Preparation, Characterization, Biological Activity and 3D Molecular Modeling of Mn(II), Co(II), Ni(II), Cu(II), Pd(II) and Ru(III) Complexes of Some Sulfadrug Schiff Bases

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Mn(II), Co(II), Ni(II), Cu(II), Pd(II) and Ru(III) complexes of Schiff bases derived from the condensation of sulfaguanidine with 2,4-dihydroxy benzaldehyde (**HL1**), 2-hydroxy-1-naphthaldehyde (**HL2**) and salicylaldehyde (**HL3**) have been synthesized. The structures of the prepared metal complexes were proposed based on elemental analysis, molar conductance, thermal analysis (TGA, DSC and DTG), magnetic susceptibility measurements and spectroscopic techniques (IR, UV-Vis, and ESR). In all complexes, the ligand bonds to the metal ion through the azomethine nitrogen and α -hydroxy oxygen atoms. The structures of Pd(II) complex **8** and Ru(III) complex **9** were found to be polynuclear. Two kinds of stereochemical geometries; distorted tetrahedral and distorted square pyramidal, have been realized for the Cu(II) complexes based on the results of UV-Vis, magnetic susceptibility and ESR spectra whereas octahedral geometry was predicted for Co(II), Mn(II) and Ru(III) complexes. Ni(II) complexes were predicted to be square planar and tetrahedral and Pd(II) complexes were found to be square planar. The antimicrobial activity of the ligands and their metal complexes was also investigated against the gram-positive bacteria *Staphylococcus aures* and *Bacillus subtilis* and gram-negative bacteria, *Escherichia coli* and *Pesudomonas aeruginosa*, by using the agar dilution method. Chloramphenicol was used as standard compound. The obtained data revealed that the metal complexes are more or less, active than the parent ligand and standard. The X-ray crystal structure of **HL3** has been also reported.

Keywords sulfaguanidine, transition metal complexes, spectral studies, biological activity, crystal structure, molecular modeling

Introduction

Sulfonamides are an important class of antibacterial drugs used in medicine and veterinary practice. They are widely used in the treatment of infections, especially for patients intolerant to antibiotics. The vast commercial success of these medicinal agents has made the chemistry of sulfonamides to become a major area of research and an important branch of commercial importance in pharmaceutical sciences.^[1]

Schiff bases still occupy an important position as ligands for the synthesis of many transition metal complexes even almost a century since their discovery. As a result, Schiff bases derived from sulfa drugs have acquired a wide interest for their useful applications in biological systems.^[2] Since it is well known that the metal complexes are much more effective than the ligand, the metal ion complexes of Schiff bases derived from sulfa drugs have gained considerable importance

due to their pronounced biological activity.^[3] There are several reports on the Schiff base metal complexes derived from sulfa drugs.^[4-7] They have been found to possess effective fungicidal and antimicrobial activity.^[4] Recently, Cu(II), Ni(II) and Co(II) complexes of biologically active Schiff bases derived from the condensation of sulfadiazine with salicylaldehyde were also studied. The increased activity of the metal chelates can be explained on the basis of chelation theory.^[8]

Depending on the fact that sulfaguanidine is a useful antibacterial drug with a typical sulfonamide structure, we report here the synthesis and characterization of Mn(II), Co(II), Ni(II), Cu(II), Pd(II) and Ru(III) complexes of Schiff bases derived from the condensation of sulfaguanidine with 2,4-dihydroxy benzaldehyde (**HL1**), 2-hydroxy-1-naphthaldehyde (**HL2**) and salicylaldehyde (**HL3**). The electrochemical and antimicrobial activities of the prepared ligands and their metal ion complexes were also studied.

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Experimental

Physical measurements and materials

Sulfadrugs and aldehyde derivatives used in this study were purchased from TCI and Wako chemical companies, Tokyo. The other solvents and chemicals were chemically pure from BDH chemicals.

Elemental analysis was carried out on a Perkin Elmer 2400II CHN analyzer. UV-Visible absorption spectra were recorded on Shimadzu UV-2450 spectrophotometer using nujol mull technique. IR spectra were achieved using Perkin-Elmer Spectrum One FT-IR spectrometer equipped with a single reflection diamond ATR accessory. TGA and DTG were obtained using a Shimadzu TG-50 thermal analyzer while DSC were recorded using Seiko SDC-6220 with TAS100 in a dynamic nitrogen atmosphere with a heating rate of 10 $^{\circ}C \cdot min^{-1}$. Magnetic susceptibility measurements at room temperature (25 °C) were determined on a Johnson Matthey magnetic susceptibility balance using Hg[(Co(SCN)₄] as calibrant; diamagnetic corrections were calculated from Pascal's constants. Conductance measurements were carried out by means of a YSI model 32 conductance meter in DMF (10^{-3} mol/L). X-band ESR spectra were recorded at 25 °C on a JEOL model JM-FE3 spectrometer provided by JEOL microwave unit using diphenylpicrylhydrazyl (DPPH) as the reference material. The nutrient agar solid medium contained 3 g of beef extract, 5 g of peptone and 15 g of agar per liter. It was sterilized under high pressure steam for 30 min, the bacteria used for testing the biological activity were provided by the Biology Department, Tanta University.

