



SYNTHESIS AND CHARACTERIZATION OF METAL COMPLEXES OF SCHIFF BASE LIGANDS DERIVED FROM 4-AMINOANTIPYRINE WITH 4-AMINO BENZOIC ACID AND BENZOIN

Rehab K. Al-Shemary^{[a]*} and Maysoon T. Tawfiq^[a]

Keywords: Benzoin; 4-aminobenzoic acid; 4-aminoantipyrine; Schiff bases, metal complexes; biological activity.

Two chelate-forming Schiff bases derived from 4-aminoantipyrine with 4-aminobenzoic acid and benzoin, namely (Z)-4-(4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino)benzoic acid (HL^1) and 4-((E)-4-((E)-((R)-2-hydroxy-1,2-diphenylethylidene)amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino)benzoic acid (H_2L^2) were prepared and complexed with copper(II), nickel(II), cobalt(II), manganese(II) and mercury(II)chlorides in ethanol. The $M(HL^1)_2Cl_2$ and $M(HL^2)_2$ type complexes could be isolated. The ligands and their metal complexes were characterized using elemental analysis, infrared and electronic, 1H and ^{13}C NMR spectroscopy, molar conductance and magnetic moment measurements. The measurements showed that the HL^1 ligand is coordinated in their complexes with N,N-bidentate mode, while HL^2 ionic ligand in NNO tridentate pattern through the azomethine nitrogen, amino-group and the deprotonated hydroxyl group of benzoin. The stability constants of complexes were determined spectrophotometrically. All the studies reveal a six coordinated octahedral structure of $M(HL^2)_2$ type complexes. In vitro tests for antibacterial and antifungal activities showed that most of the prepared compounds display a good activity towards *S. aureus*, *E. coli*, *B. subtilis*, *P. aureginosa*, *A. niger*, *A. flavus*, *R. stolonifer* and *C. albicans*.

*Corresponding Authors

E-Mail: drrehabalshemary@gmail.com;
maysoontariqwaheed@yahoo.com

[a] Department of Chemistry, College of Education for Pure Sciences / Ibn -Al-Haitham, University of Baghdad

Introduction

Schiff bases and their complexes, containing azomethine nitrogen atom coordinated to metals, belong to a widely studied ligands with high biological activity such as anticancer, antifungal, antibacterial and antimalarial activities.¹⁻³ Transition metal complexes containing 4-aminoantipyrine and its derivatives have shown a wide range of biological activity, for example copper complexes derived from 4-aminoantipyrine enhances DNA cleavage.⁴⁻¹¹

Schiff-base complexes belong to the main type of compounds used in the development of "stereochemical models" of coordination chemistry due to their structural diversity. Bidentate and multidendate ligands containing imine groups could be used as modulators of structural and electronic properties of transition metal centers.^{12,13}

In the present work, an NN bidentate Schiff base ligand, ((Z)-4-(4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylidene-amino)benzoic acid (HL^1) and an NNO tridentate Schiff base ligand, (4-((E)-4-((E)-((R)-2-hydroxy-1,2-diphenylethylidene)amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino)benzoic acid (H_2L^2) and their complexes formed by their reaction with copper(II), nickel(II), cobalt(II), manganese(II) and mercury(II) chlorides ($M(HL^1)_2Cl_2$ and $M(HL^2)_2$ types, respectively) were synthesized and characterized.

Materials and Methods

4-Aminoantipyrine, 4-aminobenzoic acid, benzoin, and the metal(II) chlorides were purchased from Merck. Anhydrous grade methanol and DMSO were purified according to standard procedures. Microanalytical data, 1H -NMR and ^{13}C -NMR spectra of the compounds were recorded on a Bruker Spectrospin Ultrashield Magnets 300 MHz instrument using tetramethylsilane (TMS) as internal standard and DMSO- d_6 as solvent. FT-IR spectra in the range of 4000-400 cm^{-1} were recorded using KBr disk on a SHIMADZUFT-IR 8300 spectrophotometer. UV-Vis spectra were recorded on a Varian Uv-Cary-100 spectrophotometers by using DMSO as solvent. The chloride content of complexes was determined using potentiometric titration method with using 686-Titro Processor-665 Dosim A-Metrohm (Switzerland) instrument. Solid state magnetic susceptibility measurement were performed at room temperature using a Bruker BM6 instrument. Microanalysis (C, H, and N) of the synthesized compounds was carried out using a Perkin Elmer 2400 series analyzer. Melting points were determined in Gallen Kamp melting point apparatus and were uncorrected.

