hg(II) complexes found to have MLCl composition and Co(II), Ni(II) and Cu(II) complexes $M(L)_2$ composition. On the basis of elemental, spectral and magnetic studies, tetrahedral geometry for Zn(II), Cd(II) and Hg(II) complexes and octahedral geometry for Co(II), Ni(II) and Cu(II) complexes have been assigned.The ligands and all the complexes have also been screened in vitro for their possible antimicrobial activity.

Keywords: Complexes, Hydrazides, Ligands, Metals, Schiff bases.

INTRODUCTION

In recent years the chemistry of hydrazones has been extensively studied, owing to their coordinating capability, pharmacological activity and biological properties[1-4]. The complexes of transition metals with hydrazone ligands have shown wide spectra of biological and pharmaceutical activities such as antimicrobial, antibacterial, antifungal, anti-inflammatory, anticonvulsant, antitubercular, antiviral, antioxidative effects and inhibition of tumor growth[5--9]. The bioinorganic chemistry paid great attention to the Schiff base complexes because many of these complexes have biologically important species[10,11]. So, the synthesis of new ligands and complexes would be important step in the development of coordination chemistry which exhibit novel properties and reactivity.

Hydrazones possessing an azomethine –NHN=CH- proton constitute an important class of compound for new drug development. It was reported that hydrazones have lower toxicity than hydrazides because of the lockage of $–NH_2$ group. In many cases it was also reported that metal chelates possess better biological activities than their corresponding ligands.

Following all these observations and as a part of our continuing research on the coordination chemistry of multidentate ligands[12-14], we report here the synthesis characterization and biological studies of the Schiff bases derived from 2[2-(2,6-dichlorophenyl amino)phenyl]acetylhydrazide derivatives and their Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Hg(II) complexes.

MATERIALS AND METHODS

All the chemicals and solvents used were of AR grade. Salicylaldehyde, Bromo-Salicylaldehyde and hydrazine hydrate were purchased from a

commercial shop and were distilled before use. The metal salts purchased from commercial sources werein their hydrated form and used as such.

i) Synthesis of ligands (Fig. 1)

a) **Preparation of hydrazide derivatives**

An equimolar mixture of 2[2(2,6-dichlorophenylamino)phenyl]aceticacid (0.01M) and hydrazine hydrate (0.01M, 99%) in 30 ml ethanol was refluxed for 6-7 hours in a round bottomed flask. The solid separated on cooling was filtered, washed several times with water, dried and recrystallised from alcohol (M.P: 100°C).

b) **Preparation of Schiff bases**

A mixture of 2[2-(2,6-dichlorophenylamino)phenyl] acetylhydrazide (0.01M) and substituted salicyladehyde (0.01M) in absolute alcohol (50 ml) containing a few drops of concentrated hydrochloric acid, was refluxed for 4 hours on a steam bath. The reaction mixture was cooled to room temperature. The Schiff bases separated was filtered, washed, dried and recrystallised from alcohol. Yield 70%, M.P: 210°C.

ii) Synthesis of complexes

To the hot solution of ligands in ethahol (0.01 mol) was added hot ethanolic solutions (10ml) of metal chloride (0.01mol). The reaction mixture was refluxed on a water bath for 4 hours to get clear solution. 1g of sodium acetate was added to the reaction mixture just to adjust the pH of the solution. The reaction mixture was further refluxed for 2 hours. The resulting mixture decomposed by pouring into the 100ml distilled water with stirring. The suspended solid complex was allowed to settle and collected by filtration, washed with sufficient quantity of distilled water and then with little hot ethanol to apparent dryness and dried in a vacuum over anhydrous calcium chloride in a dessicator. Yield 70%.

iii) Analysis and physical measurements

The elemental analysis was carried out on Heraeus CHN-O rapid analyzer. The metal contents in the complexes were determined gravimetrically by using standard procedure[15]. The molar conductance measurements were carried out at room temperature on ELICO-CM-827 Conductivity Bridge (cell constant 0.82 cm^{-1}) using 1 x 10^{-3}M solution of the complexes in DMSO. The magnetic susceptibility data at room temperature were obtained by using Lewis Coil Force Magnetometer (Model 300) of George Associates Inc. make using a Cahn 2000 electro balance. Electronic spectral measurements were carried out using ELICO SL-164 spectrophotometer in the range of 400-1200 nm. The IR spectra of the ligands and their complexes in KBr pallets were recorded on a Perkin Elmer 297 spectrophotometer in the range 4000-200 cm^{-1}. Proton ^{1}HNMR spectra of the ligand and their complexes were recorded using Varian EM-390 spectrometer in DMSO-d$_6$ with TMS as an internal reference. ESR measurements were carried out on a Varian E-109 X-band spectrometer, working at a microwave frequency of 9.05 GHz.