Preparation of the Schiff bases

The Schiff bases were prepared by condensation of sulfaguanidine with 2,4-dihydroxy benzaldehyde (HL1), 2-hydroxy-1-naphthaldehyde (HL2) and salicylaldehyde (HL3), in methanol as solvent by the molar ratio 1 : 2, 1 : 1 and 1 : 1, respectively. The reaction mixtures were refluxed in water bath for 2—3 h for HL2 and HL3 while HL1 required longer time (about 15 h). The products, which precipitated on hot, were filtered off from hot solutions, washed and dried in desiccator over anhydrous CaCl₂. The purity of the ligands was confirmed by the results of elemental analysis and IR spectra; the structure of HL2 was further confirmed by X-ray single crystal analysis.^[9] The structures of the ligands used in the present study are illustrated in Scheme 1.

Preparation of the metal complexes

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The solid metal ion complexes were prepared by mixing the appropriate amounts of the ligand in a MeOH/DMF mixture (50%, V/V) as a solvent with the hydrated metal chlorides [CuCl₂•2H₂O, CoCl₂•6H₂O, NiCl₂•6H₂O, MnCl₂•4H₂O, RuCl₃•2H₂O and K₂PdCl₄] in absolute methanol by the ratio 2 L : 1 mol/L or 1 L

: 1 mol/L in the presence of few drops of triethyl amine as basic medium. The resulting solutions were then refluxed under stirring for 4 h, the solid complexes, which were separated out on hot, were filtered off, washed with acetone and ether then dried in desiccator over anhydrous CaCl₂.

X-ray crystallography

Single crystals of HL3 were obtained by recrystallization from acetonitrile. Yellow needles were obtained by slow evaporation of the solvent over 2 d at 5 °C. A single crystal suitable for X-ray crystallography of both compounds was mounted on a glass fiber using paratone oil. Data were collected by a Bruker SMART APEX2/ CCD based diffractometer with monochromated Mo ka radiation ($\lambda = 0.710373$ Å) from a rotating anode source with mirror focusing apparatus. Cell parameters were retrieved using APEX2 software^[10] and refined using SAINT^[10] on all observed reflections. Data reduction was performed using the SAINT software. Absorption corrections were applied using SADABS.^[11] The structures were solved by direct method using SHELXS- $97^{[12]}$ and refined by the least-square method on F^2 using SHELXL-97 and KENX^[13] program. Molecular graphics for publication were prepared by TEXSAN^[14] program. The crystal structure was found to be monoclinic with space group P2(1)/c. The compound could be expressed in the formula C₁₄H₁₆N₄O₄S with unit cell parameters a=5.502(11) nm, b=7.578(15) nm, c= $35.156(7) \text{ nm}, \beta = 90.958(2)^{\circ}, V = 1465.4 \text{ Å}^3, Z = 4, \mu =$ 0.25 mm^{-1} . The crystal data have been deposited with CCDC by the number of 771136.

Molecular modeling studies

All the calculations were carried out on a Pentium



IV 3.0 GHz machine on windows xp environment using Sigress program.^[15] The structures were optimized using the molecular mechanics calculations (MM3) developed by Allinger *et al.*^[16-18]

Results and Discussion

Description of the crystal structure

The structure of the ligand, **HL3**, with atom labeling scheme is given in Figure 1. The asymmetric unit of **HL3** contains one independent molecule and water molecule. The conformation of the molecule is stabilized by the two intramolecular hydrogen bonds N(4)— H(4B)····O(3) and O(1)—H(1)····N(1), while the crystal packing is stabilized by two intermolecular hydrogen bonds [N(4)—H(4B)····O(2)(i) and O(4)—H(16)··· O(3)(ii); symmetry operations (i): x-1, y, z, (ii): -x+1, -y+1, -z+1]; no stacking interaction was found in the crystal as shown in Figure 2. The C=N double bond character of the guanidine moiety is fully delocalized over the unit as shown by the similar C—N distances within the unit.



Figure 1 The molecular structure of HL3 showing the atomlabeling scheme.



Figure 2 A view of the crystal packing of HL3.

The two planes defined with the atoms C(1)—C(6) and atoms C(14), N(2)—N(4) are declined with respect to the central benzene plane [defined by the atoms C(8)—C(13)] by 87.29(25)° and 3.00(33)°, respectively. In the best plane calculations carried out for the above-mentioned three planes, the r.m.s. deviations are in the range of 0.0011—0.067 Å, revealing that all these rings have an essentially planar geometry.

Metal complexes and characterization

The analytical and physical data of the prepared ligands and their metal ion complexes are collected in Table 1. The elemental analysis data indicate that the metal complexes have 1 : 1, 1 : 2 and 2 : 2 (metal : ligand) stoichiometry. The molar conductance values of 10^{-3} mol/L solution of the complexes in DMF were found to be within the range 8.5—26.95 $\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{mol}^{-1}$, indicating the non electrolytic nature of the metal complexes.^[19]

Thermal analysis

The thermal behavior of the metal complexes was studied using TG, DTG and DSC techniques. The stages of decomposition, temperature range, weight loss percentages as well as decomposition products are given in Table 2.