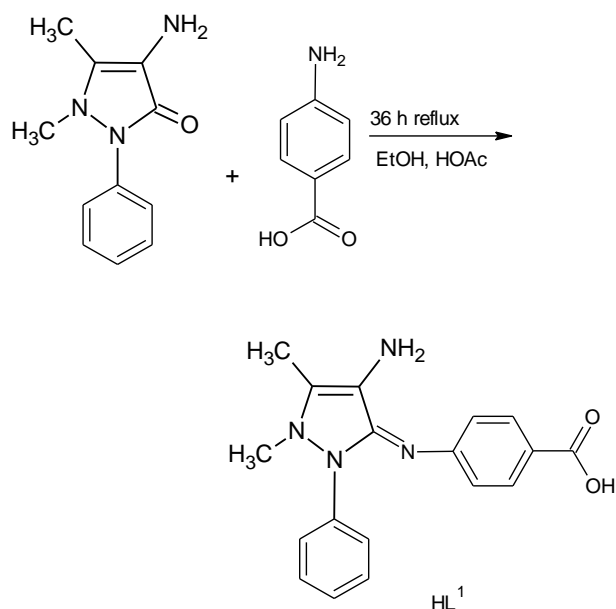
In vitro antimicrobial and antifungal activities assay were performed by well diffusion method. Ethanol was used as a solvent. The Schiff base and its complexes were tested against bacteria such as gram(-) *Bacillus subtilis*, *Escherichia Coli*, *Pseudomonas aureginosa*, gram (+) *Staphylococcus aureus* and antifungal activities of all compounds were studied against four fungal cultures such as *A. niger*, *A. flavus*, *R. stolonifer* and *C. albicans*, cultured on agar as medium. In a typical procedure, a well was made on the agar medium inoculated with bacteria or fungi. The well was filled with the test solution using a micropipette and the plate was incubated

at 37 °C for 24 h. During this period, the test solution diffused and the growth of the inoculated bacteria and fungi were affected. The inhibition zone developed on the plate was measured. The inhibitory concentration (MIC) values of the compounds were determined by serial dilution technique.

Synthesis of Schiff bases

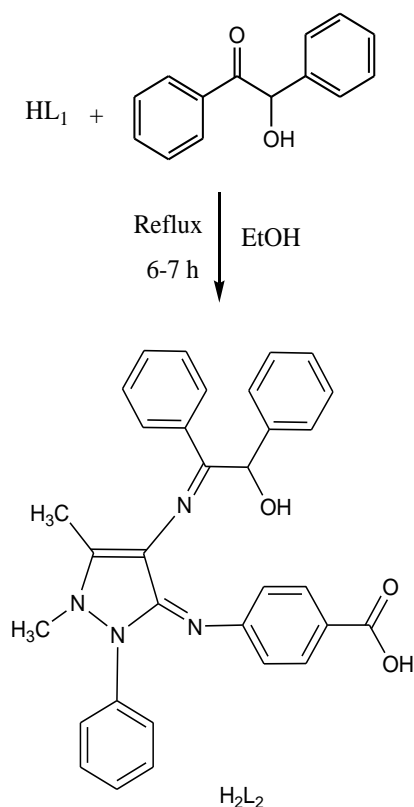
Synthesis of the (Z)-4-(4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino)benzoic acid (HL¹)

An ethanolic solution (50 mL) of 4-aminoantipyrine (0.01 mol, 2.03 g) and 4-aminobenzoic acid (0.01 mol, 1.37g) were refluxed for 36 h after addition of 3-4 drops of glacial acetic acid. The mixture was filtered, the resulting solution was concentrated to (20 mL) on a water bath. On cooling the reaction mixture, sharp yellow crystals product separated out (yield 85 %, m.p. 240 °C) which was collected by filtration and washed thoroughly with ethanol and then dried in vacuum. The purity of product was checked by TLC method and characterized by elemental and spectral analysis.