ANTIMICROBIAL ACTIVITY

The antimicrobial activity of the ligands HL_1 and HL_2 and their metal complexes were determined by agar cup-plate method[31-32]. The antibacterial activity against *Escherichia coli* and S aureus and antifungal activity against *Aspergillusniger* and A. flavous, were screened by the ligands and their metal complexes. The medium was prepared as per the instructions of the manufacturer of dry Mueller Hinton agar powder (Hi-Media). The test ligands and their metal complexes were dissolved in dimethyleformamide (DMF) at a concentration of 1 mg/ml. Streptomycin (100µg/ml) in DMF was used as a standard for antibacterial and Chlotrimazole (100µg/ml) in DMF was used as reference standard for antifungal activity. The solvent control (only DMF) was also maintained throughout the experiment. The zones of inhibition are reported in Table-6.

RESULTS AND DISCUSSION

The analytical and physical data of the compounds are given in Table-1(a-b). The results of elemental analyses of Cu(II), Ni(II) and Co(II) complexes corresponds to 1:2 stoichiometry of the type $M(L)_2$ and that of Zn(II), Cd(II) and Hg(II) complexes 1:1 stoichiometry of the type MLCl. The molar conductance values obtained for these complexes in DMF and DMSO indicates that all the complexes are nonlectrolytes. The magnetic moment of the Cu(II), Ni(II) and Co(II) complexes of HL_1 and HL_2 are in the range of 1.61-1.85 B.M., 2.8-3.2 B.M. and 5.05-5.14 B.M., respectively. The μ_{eff} values are well within the range known for six coordinated octahedral geometry[16-18] (Table-2).

The electronic spectral data of Cu(II), Co(II) and Ni(II) complexes of the ligand HL_1 and HL_2 were recorded in DMF as shown in Table 2. The

electronic spectra of Co(II) complexes of HL_1 and HL_2 exhibits two bands in the region of 8895-13000 cm^{-1} and 18000 – 21000 cm^{-1} and are attributed to $^4T_{1g} \rightarrow {}^4A_{2g}(F)$ (v_1) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively. The bands due to the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (v_2) transitioncould not observed because of its low intensity. However the position of the v_2 band has been computed 16005 cm^{-1} by the equation, $v_2 = v_1+10Dq$. The Co(II) complex under present investigation possess inter-electronic repulsion parameter (B') 927-998 cm^{-1}. The Nephelauxetic ratio (β) for the present Co(II) complex is 0.95, this is less than one, suggesting partial covalency in the metal ligand bond. The values Dq, B', β, v_2/v_1, (Table 2) suggest the octahedral geometry for the Co(II) complexes[19,20]. Ni(II) complexes exhibit three bands in the range of 8990-13810 cm^{-1}, 14088-16335 cm^{-1} and 20964-25210 cm^{-1}, assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (v_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (v_2) and $^4A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (v_3) transitions respectively and are in confirmatory with the octahedral geometry for the Ni(II) ion. The Table 2 shows the ligand field parameters such as Dq, B′, β, and v_2/v_1, calculated by using Band-fitting equation given by Underhill and Billing[21]. Racah 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 is further support the octahedral geometry around the Ni(II) ion[22]. Cu(II) complex exhibits three bands in the region 10330-11200 cm^{-1} (v_1), 15300-17500 cm^{-1} (v_2) and 19500-23000 cm^{-1} (v_3) are of equal energy and giving rise to single broad band which may be assigned to the transitions $^2B_{1g} \rightarrow {}^2A_{1g}$ (v_1), $^2B_{1g} \rightarrow {}^2B_{2g}$ (v_2), $^2B_{1g} \rightarrow {}^2E_g$ (v_3) respectively. The broadness of the band is due to the ligand field and the John-Teller effect[23]. These observations favor the octahedral geometry for the Cu(II) complexes.