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Table 1 Elemental analysis, magnetic moment values and physical properties of the prepared compounds

			· ·	<u> </u>		-	
Comp.	Formula	Colour	m.p./°C	1 ^a	Analysis found (calcd)/%		
				Λ	С	Н	Ν
HL1	HL1•H ₂ O	Deep red	200^{b}	—	53.12 (53.40)	4.28 (4.23)	12.16 (11.86)
1	$[Cu(L1)_2]$ •2H ₂ O	Brown	221 ^b	8.5	50.37 (50.12)	4.10 (3.81)	10.79 (11.13)
2	$[Co(L1)_2(CH_3OH)_2]$	Dark red	>300	15.43	51.59 (51.31)	4.34 (4.11)	10.41 (10.88)
3	[Ni(L1)Cl(H ₂ O)]•CH ₃ OH	Reddish brown	248 ^b	18.5	44.38 (44.21)	4.78 (3.88)	8.63 (9.37)
4	[Mn(L1) ₂ (CH ₃ OH)(H ₂ O)]	Reddish brown	176 ^b	12.45	51.60 (51.04)	3.59 (3.98)	11.97 (11.07)
HL2	HL2	Yellow	245	_	59.16 (58.71)	4.39 (4.34)	14.94 (15.20)
5	$[Cu(L2)_2(CH_3OH)]$	Faint brown	>300	10.7	53.29 (53.52)	4.36 (4.13)	14.16 (13.49)
6	$[Co(L2)_2(H_2O)_2] \cdot 2H_2O$	Dark brown	270 ^b	19.7	50.61 (50.00)	4.82 (4.39)	12.50 (12.94)
7	$[Ni(L2)_2]$ •CH ₃ OH	Faint green	>300	18.31	54.27 (53.83)	4.11 (4.15)	13.58 (13.57)
8	$[Pd_2(L2)_2]$	Green	>300	26.95	46.04 (45.72)	3.29 (2.98)	11.84 (11.85)
HL3	HL3 •H ₂ O	Faint yellow	240	—	50.09 (50.01)	4.84 (4.75)	16.58 (16.65)
9	$[Ru_2(L3)_2Cl_2(H_2O)_2]\bullet CH_3OH\bullet H_2O$	Deep brown	>300	26.01	34.99 (35.12)	4.07 (3.46)	12.26 (11.30)
10	$[Pd(L3)Cl(H_2O)]$	Olive green	>300	19.67	35.72 (35.23)	3.36 (3.17)	12.28 (11.74)

^{*a*} Ω^{-1} •cm²•mol⁻¹; ^{*b*} decomposition.