Synthesis of 4-((E)-4-((E)-((R)-2-hydroxy-1,2-diphenylethylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazole-3(2H)-ylideneamino)benzoic acid (H₂L²)

An ethanolic solution (50 mL) of Schiff base (HL¹) (0.01mol, 3.62 g) and benzoin (0.01 mol, 1.37 g) were mixed and refluxed at 70 °C for 6-7 h after adding anhydrous potassium carbonate. The mixture was filtered and the resulting solution was evaporated to 20 mL on a water bath. The product was filtered off, washed thoroughly with ethanol and subsequently dried at ambient temperature. The purity was confirmed by TLC (yield 82 % , m.p.>280 °C).¹⁵



Synthesis of metal complexes

The solutions of the hydrated chloride salts and HgCl₂ (0.001 mol) and the Schiff base ligands (HL¹ or H₂L²) (0.002 mol) in ethanol (50 mL) was refluxed for 1 h. The solution was evaporated to 15 mL and the mixture was cooled to room temperature. The solid complex formed was removed by filtration, washed with hot ethanol until the filtrate becomes colourless. The resulting product was recrystallized from EtOH and dried in a vacuum desiccator over anhydrous CaCl₂ (yields = 70-85 %).

Results and Discussion

The analytical values for the ligands (HL¹ and H₂L²) and their complexes together with some physical characteristics are outlined in table 1. The analytical data of the complexes confirm the general formula [M(HL¹)₂]Cl₂ for HL¹ = C₁₈H₁₈N₄O₂ and [M(HL²)₂] for H₂L² = C₃₂H₂₈N₄O₃ ligands, where M = Cu(II), Ni(II), Co(II), Mn(II) and Hg(II).

All the metal complexes are coloured solids, stable in air at room temperature. The ligands are soluble in most of the organic solvents and all the complexes found to be insoluble in water and freely soluble in methanol and ethanol, CHCl₃, DMF and DMSO. The metal complexes exhibit 1:2 (metal-ligand) stoichiometry of the type [M(HL¹)₂]Cl₂ and [M(HL²)₂] where HL¹ acts as bidentate and HL²(1-) acts as a tridentate ligand.

Table 1. Physical characterization data of the Schiff base ligands (HL¹ and H₂L²) and their complexes

Comp.	Molecular formula	Color	Yield %	MP, °C	Elemental analysis %, Found(calculated)			
					C	H	N	M
HL ¹	C ₁₈ H ₁₈ N ₄ O ₂	yellow	85	232	67.27(67.07)	5.43(5.63)	16.93(17.3)	-----
[Co(L ¹) ₂]Cl ₂	C ₃₆ H ₃₆ Cl ₂ CoN ₈ O ₄	blue	78	265	55.30(55.73)	4.21(4.68)	14.54(14.47)	7.54(7.58)
[Ni(L ¹) ₂]Cl ₂	C ₃₆ H ₃₆ Cl ₂ NiN ₈ O ₄	green	91	270	55.27(55.67)	4.22(4.69)	14.54(14.47)	7.14(7.58)
[Cu(L ¹) ₂]Cl ₂	C ₃₆ H ₃₆ Cl ₂ CuN ₈ O ₄	Black	69	310	55.09(55.49)	4.51(4.66)	14.24(14.38)	6.88(7.13)
[Mn(L ¹) ₂]Cl ₂	C ₃₆ H ₃₆ Cl ₂ MnN ₈ O ₄	Brown	74	282	55.87(56.11)	4.61(4.71)	14.4(14.59)	7.54(7.89)
[Hg(L ¹) ₂]Cl ₂	C ₃₆ H ₃₆ Cl ₂ HgN ₈ O ₄	Colourless	88	295	46.92(47.14)	3.63(3.96)	12.13(12.23)	12.54(12.89)
H ₂ L ²	C ₃₂ H ₂₈ N ₄ O ₃	Pale brown	82	245	73.83(74.40)	5.13(5.46)	10.59(10.85)	-----
[Co(L ²) ₂]	C ₆₄ H ₅₄ CoN ₈ O ₆	Dark brown	85	276	70.24(70.52)	4.73(4.99)	9.87(19.28)	5.63(5.41)
[Ni(L ²) ₂]	C ₆₄ H ₅₄ NiN ₈ O ₆	Dark brown	78	267	70.28(70.53)	4.70(4.99)	9.83(10.28)	5.59(5.39)
[Cu(L ²) ₂]	C ₆₄ H ₅₄ CuN ₈ O ₆	Dark brown	70	298	70.17(70.22)	4.75(4.82)	9.76(9.88)	5.46(5.32)
[Mn(L ₂) ₂]	C ₆₄ H ₅₄ MnN ₈ O ₆	Dark brown	74	252	70.09(70.77)	4.65(5.01)	9.92(10.32)	5.31(5.06)
[Hg(L ²) ₂]	C ₆₄ H ₅₄ HgN ₈ O ₆	Dark brown	76	213	61.86(62.41)	4.63(4.42)	8.78(9.10)	16.00(16.28)