The important infrared frequencies exhibited by the ligands (HL_1& HL_2) and their complexes are given in Table 3. Comparison of IR spectra of the ligands with those of complexes is based on earlier studies of similar ligands[24]. The ligands HL_1& HL_2 have shown bands at 1725 cm^{-1} and 1720 cm^{-1} respectively due to v(C=O) and in the complexes the lower frequency shift by 15 to 20 cm^{-1} are observed. The infrared spectra of the ligands also exhibits high intensity band in the region 1646-1643 cm^{-1} due to v(C=N) and the bands between 3450-3445 cm^{-1} due to phenolic OH. In the complexes, the low frequency shift (15-20 cm^{-1}) are observed around 1616 cm^{-1} due to v(C=N) is suggestive of coordination through nitrogen of the azomethine group[25]to the metal(II) Chloride.. The band around 3450 cm^{-1} due to phenolic OH, which is observed in the ligands, disappeared in the complexes, this indicates that the ligands coordinated to the metal ion through phenolic oxygen atom of OH group via deprotonation[25]. Appearances of three new bands in the region 520-550 cm^{-1}, 420-432 cm^{-1} 350-366 cm^{-1}, are due to M-N, M-O and M-Cl bands respectively.

The ^{1}HNMR spectrum of the ligands HL_1& HL_2 showed singlets at 12.59 – 12.291 δ (s, 1H, OH) due to proton of phenolic –OH group, two singlets of azomethine protons in the range of 8.65 – 9.63 δ and 8.77 – 9.82 δ (s, 1H, CH=N). The sixteen aromatic protons have resonated in the region 6.9-8.15 δ as multiplet (Table 4).

In the ^{1}HNMR spectra of Zn(II), Cd(II) and Hg(II) complexes, the sixteen aromatic protons have resonated in the region 7.2 – 8.25 δ as multiplets. This lower shift confirms the complex formation. The signal due to OH protons of the ligands HL_1 and HL_2 at 12.59 δ and 12.29 δ respectively disappeared in the complexes indicating the involment of OH group in the complex formation via deprotonation[26-28]. The HC=N proton signals have shifted to downfield in the complexes of HL_1 and HL_2, which indicates the desielding of C=N group through nitrogen due to coordination.

The ESR spectra of the copper complexes as polycrystalline sample have been recorded at room temperature (Table 5), (ESR chart was calibrated with DPPH). The observed g values for the Cu(II) complexes of the ligand HL_1 are $g_{\parallel}$=2.2277, $g_{\perp}$=2.1228, g_{av} =2.1932 and G = 4.314 and of HL_2 are $g_{\parallel}$=2.052 $g_{\perp}$= 2.024 g_{av}= 2.030 and G = 4.22. The isotropic g values have been calculated by Kneubuhl`s methods[29] and methods reported earlier $G = (g_{\parallel}-2)/(g_{\perp}-2)$, which measures the exchange interaction between copper centers. According the Hathaway[30] if the G value is greater than 4, the exchange interaction is negligible, while a value of G less than 4 indicates a considerable exchange in the solid complexes. As G=4.314 and G= 4.22 for Cu (HL_1)and Cu (HL_2) complexes respectively, indicates that there is no spin exchange interaction in the complexes and hence distorted octahedral geometry is proposed for the copper complexes.

Table 1a: Physical and analytical data of the ligand HL_1 and its Metal Complexes

Ligands/ Complexes	Empirical formula	M. P. (°C) Yield (%)	Elemental analysis (%), Found (Calculated)					
			C	H	N	O	Cl	M
HL_1	$C_{21}H_{17}N_3O_2Cl_2$	210 (75)	60.88 (60.85)	4.14 (4.12)	10.14 (10.12)	7.72 (7.50)	17.12 (11.11)	--
$Cu(L_1)_2$	$Cu(C_{21}H_{17}N_3O_2Cl_2)_2$	280 (69)	56.67 (56.62)	3.62 (3.60)	9.44 (9.40)	7.19 (7.18)	15.93 15.91	7.14 (7.13)
$Ni(L_2)_2$	$Ni(C_{21}H_{17}N_3O_2Cl_2)_2$	290 (73)	56.98 (56.96)	3.64 (3.62)	9.49 (9.48)	7.23 (7.04)	16.02 (16.00)	6.63 (6.62)
$Co(L_2)_2$	$Co(C_{21}H_{17}N_3O_2Cl_2)_2$	300 (76)	53.72 (53.70)	3.44 (3.21)	8.95 (8.91)	6.82 (6.80)	11.97 (11.95)	6.68 (6.56)
$Zn(L_1)$	$Zn(C_{21}H_{17}N_3O_2Cl_3)$	283 (70)	49.06 (48.76)	3.14 (3.12)	8.17 (8.15)	6.22 (6.17)	20.69 (20.68)	12.72 (12.71)
$Cd(L_1)$	$Cd(C_{21}H_{17}N_3O_2Cl_3)$	273 (72)	44.95 (44.86)	2.87 (2.83)	7.49 (7.48)	5.70 (5.59)	18.95 (18.84)	20.03 (19.90)
$Hg(L_1)$	$Hg(C_{21}H_{17}N_3O_2Cl_3)$	270 (67)	38.84 (38.80)	2.48 (2.45)	6.47 (6.45)	4.93 (4.91)	16.38 (16.32)	30.89 (30.88)