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$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$I-SO_2-C_6H_4) +$ and formation
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$I-SO_2-C_6H_4) +$ and formation
$ \begin{array}{c} 1 \\ [Cu(L1)_2]^{\bullet}2H_2O \\ (1006.4) \end{array} \begin{array}{c} 40 - 91 & 83 & 66 (-) \\ 91 - 216 & 151 & 148 (-) \\ 216 - 399 & 392 & 393 (+) \\ (1006.4) \end{array} \begin{array}{c} (3.57) 3.00 & \text{Loss of lattice water} \\ (10.13) 10.12 & \text{Loss of } 6(OH) \text{ groups} \\ (62.2) 62.73 & \text{Loss of } 2(CH = N-C = NH-HN) \\ 2(CH = N) \\ (2CH = N) \\ (2CH = N) \end{array} $	$1-SO_2-C_6H_4) +$ and formation
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$1-SO_2-C_6H_4) +$ and formation
$ \begin{bmatrix} Cu(L1)_2] \cdot 2H_2O \\ C_{42}H_{38}N_8O_{14}S_2Cu \\ (1006.4) \end{bmatrix} $ $ \begin{bmatrix} 216-399 & 392 \\ 399-421 & 412 \\ 421-507 & 455 \end{bmatrix} $ $ \begin{bmatrix} 399-421 & 412 \\ 414(+) \\ 421-507 & 455 \end{bmatrix} $ $ \begin{bmatrix} 9.24 \\ 9.06 \\ 108 \\ 506 \end{bmatrix} $ $ \begin{bmatrix} 9.24 \\ 9.06 \\ 108 \\ 108 \end{bmatrix} $ $ \begin{bmatrix} 9.24 \\ 9.06 \\ 108 \\ 108 \end{bmatrix} $ $ \begin{bmatrix} 9.24 \\ 9.06 \\ $	$1-SO_2-C_6H_4) +$ and formation
$\begin{array}{c} 2 \\ C_{42}H_{38}N_8O_{14}S_2Cu \\ (1006.4) \\ \end{array} \begin{array}{c} 399-421 \\ 421-507 \\ 455 \\ \end{array} \begin{array}{c} 414(+) \\ 468(+) \\ \end{array} \begin{array}{c} 9.24 \\ 9.06 \\ (7.66) \\ 7.58 \\ \end{array} \begin{array}{c} 2 \\ Further \ decomposition \ of \ ligand \\ of \ CuO \\ \end{array}$	and formation
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	and formation
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	and formation
$\begin{array}{c} 2 \\ Co(L1)_2(CH_3OH)_2 \end{array} 35-130 88 90 (-) \\ \hline \end{array} (6.21) 6.69 Loss of coordinated MeOH \\ \hline \end{array} (200 (-) \\ \hline \end{array} (6.21) 6.69 Loss of coordinated MeOH \\ \hline \end{array} (200 (-) \\ \hline \bigg) (200 (-) \\ \bigg) (200 (-)$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
$[Co(L1)_{2}(CH_{3}OH)_{2}] \qquad 35-130 88 \qquad 90 (-) \qquad (6.21) 6.69 Loss of coordinated MeOH$	
$\frac{130-320}{C_{44}H_{42}N_8O_{14}S_2Co} = \frac{130-320}{200} = \frac{210}{180(+)} = \frac{180(+)}{(23.10)} = \frac{23.87}{Loss of 2[C_6H_3OH+CH=N]}$	1.6
(1029.9) $320-550$ 480 $410(+), 490(+)$ (62.91) 61.99 Further decomposition of ligand	and formation
72 ()	
3 33-81 52 $\frac{75(-)}{125(-)}$ (5.35) 5.14 Loss of lattice MeOH	
$[Ni(L1)Cl(H_2O)]$ •CH ₃ OH 81-245 135, 241 $\frac{125}{258}(-)$ 304 (8.95) 8.99 Loss of coordinated water and Cl ⁻	
$C_{22}H_{23}N_4O_8SCINi$ 245-436 357 256 (-), 504 (22.75) 22.28 Loss of $C_6H_3(OH)_2+CH=N$	
(597.6) $436-911499, 627 \frac{(+)}{493} \frac{(+)}{(+)} \frac{537}{537} \frac{(+)}{(+)} (50.46) 50.05$ Further decomposition of ligand	and formation
$(+), (+), (+)$ of $0.5(Ni_2O_3)$	
4 $33-160\ 111\ 145\ 120\ (-)\ (4.94)\ 5.52\ Loss of coordinated MeOH & H_2O$)
$[Mn(L1)_2(CH_3OH)(H_2O)] = 160-357 - 230 - 220 (+), 310 (+) (23.52) 24.33 \text{ Loss of } 2[C_6H_3OH+CH=N]$	
$C_{43}H_{40}N_8O_{14}S_2Mn$ 357–620 530 440 (+) (64.43)65.32 Further decomposition of ligand	and formation
(1011.8) of MnO	
28—115	
5 $115-165$ $149(-)$ (3.86) 4.41 Loss of one coordinated MeOH	
$[Cu(L2)_2(CH_3OH)] \qquad Thermal stability$	
$C_{37}H_{34}N_8O_7S_2Cu$ 161–262 298 (-) (38.39) 38.84 Loss of $2SO_2-N=C-NHNH_2+C_6I_3$	H_4
(828.3) $262-355 + 483 (+), 553 = (46.24) 45.96$ Further decomposition of ligand	and formation
355-505 (+), 612 (+) of 0.5 (Cu ₂ O ₃)	
33-136 127 $108(-)$ (4.16) 4.38 Loss of lattice water	
6 $136-198$ 188 $146(-)$ (4.16) 4.81 Loss of coordinated water	
$[Co(L2)_2(H_2O)_2] \cdot 2H_2O \qquad 198-273 260 \qquad 256 (-) \qquad (10.40) \ 10.12 \ \text{Loss of } 4NH_2 \text{ and } C=N \text{ group}$	
$(C_{36}H_{38}N_8O_{10}S_2Co) = 273-437 348 285(-), 402(+) (26.59) 26.21 \text{Loss of } C=N+2SO_2+C_6H_4$	1.0
(864.9) $43/-534$ 523 $439(+)$, $514(+)$ (46.88) 46.23 Further decomposition of ligand	and formation
of CoO as final product	
28-55	
7 $33 122 103 99()$ $(3.87) 3.13$ Loss of lattice MeOH molecule 7 $122-262 - $ Thermal stability	
$[Ni(L2)_2]CH_3OH \qquad \begin{array}{c} 122 & 202 \\ 262-325 & 310 \\ 262-325 & 318 \\ \end{array} \qquad \begin{array}{c} 318 \\ (-) \\ (14 \\ 05) \\ 13 \\ 96 \\ Loss \\ of \\ 2(N=C(NH_2)_2) \\ \end{array}$	
$ \begin{array}{c} (C_{37}H_{34}N_8O_7S_2Ni) \\ 325-420 \\ 325-420 \\ 325-420 \\ 413 \\ 412(+) \\ 318(-) \\ (24,71) \\ 24,46 \\ 1055 \\ 012(N-C(NH_2)_2) \\ (24,71) \\ (24,71) \\ 24,46 \\ 1055 \\ 012(N-C(NH_2)_2) \\ (24,71) \\ (24,$	
$\begin{array}{c} (825.5) \\ 420-530 \\ 515 \\ 420-530 \\ 515 \\ 517(+) \\ (46.25) \\ 46.73 \\ Further decomposition of ligand \\ 612 \\ 614 \\ 712 $	and formation
(10,20) ($10,20$) ($10,20$) ($10,20$) as final product	unu ronnunon
$29-233$ 188 - (6.13) 6.56 Loss of $2NH_2+C=N$	
8 233-447 393 373 (+) (64.72) 64.68 Loss of $C=N+2C_{10}H_6+2C_6H_1$	+2N = CH +
$[Pd_2(L2)_2] $ $2SO_2$	
$C_{36}H_{28}N_8O_6S_2Pd_2$ 447-777 732 549 (+), 621 (+) (3.17) 2.81 further decomposition of ligand an	nd formation of
(945.6) 2PdO	
2 9-95 52 57 (-) (5.04) 5.60 Loss of lattice water and MeOH	
$[P_{11}(L_3) C1(H_0)] + CH_0 CH_0 H + O 95 - 163 151 153(-) (3.63) 3.71 Loss of coordinated water$	
$\begin{array}{c} 163-394 \\ C_{2}-H_{2}, N_{2}, O_{2}, S_{2}, C_{1}, R_{1}, S_{2}, $	$_{2}+2C_{6}H_{4}$
(991.8) 394—483 444 426 (+) (20.78)19.84 Further decomposition of ligand	and formation
of 2RuO ₂	
39–98 – – Thermal stability	
10 98-127 119 122 (-) (3.77) 3.16 Loss of coordinated water.	
$[Pa (L3)Cl(H_2O)] \qquad 127-282 281 259 (+) \qquad (7.43) \ 7.55 Loss of coordinated chloride$	
$C_{14}H_{15}N_4O_4SCIPd$ 282–349 345 (sn) 345 (+), sh (25.56) 24.78 Loss of 2SO ₂ -N=C-(NH ₂) ₂ +2C ₆	H ₄
(+//.2) 549-594 500 558 $(+)$ (5/.50) 5/.28 Further decomposition of ligand of D4O	and iormation