IR spectra

In order to study the binding mode of the Schiff bases in the complexes, IR data of the ligands and complexes have been compared (Table 2). The peaks appearing in the region of 3444-3359 cm⁻¹ are assigned to the uncoordinated O-H stretchings of the ligand (alcoholic and carboxylate OH) in the complexes.

The ligand L¹ shows the characteristic -C=N- band at 1637-1625 cm⁻¹ and two NH₂ bands at 3336 and 3215 cm⁻¹, which shifts in the complexes to the range 3423 ~ 3305 cm⁻¹ and 3371~3209 cm⁻¹, while in the ligand L² two peaks of characteristic -C=N- bands appear at 1647~1616 cm⁻¹, which are shifted toward lower frequencies in the spectra of complexes (1638~1589 cm⁻¹). The metal coordination causes appearing of new frequencies in the range 482~450 cm⁻¹ and 594~570 cm⁻¹, which are assigned to the fashioning of M-O and M-N bonds, respectively.^{7,8} It can thus be concluded that the ligand HL¹ acts as bidentate neutral unit with NN coordination mode, while the ligand H₂L² behaves as anionic tridentate unit and coordination to the metal ion through deprotonated alcoholic oxygen and via the two azomethine nitrogen atoms of the Schiff base.

NMR spectra

¹H-NMR (DMSO-d₆) of HL¹: δ = 2.26 (3H, -C-CH₃), 2.47 (DMSO), 3.11 (3H, =N-CH₃), 4.95 (2H, -NH₂), 6.5-8.12 (5H, m, C₆H₅), 12.83 (1H, COOH).⁹

¹H-NMR (DMSO-d₆) of H₂L²: δ = 2.26 (1H, OH in benzoin), 2.37 (3H, -C-CH₃), 2.479 (DMSO), 2.53 (3H, -N-CH₃), 5.21 (1H, -CH₂-OH), 6.4-7.98 (5H, m, C₆H₅), 12.82 (1H, COOH).¹⁰

¹³C-NMR (DMSO-d₆) of HL¹: δ = 10.12 (=C-CH₃), 33.70 (-N-CH₃), 40.38 (DMSO), 106.14 (-N-CH₃), 115.38 (-C-CO), 123.56-149.97 (m, C₆H₅), 161.17 (-C=O), 165.79 (C=N).¹¹

¹³C-NMR (DMSO-d₆) of H₂L²: δ = 10.12 (=C-CH₃), 33.70 (-N-CH₃), 40.38 (DMSO), 75.66 (-C-OH), 106.08 (=C-N), 115.34 (-C-CO), 123.57-149.54 (m, C₆H₅), 161.17-162.54 (-C=N groups), 165.79 (COOH).¹²

Electronic absorption spectra

UV-Vis spectra provide the most detailed information about the structure. Electronic spectrum of the HL¹ ligand displays two bands at 37453 cm⁻¹ and 28571 cm⁻¹ attributed to π-π* and n-π* transitions. In the spectrum of the complexes of HL¹, the bands observed at range 35714-34722 cm⁻¹ and 29154-27548 cm⁻¹ are assigned ligand field and LMCT charge transfer transitions. Weak and broad peaks can be shown in the spectrum of the complexes at 23870-14104 cm⁻¹ and are assigned to the d-d transitions. The cobalt(II) complex showed one band from d-d transition at 17982 cm⁻¹ which may be assigned to ¹A₁ → ¹B₁ transition in case of tetrahedral environment around the Co²⁺ ion. The magnetic moment of Co(II) complex was found to be 3.9 B.M. which is at the lower end of magnetic moments expected for tetrahedral Co(II) complex.¹³

The absorption spectrum of copper complex showed a band at about 18635 cm⁻¹ attributed to ²B₂ → ²A₁ transition of a Cu-complex with tetrahedral geometry. The magnetic moment (μ_{eff}) for this complex was found to be 2.2 B.M. per Cu ion which was in usual range for tetrahedral copper complex.¹⁴

Table 2. Infrared spectral data(ν wave number) cm^{-1} for the ligands (HL^1 , H_2L^2) and their complexes.