Table 1b: Physical and analytical data of the ligand HL_2 and its Metal Complexes

Ligands/ Complexes	Empirical formula	M. P. (°C) Yield (%)	Elemental analysis (%), Found (Calculated)						
			C	H	N	O	Cl	Br	M
HL_2	$C_{21}H_{17}N_3O_2Cl_2Br$	230 (72)	51.01 (50.85)	3.44 (3.32)	8.50 (8.12)	6.48 (6.30)	14.37 (14.11)	16.17 16.11	--
$Cu(L_2)_2$	$Cu(C_{21}H_{17}N_3O_2Cl_2Br)_2$	296 (70)	48.02 (47.62)	3.24 (3.15)	8.00 (7.40)	6.10 (5.98)	13.53 12.91	15.22 15.09	6.05 (6.03)
$Ni(L_2)_2$	$Ni(C_{21}H_{17}N_3O_2Cl_2Br)_2$	298 (75)	48.25 (47.96)	3.25 (3.15)	8.04 (7.87)	6.13 (6.04)	13.59 (13.47)	15.29 (15.16)	5.65 (5.62)
$Co(L_2)_2$	$Co(C_{21}H_{17}N_3O_2Cl_2Br)_2$	305 (80)	48.24 (47.70)	3.24 (3.21)	8.03 (7.97)	6.12 (6.04)	13.58 (13.55)	15.30 (15.21)	5.64 (5.56)
$Zn(L_2)_2$	$Zn(C_{21}H_{17}N_3O_2Cl_3Br)$	299 (73)	42.36 (42.21)	2.86 (2.82)	7.06 (7.02)	5.38 (5.33)	17.09 (17.07)	13.44 (13.41)	10.99 (10.88)
$Cd(L_2)_2$	$Cd(C_{21}H_{17}N_3O_2Cl_3Br)$	285 (70)	39.26 (39.18)	2.65 (2.63)	6.54 (6.48)	4.98 (4.93)	16.59 (16.54)	12.45 (12.36)	17.51 (17.49)
$Hg(L_2)_2$	$Hg(C_{21}H_{17}N_3O_2Cl_3Br)$	292 (71)	34.52 (34.50)	2.33 (2.25)	5.75 (5.72)	4.39 (4.24)	14.59 (14.52)	10.95 (10.85)	27.48 (27.43)

Table 2: Magnetic moments, Electronic spectral data and ligand field parameters of Cu(II), Ni(II) and Co(II) complexes of the Ligand HL_1& HL_2

Complexes	v_1	v_2	v_3	Dq(cm^{-1})	B′	β	v_2/ v_1	μ_{eff} B.M
$Cu(L_1)_2$	12280	16263	22679	--	--	--	--	1.61
$Ni(L_1)_2$	10057	16005	20015	863.83	927	0.95	1.59	2.80
$Co(L_1)_2$	13810	15151	25316	899.00	865	0.82	1.41	5.05
$Cu(L_2)_2$	12030	15622	21478	--	--	--	--	1.85
$Ni(L_2)_2$	10362	16260	20325	1036	740	0.72	1.57	3.20
$Co(L_2)_2$	12163	16896	22725	1036	715	0.73	1.39	5.14