The TG curves of complexes 1 and 3 show mass losses of 3.00% and 5.14% within the temperature ranges 40-91 and 33-81 °C, which are attributed to the removal of two lattice water and one methanol molecules, respectively. These peaks are associated with endothermic peaks at 66 and 73 °C, respectively. The mass losses within the temperature ranges 91-216 and 81-245 °C are attributed to partial decomposition of ligand with the loss of six hydroxyl groups for 1 and the removal of one coordinated water molecule and chloride ion for 3 with endothermic DSC peaks at 148 and 125 $^{\circ}$ C, respectively. For complex 1, the organic ligand is further decomposed in 3 steps within the temperature ranges 216-399, 399-421 and 421-507 ℃ with exothermic DSC peaks at 393, 414 and 468 °C, while complex 3 undergoes decomposition of ligand only in 2 stages within the temperature ranges 245-436 and 436 -911 °C with DSC peaks at 258, 304, 493 and 537 °C.

The TG thermogram of complex 5 shows mass loss within the temperature ranges 115-165 °C, which is attributed to the removal of one coordinated methanol with endothermic peak at 149 °C. For complex 8, the mass loss within the temperature range 29-233 °C corresponds to partial decomposition of ligand with the loss of one azomethine and two amino groups. The two metal ion complexes undergo decomposition of ligand in the temperature ranges 262-505 for 5 and 233-777 $^{\circ}$ C for complex 8, within two successive decomposition steps with formation of the metal oxide as final product.

The TG curves of complexes 9 and 10 show mass loss within the temperature ranges 29-95 and 98-127 °C attributed to loss of one lattice water and methanol for complex 9 and one coordinated water molecule for complex 10 associated with maximum endothermic DSC peaks at 57 and 122 $^{\circ}$ C for complexes 9 and 10. respectively. The second decomposition step appearing in the temperature ranges 95-163 and 127-282 °C for complexes 9 and 10, respectively, corresponds to the removal of two coordinated water molecules for complex 9 and one coordinated chloride ion for complex 10. The two metal ion complexes undergo decomposition of ligand in two steps within the temperature ranges 163-483 and 282–394 °C for complexes 9 and 10, respectively, associated with endothermic or exothermic DSC peaks within the same temperature ranges. The thermal behavior of the other metal complexes is illustrated in Table 2.

IR spectra

By comparing the IR spectra of the free ligands with those of the metal complexes, the following evidences can be pointed out:

(i) The band appearing at 2923 cm^{-1} in the spectra of HL3 due to the intramolecularly hydrogen bonded OH group disappears from the spectra of its complexes, indicating the participation of the o-OH in complex formation through proton displacement.^[20] The bonding of the phenolic oxygen is further supported by the shift of v_{C-O} band in the spectra of the metal complexes to higher or lower wave numbers compared with the free ligands (Table 3).^[21,22]

(ii) The bands which appear around 3330 cm^{-1} in the ligand spectra are attributed to $v_{\rm NH}$ of sulfonamide or amino groups. These bands remain unchanged in the spectra of complexes 1-4 and 10. This denotes that the nitrogen atoms of sulfonamide or amino groups are not taking part in coordination to metal ion. In the spectra of complexes 5-9, these bands are shifted to higher or lower wavenumbers. In the case of complexes 5, 6 and 7 this shift is due to the hydrogen bonding involved in the amino groups, while in the case of complexes 8 and 9 this shift is due to the coordination of one amino nitrogen atom to the metal ion through deprotonation.^[23]

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Table 3 Important IR spectral bands and their assignments of ligands and their metal complexes^a Comp. v(OH)v(NH₂)_{asy} v(NH₂)_{sym} v(NH)v(C=N) $v(SO_2)_{asy}$ $v(SO_2)_{sym}$ v(M - O)v(M-N)HL1 3431(w) 3337(m) 1343(w) 1170(m) 1615(s), 1580(sh), 1570(m) 1 3430(w) 3323(m) 1615(m), 1580(s), 1539(s) 1344(m) 1171(m) 551(m) 407(m) 2 3431(w) 3338(m) 1614(m), 1582(m), 1538(s) 1339(m) 1172(m) 550(m) 470(w) 3 3439(w) 3335(m) 1338(w) 1170(m) 552(m) 479(w) 1614(m), 1581(m), 1538(s) 4 3437(w) 1338(m) 3441(w) 1615(m), 1580(w), 1542(s) 1172(m) 537(w) 425(w) HL2 1347(m) 3392(m) 3316(m) 1614(s), 1591(m) 1175(m) 5 3431(m) 1342(m) 549(m) 3431(m) 3332(w) 1616(m), 1601(s) 1165(m) 415(s) 6 3423(m) 3423(m) 3330(m) 1615(m), 1601(m) 1341(m) 1175(m) 568(w) 421(m) 7 3454(m) 3436(m) 3332(m) 1617(s), 1600(s) 1341(m) 1172(m) 572(m) 482(m) 8 3436(m) 3332(m) 1616(m), 1601(s) 1338(m) 1172(m) 550(m) 418(w) 3484(w) HL3 3438(w) 3353(m) 1617(s) 1364(m) 1176(s) 2923(m) 9 3430(w) 3430(w) 3332(w) 1641(m) 1361(w) 1180(m) 502(w) 459(m) 10 3498(w) 3441(m) 3356(m) 1633(w), 1606(s) 1366(m) 1171(m) 524(w) 407(w) ^a s: strong, m: medium, w: weak, sh: shoulder.