Compound	$\nu(\text{OH})$	$\nu(\text{NH}_2)$	$\nu(\text{C-H})$ aromatic	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C=O})$ carboxylic	$\nu(\text{C=N})$ imine	$\nu(\text{C=C})$	$\nu(\text{C-O})$	$\nu(\text{M-N})$ $\nu(\text{M-O})$
L^1	3444	3336 3215	3051	2970	1668	1597	1566	----	----
$[\text{Co}(\text{L}^1)_2]\text{Cl}_2$	3441	3413 3371	3062	2954	1665	1588	1563	-----	610 464
$[\text{Ni}(\text{L}^1)_2]\text{Cl}_2$	3445	3423 3371	3011	2904	1667	1589	1562	-----	582 443
$[\text{Cu}(\text{L}^1)_2]\text{Cl}_2$	3447	3394 3236	3066	2975	1666	1592	1559	-----	624 462
$[\text{Mn}(\text{L}^1)_2]\text{Cl}_2$	3456	3305 3243	3078	2981	1666	1590	1546	-----	555 451
$[\text{Hg}(\text{L}^1)_2]\text{Cl}_2$	3459	3367 3209	3070	2993	1666	1587	1558	-----	612 466
L^2	2800- 3240	---	3059	2904	1668	1600 1658	1587	1165	----
$[\text{Co}(\text{L}^2)_2]$	3419	---	3105	2976	1667	1638 1618	1565	1205	570 478
$[\text{Ni}(\text{L}^2)_2]$	3407	----	3109	2964	1665	1623 1597	1559	1189	574 468
$[\text{Cu}(\text{L}^2)_2]$	3429	----	3127	2976	1666	1629 1618	1561	1193	594 468
$[\text{Mn}(\text{L}^2)_2]$	3444	----	3121	2988	1668	1620 1589	1560	1185	582 482
$[\text{Hg}(\text{L}^2)_2]$	3402	----	3111	2996	1663	1643 1624	1556	1176	578 442

The electronic spectra of the Ni(II) complex showed bands at 23870 cm^{-1} and 17233 cm^{-1} that may be assigned to the $^1\text{A}_1 \rightarrow ^1\text{A}_2$ and $^1\text{A}_1 \rightarrow ^1\text{B}_1$ transitions, indicating a tetrahedral environment around the nickel(II) metal ions.

The peak at 14104 cm^{-1} , which may be assigned to $^6\text{A}_1 \rightarrow ^4\text{E}_{\text{G}}$, transition is characteristic for tetrahedral Mn(II) complexes.¹⁵ The magnetic moment of manganese(II) complex is 5.70 B.M. which suggest that the complex is four coordinated.

The electronic spectrum of free Schiff base (H_2L_2) showed two bands at 36363 cm^{-1} and 32362 cm^{-1} due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. In the spectrum of the complexes, these bands observed at the range $36496\text{--}35842 \text{ cm}^{-1}$ and $31250\text{--}30303 \text{ cm}^{-1}$, which are assigned to ligand field and charge transfer (LMCT) transitions.

UV-Vis spectrum of the cobalt(II) complex of H_2L_2 showed the d-d transition bands at 10710 , 15943 and 22765 cm^{-1} , which are assigned to $^4\text{T}_{1\text{g}(\text{F})} \rightarrow ^4\text{A}_{2\text{g}(\text{F})}$, $^4\text{T}_{1\text{g}(\text{F})} \rightarrow ^4\text{A}_{2\text{g}(\text{F})}$ and $^4\text{T}_{1\text{g}(\text{F})} \rightarrow ^4\text{T}_{1\text{g}(\text{P})}$ transitions, respectively. These transitions correspond to the octahedral configuration of the complex, which is also supported by the magnetic moment value ($4.86 \mu\text{B}$) of the complex.¹⁶

The electronic spectrum of the copper (II) complex displayed in the region of 13523 cm^{-1} . This transition may be attributed to the charge transfer band or the d-d transition band which of $^2\text{E}_{\text{g}} \rightarrow ^2\text{T}_{2\text{g}}$ transition. This d-d transition band supports a distorted octahedral configuration around the metal ion, which is also supported by its magnetic moment value ($1.66 \mu\text{B}$).¹⁷