Table 3: Infrared spectral Data of the ligands HL_1& HL_2 and their complexes

Ligands/ Complexes	ν_{OH}	$\nu_{C=O}$	$\nu_{C=N}$	ν_{C-O}	ν_{N-H}	ν_{M-N}	ν_{M-O}	ν_{M-Cl}
HL_1	3449.40	1725	1645	1284	3239	--	--	--
$Cu(L_1)_2$	--	1705	1622	1301	3210	528	422	--
$Ni(L_1)_2$	--	1708	1623	1306	3221	530	421	--
$Co(L_1)_2$	--	1704	1622	1310	3220	549	428	--
$Zn(L_1Cl)$	--	1703	1616	1316	3218	519	432	365
$Cd(L_1Cl)$	--	1711	1615	1309	3209	520	433	357
$Hg(L_1Cl)$	--	1709	1621	1311	3215	515	429	363
HL_2	3438.67	1720	1643	1287	3240	--	--	--
$Cu(L_2)_2$	--	1698	1619	1298	3215	534	428	--
$Ni(L_2)_2$	--	1702	1620	1305	3218	542	424	--
$Co(L_2)_2$	--	1695	1618	1310	3221	526	431	--
$Zn(L_2Cl)$	--	1697	1625	1312	3220	520	436	370
$Cd(L_2Cl)$	--	1705	1619	1307	3211	529	427	364
$Hg(L_2Cl)$	--	1703	1617	1314	3218	545	439	369

Table 4: ^1H NMR spectral data of Zn(II), Cd(II) & Hg(II) complexes of HL_1 and HL_2 ligands

Ligand/Complexes	OH Protons	CH=N Protons	Aromatic Protons
HL_1	12.59	8.65, 9.63	6.90 – 7.20
$Zn(L_1Cl)$	--	8.47, 9.28	7.12 – 7.26
$Cd(L_1Cl)$	--	8.29, 9.23	7.28 – 7.57
$Hg(L_1Cl)$	--	8.19, 9.16	7.35 – 8.25
HL_2	12.29	8.77, 9.82	7.00 – 7.25
$Zn(L_2Cl)$	--	8.52, 9.46	7.18 – 7.32
$Cd(L_2Cl)$	--	8.34, 9.69	7.20 – 7.40
$Hg(L_2Cl)$	--	8.49, 9.58	7.18 – 7.35

Table 5: ESR Spectral data Cu(II) complexes

Complexes	$g_{\parallel}$	$g_{\perp}$	g_{av}	G
$Cu(L_1)_2$	2.2277	2.1228	2.175	4.314
$Cu(L_2)_2$	2.052	2.024	2.038	4.22

Table 6: Antibacterial and antifungal activities of the ligands and their metal complexes (Zone of inhibition in mm)

Ligands/ Complexes	Antibacterial		Antifungal		Ligands/ Complexes	Antibacterial		Antifungal	
	E. coli	S. aureus	A. niger	A. flavous		E. coli	S. aureus	A. niger	A. flavous
HL_1	12	14	10	11	**HL_2**	14	12	10	10
$Cu(L_1)_2$	18	17	11	10	$Cu(L_2)_2$	21	19	14	13
$Ni(L_1)_2$	15	18	17	16	$Ni(L_2)_2$	18	17	18	19
$Co(L_1)_2$	20	19	10	12	$Co(L_2)_2$	19	18	17	17
$Zn(L_1)$	13	15	12	14	$Zn(L_2)$	17	19	16	13
$Cd(L_1)$	12	17	13	14	$Cd(L_2)$	15	17	15	18
$Hg(L_1)$	14	14	16	12	$Hg(L_2)$	16	18	16	20
Streptomycin	24	21	--	--	Chlotrimazole	--	--	24	23
Chlotrimazole	--	--	24	23	Streptomycin	24	21		