(iii) The two bands appearing at 1615 and 1580 cm⁻¹ in the spectra of HL1 correspond to $v_{C=N(1)}$ and $v_{C-N(2)}$, respectively. These two bands are found to appear at the same position in the spectra of metal complexes. On the other hand, the band appearing at 1570 cm⁻¹ corresponding to $v_{C-N(3)}$ shifted to lower wavenumbers by 28—32 cm⁻¹, indicating its coordination to the metal ion through the nitrogen donor.

(iv) The band appearing at 1614 cm⁻¹ in the spectra of **HL2**, which corresponds to $v_{C=N}$ of sulfonamide moiety appeared at the same position in the spectra of its metal complexes. The second azomethine group appearing at 1591 cm⁻¹ in the ligand spectra is shifted to higher wavenumbers by 10—12 cm⁻¹, which indicates its coordination to the metal ion.

(v) The strong band appearing at 1617 cm⁻¹ in the spectra of **HL3**, corresponding to $v_{C=N}$ of both azomethine groups is found to split into two bands in the spectra of all complexes, except for complex 9. This splitting reveals that the two azomethine groups are in different chemical environment. The first band is shifted to higher wavenumbers by 11–23 cm⁻¹, which indicates the coordination of the azomethine proup band is assigned to uncoordinated azomethine group.^[24]

(vi) The new bands appearing in the ranges 572— 502 and 482—407 cm⁻¹, which are assigned to v_{M-O} and v_{M-N} , respectively, can be taken as a good evidence for coordination of both oxygen and nitrogen atoms to the metal ion.^[25]

(vii) The presence of lattice or coordinated water molecules in most of the prepared metal complexes is indicated by the band appearing in the range 3498— 3423 cm^{-1} , which corresponds to v_{OH} of water molecules.

Magnetic moment and electronic spectra

The room temperature magnetic moments of the Cu(II) complexes 1 and 5 are found to be 1.65 and 1.75 B.M., respectively, which are close to the spin only value of one unpaired electron. These values are also in the range expected for monomeric Cu(II) complexes.^[26] The magnetic moments of the Co(II) complexes, 2 and 6 are found to be 4.64 and 4.47 B.M, respectively, which correspond to three unpaired electron in an octahedral environment of these complexes.^[27] The Ni(II) complex 7 exhibits diamagnetic character denoting square planar geometry,^[28] while the the Ni(II) complex 3 has magnetic moment value of 3.30 B.M. expected for spin free tetrahedral^[29] geometry. The magnetic moment of Mn(II) complex 4 is 5.29 B.M. which confirms the high spin octahedral structure.^[30] The diamagnetic nature of Pd(II) complexes 8 and 10 indicate square planar geometry.^[31] The Ru(III) complex 9 has a magnetic moment value of 1.83 B.M., which is close to the spin only value of one unpaired electron, indicating the presence of Ru in low spin+3 oxidation state (low spin d^5 , S=1/2).^[31]

The electronic spectrum of Cu(II) complex 1 dis-

plays two bands at 19455 and 25707 cm⁻¹, which can be assigned to ${}^{2}T_{2g} \rightarrow {}^{2}E_{g}$ and charge transfer (M \rightarrow L or L \rightarrow M) interactions in distorted tetrahedral configurations.^[32,33] The nujol mull spectrum of complex **5** has absorptions at 13333 and 18148 cm⁻¹, which are attributed to E" \rightarrow A'₁ and E' \rightarrow A'₁ transitions of Cu(II) ions in a five-coord- inate square pyramidal geometry.^[34]

The electronic spectra of Co(II) complexes **2** and **6** show two bands at 14598 & 18726 cm⁻¹ for **2** and 14684 & 17921 cm⁻¹ for **6**, which may be assigned to ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(P)$ transition of octahedral complexes.^[35]

The electronic spectrum of Ni(II) complex **3** shows a weak absorption band at 17699 cm⁻¹, which probably corresponds to ${}^{3}T_{1} \rightarrow {}^{3}T_{1}(P)$ transition in a tetrahedrally coordinated Ni(II) complexes. Complex **7** exhibits two bands at 16393 and 20833 cm⁻¹ due to ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transitions, respectively, of square planar geometry.^[36]

The electronic spectra of the Mn(II) complex 4 shows two bands at 18691 and 22935 cm⁻¹, which are assigned to ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}(4G)$ and ${}^{6}A_{1g} \rightarrow {}^{4}E_{g}(G)$ transitions, respectively, corresponding to octahedral structure.^[37]