The UV-Vis spectrum of the nickel(II) complex shows d-d peaks at 10309 , 15587 and 26130 cm^{-1} due to $^3\text{A}_{2\text{g}(\text{F})} \rightarrow ^3\text{T}_{1\text{g}(\text{F})}$, $^3\text{A}_{2\text{g}(\text{F})} \rightarrow ^3\text{T}_{2\text{g}(\text{F})}$ and $^3\text{A}_{2\text{g}(\text{F})} \rightarrow ^3\text{T}_{1\text{g}(\text{P})}$ transitions, respectively, indicating an octahedral geometry. This configuration is further supported by its magnetic moment value ($2.89 \mu\text{B}$).¹⁸

The electronic spectrum of Mn(II) complex shows an absorption peak at 17605 cm^{-1} assigned to d-d electronic transition type $^6\text{A}_{1\text{g}} \rightarrow ^4\text{T}_{1\text{g}(\text{G})}$ which suggests octahedral geometry around Mn(II). This geometry is further supported by the magnetic susceptibility value ($5.64 \mu\text{B}$).

The complex of Hg(II) is diamagnetic. According to the empirical formula, the same octahedral geometry might be supposed for this complex as well.¹⁹

Molar conductivity

The molar conductivities of 10^{-3} M of ethanol solution at room temperature were measured. The molar conductivity data of Co(II), Cu(II), Ni(II), Mn(II), and Hg(II) chelates of HL^1 were found to be 72 , 77 , 86 , 82 and $88 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively. It is obvious from these data that these chelates are ionic in nature and they belong to the type of 1:2 electrolytes.²⁰

In addition the low conductance values of Co(II), Cu(II), Ni(II), Mn(II), and Hg(II) chelates of H_2L^2 lie in the range $1.2\text{--}2.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ showing their non-ionic nature.

Table 3. Electronic spectral data of the ligands and their metal complexes

Compounds	μ_{eff}	Λ_m , ohm.cm ² molar ⁻¹	Absorption band (nm, cm ⁻¹)	Transition	Proposed structure
L ¹	-	-	267 nm (37453cm ⁻¹) 350 nm (28571cm ⁻¹)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	--
[Co(L ¹) ₂]Cl ₂	3.9	72	297 nm (33670cm ⁻¹) 371 nm (26954cm ⁻¹) 556nm (17982cm ⁻¹)	F.T C.T $^1A_1 \rightarrow ^1B_1$	Tetrahedral
[Cu(L ¹) ₂]Cl ₂	2.2	77	280 nm (35714cm ⁻¹) 363 nm (27548cm ⁻¹) 536 nm (18635cm ⁻¹)	F.T C.T $^2B_2 \rightarrow ^2A_1$	Tetrahedral
[Ni(L ¹) ₂]Cl ₂	3.4	86	288 nm (34722cm ⁻¹) 368 nm (27173 cm ⁻¹) 418.nm (23870 cm ⁻¹) 580nm (17233 cm ⁻¹)	F.T C.T $^1A_1 \rightarrow ^1A_2$ $^1A_1 \rightarrow ^1B_1$	Tetrahedral
[Mn(L ¹) ₂]Cl ₂	5.70	82	282nm (35460 cm ⁻¹) 360 nm (27777cm ⁻¹) 709 nm(14104 cm ⁻¹)	F.T C.T $^6A_1 (F) \rightarrow ^4E (D)$	Tetrahedral
[Hg(L ₁) ₂]Cl ₂	Dia	88	343 nm (29154 cm ⁻¹) 432 nm (23148cm ⁻¹)	F.T C.T	Square planar
L ²	-	-	275 nm (36363 cm ⁻¹) 309 nm (32362 cm ⁻¹)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi$	----
[Co(L ²) ₂]	5.42	1.2	278 nm (35971 cm ⁻¹) 322 nm (31055cm ⁻¹) 439nm (22765 cm ⁻¹) 627nm (15943 cm ⁻¹) 933nm (10710 cm ⁻¹)	F.T C.T $^4T_{1g(F)} \rightarrow ^4T_{2g(P)}$ $^4T_{1g(F)} \rightarrow ^4A_{2g(F)}$ $^4T_{1g} \rightarrow ^4T_{2g(F)}$	Octahedral
[Cu(L ²) ₂]	1.81	1.8	279 nm (35842cm ⁻¹) 322 nm (31055cm ⁻¹) 739nm(13523 cm ⁻¹)	F.T C.T $^2E_g \rightarrow ^2T_{2g}$	Octahedral
[Ni(L ²) ₂]	3.23	2.9	275 nm (36363cm ⁻¹) 328 nm (30487cm ⁻¹) 970nm (10309 cm ⁻¹) 641nm (15587 cm ⁻¹) 382nm (26130 cm ⁻¹)	F.T C.T $^3A_{2g(F)} \rightarrow ^3T_{1g(F)}$ $^3A_{2g(F)} \rightarrow ^3T_{2g(F)}$ $^3A_{2g(F)} \rightarrow ^3T_{1g(P)}$	Octahedral
[Mn(L ²) ₂]	5.72	2.0	277nm (36101cm ⁻¹) 330 nm (30303cm ⁻¹) 568 nm (17605cm ⁻¹)	F.T C.T $^6A_{1g} \rightarrow ^4T_{1g(G)}$	Octahedral
[Hg(L ²) ₂]	-	2.6	274 nm (36496cm ⁻¹) 320 nm (31250cm ⁻¹) 414 nm (24154cm ⁻¹)	F.T C.T C.T	Octahedral