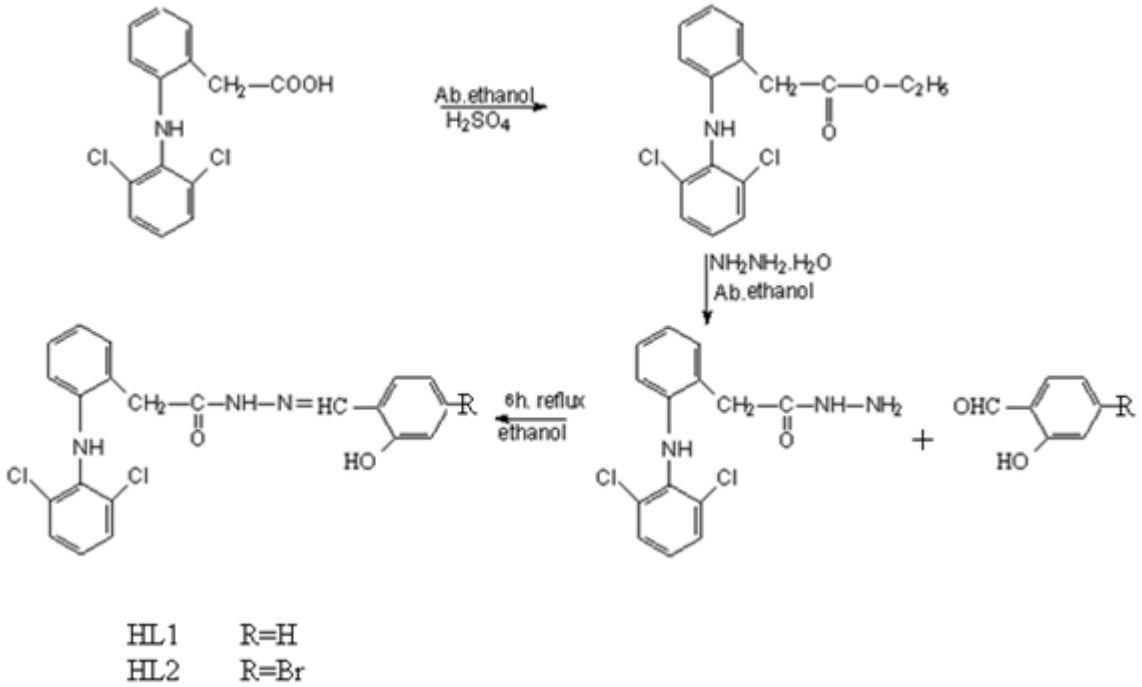
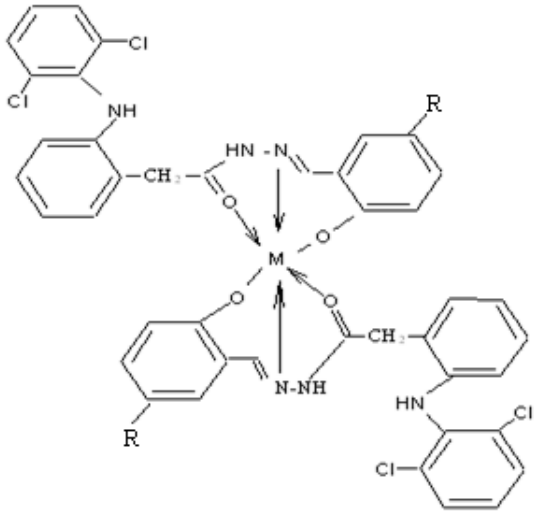
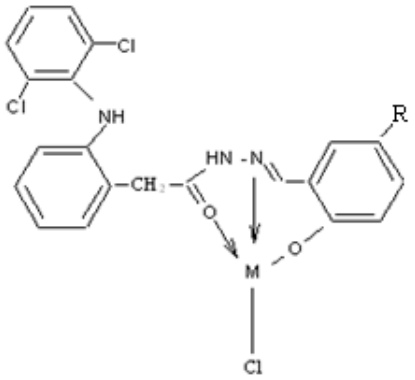


Fig. 1: Scheme of Synthesis of ligands (HL_1 and HL_2)

CONCLUSION

On the basis of elemental analysis, molar conductance, magnetic susceptibility measurements, electronic, IR, 1HNMR, and ESR spectral observations, octahedral geometry with coordination number six (Fig.2) has been proposed for the Cu(II), Ni(II) and Co(II) complexes and Tetrahedral geometry (Fig.3) with coordination number four for Zn(II), Cd(II) and Hg(II) complexes. The following structures have been proposed for the complexes;





Where R = H, Br

Fig. 2: M = Cu(II), Ni(II) and Co(II) **Fig.3:M = Zn(II), Cd(II) and Hg(II)**

From the Table-6, it is clear that the ligands HL_1 and HL_2 show moderate activity against the tested microorganisms. But their metal complexes show moderate to high activity against the tested microorganisms[33-37]. Even though the test compounds are less active with reference to the standard drug, the data reported in this article may be a helpful guide for the medicinal chemists who are working in the area.

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