The electronic spectrum of the Ru(III) complex **9** shows two broad bands at 24271 and 18518 cm⁻¹, corresponding to MLCT and ${}^{2}T_{2g} \rightarrow {}^{2}A_{2g}$ transitions, respectively, which is in confirmatory with octahedral Ru(III) complexes.^[38,39]

The electronic spectrum of the Pd(II) complexes **8** and **10** show 3 bands at 15847, 20661 and 22573 cm⁻¹ for **8** and 15360, 22831 and 23419 cm⁻¹ for **10**, which can be assigned to ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$, ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$ transitions, respectively, indicating square planar geometry of these complexes.^[36,40]

ESR spectra

The X-band ESR spectrum of Cu(II) complex **1** shows an isotropic signal without any hyperfine line with $g_{eff}=2.141$. This value indicates tetrahedral structure with tetragonal distortion around the Cu(II) ion, ^[41,42] while the ESR spectrum of the Cu(II) complex **5** shows g_x , g_y and g_z values of 2.311, 2.113 and 2.09, respectively, indicating that the unpaired electron is in $d_{x^2-y^2}$ orbital of Cu(II). These features are characteristic of elongated tetragonally distorted square pyramidal Cu(II) complexes. ^[43,44]

Broad signals are observed in case of Co(II) complexes **2** and **6** with obvious hyperfine splitting. The spectrum shows eight lines (2*I*+1 where *I*=7/2, nuclear spin) characteristic of Co(II). Complex **2** has $g_{\perp} =$ 2.26 and $g_{\parallel} =$ 2.14. For complex **6**, $g_{\perp} =$ 2.30 and $g_{\parallel} =$ 2.08. The ESR pattern as well as the ESR parameters ($g_{\perp} > g_{\parallel} >$ 2.0023) prove octahedral geometry, and indicate that the unpaired d-electron is present in the d_{z^2} orbital with slight distortion of the symmetry around *Z* axis.^[45]

The Mn(II) complex 4 shows a broad ESR signal with no obvious hyperfine structure with $g_{eff}=2.11$. The

line broadening and the pattern of g value indicate octahedral geometry around the Mn(II) center.^[46]

Molecular modeling and analysis

Based on the stereochemistry of the metal complexes proposed on the basis of analytical and spectroscopic studies, the possible structures of some selected metal complexes have been computed using the molecular mechanic calculations. The metal complexes under study can be classified into 3 classes based on the mode of bonding and the ratio of metal to ligand, *i.e.* stoichiometry, as follows:

(i) The first class includes Cu(II) complex 1 and Ni(II) complex 7. In the case of Cu(II) complex 1, the metal center is legated by two chelates through imine nitrogen and phenolate oxygen donors, resulting in the formation of tetrahedral structure as shown in Figure 3. The mode of chelation in the Ni(II) complex 7 is quite similar to that of complex 1 in which the ligands act as bidentate coordinating to the Ni(II) center, through phenolate oxygen and imine nitrogen atoms, resulting in a square planar geometry around the metal center. The two chelates are oriented in a *trans* fashion as shown in Figure 4, however it is impossible to locate the two chelates in a *cis* manner as a result of steric hinderence.

(ii) The second class contains Pd(II) complex **8** and Ru(III) complex **9**. The structure of Pd(II) complex **8** is now found out to be polynuclear in which two chelates are coordinated to the metal center through azomethine nitrogen and phenolate oxygen. The phenolate oxygen bridges to another Pd atom (see Figure 5). One nitrogen atom of a guanidine moiety from adjacent molecule is coordinated to the metal center through deprotonation, presumably resulting in the formation of an infinite structure. A similar mode of bonding is predicted for Ru(III) complex **9**, Figure 6, while in this case the metal center has an octahedral stereochemistry via coordination of a water molecule and chloride ion to the metal center. Such polynuclear geometries explain the low solubility of these compounds.

(iii) The third class of compounds contains Ni(II) complex **3** and Pd(II) complex **10**. In the structure of complex **10** (Figure 7), The metal center is coordinated to the ligand in the same manner as predicted for com-

plexes 1 and 7 in the molar ratio 1 : 1 (ligand : metal). The square planar geometry around the metal center was completed by coordination of a water molecule and chloride ion to the metal center. The water molecule and chloride ion can be oriented in two ways. In the first way the phenolate and water oxygen atoms are located in a *cis* fashion (E=-796.16 kJ/mol), Figure 7, and in the other conformer the two oxygen atoms are directed in a *trans* manner (E=-725.8 kJ /mol). The same mode of bonding is predicted for complex **3**, resulting in a tetrahedral geometry around the metal center (Figure 8).

Antimicrobial activity

The antimicrobial activity of free ligands and a number of their metal complexes was determined against two types of gram-positive (Staphylococcus aures and Bacillus subtilis) and gram-negative bacteria (Escherichia coli and Pesudomonas aeruginosa) by using the agar dilution method.^[47] The sterile nutrient agar plates were aseptically seeded with the test bacteria. After solidification, wells were made inside the plates and filled with 0.2 mL of the tested compounds dissolved in DMF. The plates were incubated at 37 $\,^{\circ}\text{C}$ for 24 h. The activity of DMF alone was also checked against each organism of the tested bacteria under the same conditions; the antimicrobial activities were calculated as a mean of two replicates after subtracting the diameter of inhibition zone resulting with DMF that was obtained in each case.