Table 4. Results of antibacterial bioassay (concentration used 100 $\mu\text{g mL}^{-1}$ of DMSO). (a) *E. coli*, (b) *S. aureus* (c) *B. subtilis* (d) *P. aeruginosa*, antifungal bioassay (concentration used 200 $\mu\text{g mL}^{-1}$). (a) *A. niger* (b) *A. flavus* (c) *R. stolonifer* and (d) *C. albicans*. 10<: weak; >10: moderate; >16: significant.

Compounds	Bacteria				Fungi			
	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
L ¹	2	3	1	1	17	18	20	19
[Co(L ¹) ₂]Cl ₂	7	15	11	10	20	23	26	22
[Cu(L ¹) ₂]Cl ₂	9	14	12	13	25	27	30	24
[Ni(L ¹) ₂]Cl ₂	16	11	17	13	28	30	32	26
[Mn(L ¹) ₂]Cl ₂	9	10	14	12	30	24	29	27
[Hg(L ¹) ₂]Cl ₂	8	6	12	14	32	32	34	30
L ²	2	3	4	2	33	28	28	32
[Co(L ²) ₂]	7	15	11	9	30	35	25	34
[Cu(L ²) ₂]	9	14	9	12	34	27	28	36
[Ni(L ²) ₂]	14	11	5	6	35	37	26	30
[Mn(L ²) ₂]	16	10	13	14	31	32	30	32
[Hg(L ²) ₂]	9	6	11	17	33	31	34	30

Antibacterial and antifungal activities

The ligands and their complexes have been tested for in vitro growth inhibitory activity against gram(+) (*Staphylococcus aureus*) and gram(-) (*Escherichia Coli*, *Bacillus subtilis*, *Pseudomonasaureginosa*) by using well-diffusion process. The minimum inhibitory concentration (MIC) values of the investigated compounds are summarized in Table 4. As it can be seen from the Table 4, the complexes have high antimicrobial and intermediate antifungal activities. The metal complexes have higher antimicrobial activity than the ligands. The increase in antimicrobial activity might be the consequence of easier diffusion of metal complexes and higher cell permeability.²¹⁻²³

Conclusions

Two new Schiff ligands, namely (Z)-4-(4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino)benzoic acid (HL¹) and 4-((E)-4-((E)-(R)-2-hydroxy-1,2-diphenylethylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino)benzoic acid (H₂L²) and their metal complexes were synthesized. Based on the results of molar conductivity, elemental analysis, UV-Vis, ¹H- and ¹³C-NMR and FT-IR spectral studies, it is concluded these ligands form [M(HL¹)₂]Cl₂ and [M(L²)₂] type metal complexes, where M=Co(II), Cu(II), Ni(II), Mn(II) and Hg(II).