The data obtained (Table 4) showed that the most active ligand among the three ligands is **HL3**; it displayed high activity against both gram-negative and gram-positive bacteria. By comparing the activity of **HL3** with its Pd(II) complex **10**, the obtained data showed that the Pd(II) complex was more active than its ligand. **HL1** caused only partial inhibition against both gram-positive and gram-negative bacteria while its Cu(II) and Co(II) complexes **1** and **2** cause a complete inhibition of the growth of two types of the tested bacteria. **HL2** was found to be active against only one type of the tested bacteria (St-aur) while its Cu(II) and Pd(II) complexes **5** and **8** are found to be more active against a wider range of the tested bacteria.



Figure 3 3D structure of complex 1.



Figure 4 3D structure of complex 7.



Figure 5 3D structure of complex 8.



Figure 6 3D structure of complex 9.



Figure 7 3D structure of complex 10.



Figure 8 3D structure of complex 3.

 Table 4
 Minimum inhibitor concentration and minimum actual inhibition zone diameter of ligand HL1, HL2 and some of their metal complexes against gram-positive and gram-negative bacteria

	MIC/(µg/mL) [Minimum actual inhibition zone/mm]							
Comp.	Gram+ve bacteria		Gram-ve bacteria					
_	B. subtilis	S. aures	E. Coli	P. aeruginosa				
HL1	25 ^{<i>a</i>} (10)	25 ^{<i>a</i>} (15)	25 ^{<i>a</i>} (12)	$25^{a}(20)$				
1	2500 (9)	-ve	2500 (20)	-ve				
2	-ve	12.5 (13)	25 (15)	-ve				
HL2	-ve	12.5 (13)	-ve	-ve				
5	25 (15)	25 (9)	-ve	-ve				
8	-ve	0 (0)	250 (8)	6.1 (7)				
HL3	200 (14)	200 (14)	50 (15)	50 (16)				
10	100 (14)	100 (14)	7.5 (17)	12.5 (15)				
\mathbf{St}^b	1000 (8)	1000(6)	1000(10)	-ve				

^{*a*} Partial inhibition; ^{*b*} reference standard (chloramphenicol).

The obtained data revealed that both ligands and metal complexes displayed higher activity against

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E. coli

B. subtilis

S. aureus

1.5

2.0

Sp. serratia

Ps. aeruginosa

K. pneumoniae

b

с

d

e

gram-positive than gram-negative bacteria. The reason is the difference in the structures of the cell walls while the walls of gram-negative cells are more complex than the gram-positive cells.^[48] From the obtained data also we can realize that the tested metal complexes are, to some extent, more active than the parent ligand and the tested standard, chloramphenicol. The increased activity of metal complexes may be due to the effect of the metal ion configuration and charge on the normal cell, which can be explained on the basis of chelation theory.^[8] The other metal complexes were found to be completely inactive against the tested microorganisms.

Complex 8 was further assaved at different concentrations in aqueous suspensions of diluted nutrient broth to quantify its inhibitory effects against a wider range of bacteria. A loopful of each culture was placed in 10 mL of ten times diluted broth which was incubated overnight at 37 °C. At this stage, the cultures of the test bacteria were then used for the antimicrobial test. The ratio of the colony numbers for the media containing the complex (M) to those without the complex (C) was taken as an indicator for the surviving cell number; the antimicrobial activity was evaluated using this value. Figure 9 illustrates that the growth inhibitory effect of the complex differs among the bacterial strains. The data obtained showed that concentrations of 0.29, 0.34, 0.43, 0.6, 0.69 and 0.75 mg/mL of the complex were enough to inhibit the growth of 50% of S. aureus, K. pneumoniae, Sp. serratia, E. coli, B. subtilis and Ps. aur, respectively.

Conclusions

From the above findings, it is inferred that the ligands are coordinated to metal centers through the imine nitrogen and phenolate oxygen in the metal:

Scheme 2 Predicted structures of the metal complexes



 $\mathsf{R} = o, p \text{-} \mathsf{OH}\text{-} \mathsf{C}_6\mathsf{H}_3\text{-} \mathsf{CH}\text{=}\mathsf{N}\text{-} \mathsf{C}_6\mathsf{H}_4\text{-} \mathsf{SO}_2\text{-}\mathsf{NH}\text{-} \mathsf{C}\text{=}\mathsf{NH}$

Complex 1, M = Cu(II), X1 = X2 = 0, y = 2; complex 2, M = Co(II), X1 = X2 = MeOH, y = 0; complex 4, M = Mn(II), X1 = H₂O, X2 = MeOH, y = 0





• xMeOH

Figure 9 Growth inhibition of different concentrations of complex 8.

1.0

 $C/(g \cdot L^{-1})$

Ratio of surviving cell number (M/C)

1.0

0.8

0.6

0.4

0.2

0.0

0.0

0.5

ligand ratio 1:1, 1:2 and 2:2 resulting in the formation of neutral complexes. The comparison of antimicrobial activities of the ligands and complexes indicated that the prepared complexes, in some cases, demonstrated higher antimicrobial activity than both the parent ligand and standard which can be explained on the basis of chelation theory.^[8] Moreover, molecular mechanics calculations were performed for some selected metal complexes in order to gain a better under standing of their structures. These studies revealed that, in the case of complexes 8 and 9, one nitrogen atom of a guanidine moiety from adjacent molecule is coordinated to the metal center through deprotonation. It also showed that two conformers are possible for complex 10. In the case of complex 7, the two chelates should be oriented in a trans fashion. Based on the previous studied, the predicted structures of the metal complexes are illustrated in Scheme 2.



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