The metal (II) ions are coordinated by NN mode with involving the imine (H-C=N) and the amine (NH₂) groups in the case of HL¹ and one deprotonated alcoholic O atom and two imine (H-C=N) groups in the case of H₂L². UV-VIS spectroscopic and magnetic data show that all complexes are four-coordinated in the case of HL¹ and six-coordinated in the case of H₂L² ligands. The synthesized compounds showed strong antibacterial and intermediate antifungal properties. The microbicide actions of complexes are higher than those of the free ligands.

Acknowledgments

Sincere thanks are expressed to the Department of Chemistry, College of Education for Pure Sciences, Ibn-Al-Haitham, University of Baghdad for financial support.

References

- Barboiu, C. T., Luca, M., Pop, C., Brewster, E., Dinculescu, E. M., *Eur. J. Med. Chem.*, **1996**, 31, 597.
- El-Ansary, A. L., Abdel-Fattah, H. M. and Abdel-Kader, N. S., *J. Coord. Chem.*, **2008**, 61(18), 2950–2960.
- Reham, H., Hassan, A., Manal, M., Nehad, A. L., *J. Chem.*, **2013**, 20(13), 10.
- Azzellini, M. A. A. Bagatin I. A. and Ferreira, A. M. D. C., *Redox Report*, 11, 25 (1996).
- Raman, N., Kulandaisamy, A., S. hunmugasundaram, A., Jeyasubramaniam, K., *Transito. Met. Chem.*, **2001**, 26, 131–135.
- Raman, N., Sakthivel, A., Rajasekaran, K., *Mycobiology*, **2007**, 35(3), 150–153.
- Tabassum, S., Parveen, S., Arjmand, F., *Indian J. Chem.*, **2004**, 43, 270–277.
- Mishra A. P., Pandey, L. R., *Indian J. Chem.*, **2005**, 44A, 1800–1805.
- Raman, N. S., Sobha, S. Mitu, L., *J. Saudi Chem. Soc.*, **2013**, 17, 151–159.
- Santos, M. L. P., Faljoni, A. A., Mangrich, A. S., Ferreira, A. M. D. C., *J. Inorg. Biochem.*, **1998**, 71, 71.
- Santos, M. L. P., Bagatin, I. A., Pereira, E. M., Ferreira, A. M. D. C., *J. Chem. Soc. Dalton Trans.*, **2001**, 838.
- Sumathi, A. S., Tharmaraj, P., Sheela, C. D., *Int. J. Inorg. Chem.*, **2011**, 8.
- Kalanithi, M.; Rajarajan, M.; Tharmaraj, P., *J. Coord. Chem.*, **2011**, 64, 1436–1445.

- ¹⁴Dharmaraj, N., Viswanathamurthi, P., Natarajan, K., *Transition Met. Chem.*, **2001**, 26, 105–109.
- ¹⁵Muna, A. H., *Acta Chim. Pharm. Indica*, **2013**, 3(2), 127-134.
- ¹⁶Sharma, R., Samadhiya, P., Srivastava, S. D., Srivastava, S. K., *Org. Commun.*, **2011**, 4(2), 42-51.
- ¹⁷Suresh, M.S., Praksh, V., *E-J. Chem.*, **2011**, 8(3), 1408-1416.
- ¹⁸Fernandez-Torres, M. J., *Int. J. Chem.*, **2013**, 9(2), 33-40.
- ¹⁹Raman, T. S., Dhaweethuraja, J., Neelakadan, M.A., Banerjee, S., *J. Chilean Chem. Soc.*, **2008**, 53(1), 1450.
- ²⁰Bahl, B. S., Bahl, A., *Elementary Organic Chemistry*, S. Chand and Company Ltd., New Delhi, **1993**, 60-66.
- ²¹Ergene, E., Sivas, H., Benkli, K., *Turk. J. Biol.*, **2010**, 34, 379-387.
- ²²Layla, A. M., Muna, A. H., Methaq S.M., *J. Chem. Chem. Sci.*, **2013**, 3, 48-96.
- ²³Gupta, A. K. S., Barhate, V. D., *Res. J. Pharm., Biol. Chem. Sci.*, **2012**, 3(3), 1014-1020.
- ²⁴Singh, P., Dhakarey, R. K. S., *Rasayan J. Chem.*, **2009**, 2(4), 869-874.
- ²⁵El-Ansary, A. L., Abdel-Kader, N. S., *Int. J. Inorg. Chem.*, **2012**, 13.

Received: 27.09.2016.

Accepted: 06.01.2017.