



Synthesis and Spectral Studies of some Metal Complexes With N₁,N₂-bis(2-amino-3,5-dibromo-benzylidene)ethane -1,2-diamine and N₁,N₄-bis(2-amino-3,5-dibromo benzylidene) butane-1,4-diamine

Angham T. Ali¹, Haider A. Mahdi¹ & Falih H. Musa^{2*}

¹ Department of Chemistry, College of Science, Thi-Qar University, IRAQ

² Department of Chemistry, College of Science, Thi-Qar University, IRAQ

* Correspondence: E-mail: dr.Falihhassan@yahoo.com

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ABSTRACT: Microwave assisted synthesis, a green chemistry approach, is now a day's widely practice in the synthetic laboratories. In the present work two Schiff bases are synthesized using microwave irradiation. Co(II), Cu(II) and Cr(III) complexes of the two new Schiff bases L₁= N1, N2-bis(2-amino-3,5-dibromobenzylidene) ethane 1,2-diamine and L₂= N1, N4-bis(2-amino-3,5-dibromobenzylidene)butane-1,4-diamine are synthesized and characterized by microanalysis conductance, HNMR, IR, UV-Visible and mass spectral measurement. The two ligands coordinates through two imine N atoms and two amine N atoms to the metal ions as shown by IR and electronic measurement resulting in six-coordinated Metal ion. The complexes are non electrolyte in the solvent except Cr-complexes are electrolyte (1:1). Studies showed the new Schiff base and their complexes have various activity towards Staphylococcus aureus, Escherichia coli, Bacillus and Pseudomonas.

Keywords: Synthesis; Schiff bases; Microwave radiation; Complexes; Bioactivity.

INTRODUCTION: Schiff bases usually have variable donation sites, e.g., nitrogen, sulphur, and/or oxygen markedly affected the activity of the compounds. They could be monodentate, bidentate, tridentate or tetradentate forming mono-or polynuclear complexes¹. Also for this class of compounds, many applications such as antidepressant, antiphlogistic, antinematocide, and other medicinal agents have been reported². Microwave radiation has been using solvent free or organic solvents such as ethanol, dimethylformamide, dichloromethane etc. As energy transfer media which absorb microwave energy efficiently through dipole rotation. The salient features of microwave approach are shorter reaction times, simple reaction conditions and enhancements in chemical yields^{3 & 4}. In the present study, preparations of two new Schiff bases by using microwave irradiation have carried out with good yield and short time. Their complexes with Co(II), Cu(II), Cr(III) are prepared and characterized. Their antibacterial studies are focused too.

MATERIAL AND METHODS: All chemicals are purchased from BDH, and used without further purifications. FT-IR spectra are recorded in KBr, Shimadzu spectrophotometer in the range of 4000-200 cm⁻¹ used KBr disc to the ligands and CsI disc to the complexes. Electronic spectra in DMSO are recorded using UV-

Visible spectrophotometer type Shimadzu in the range of 200-1100 nm with quartz cell of (1cm) path length. Melting points are measured with an electro thermalsturat apparatus, model SMP30. Electrical conductivity measurements of the ligands and their complexes were recorded at (25°C) for 10⁻³ molL⁻¹ solution of the sample in DMSO using Ltd 4071 digital conductivity meter.

¹HNMR spectra are recorded on a Bruker 300 MHz spectrometer in CDCl₃, chemical shift in ppm relative to internal Me₄Si. The micro analysis (C, H, N) of ligands are carried out by using CHNS-O PerkinElmer model 2400-11-Mass spectra are recorded with Agilent technologies 5975 mass spectrometer.

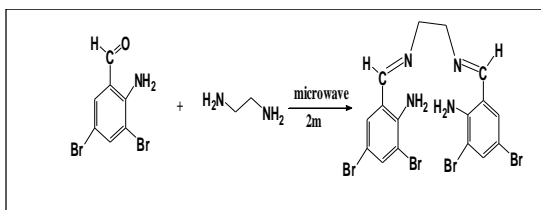
Synthesis of Ligands L₁, L₂: In microwave method synthesis of L₁, L₂ are prepared by condensation of (1.11gm, 0.002 mol) of 2-amino-3,5-dibromobenzyldehyde with secondary ethylene diamine (0.13 gm, 0.001 mol) or with 1,4-butane diamine dissolved in 5 ml ethyl estate with a few drops of acetic acid. The content is allowed to react in a Teflon beaker in microwave oven 300 w for two minutes giving solid product. Recrystallized by ethanol, their physical properties and analytical data are recorded in Table 1. **Synthesis of Co(II), Cu(II) & Cr(III) complexes:** To a solution of the L₁, L₂ (0.001mmol) in (20ml ethanol) a solution of (0.001 mmol) of metal chloride in (10 ml methanol) was added .

Table 1: Physical properties and analytical data for the synthesized ligands (L₁, L₂) and their complexes.

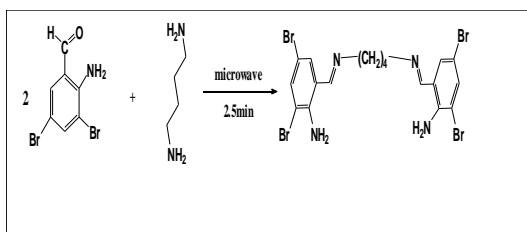
Compound	Molecular Formula	Molecular Weight	Melting Point (°C)	Colour	Yield%	Molar Conductance (Λm)(S.cm ² .mole ⁻¹)	Elemental Analysis		
							C% Found (cal)	H% Found (cal)	N% Found (cal)
L ₁	C ₁₆ H ₁₄ Br ₄ N ₄	581.925	225-227 d*	Yellow	90.5	-	33.02 (33.029)	2.42 (2.505)	9.63 (8.970)
(CoL ₁ Cl ₂)	[Co(C ₁₆ H ₁₄ Br ₄ N ₄ Cl ₂)	711.76	321-322 d*	Sepia	88	19	-	-	-
(CrL ₁ Cl ₃)	[Cr(C ₁₆ H ₁₄ Br ₄ N ₄ Cl ₃)	740.28	345-347 d*	Yellow Greenish	79.49	32	-	-	-
(CuL ₁ Cl ₂)	[Cu(C ₁₆ H ₁₄ Br ₄ N ₄ Cl ₂)	716.377	290-291 d*	Greenish yellow	74	18	-	-	-
L ₂	C ₁₈ H ₁₈ Br ₄ N ₄	609.978	222-224 d*	Yellow	81	-	75.68 (75.75)	5.00 (5.05)	7.01 (7.07)
(CoL ₂ Cl ₂)	[Co(C ₁₈ H ₁₈ Br ₄ N ₄ Cl ₂)	739.81	335-238 d*	Reddish-brown	73	16	-	-	-
(CrL ₂ Cl ₃)	[Cr(C ₁₈ H ₁₈ Br ₄ N ₄ Cl ₃)	768.33	349-350 d*	Black	84.4	34	-	-	-
(CuL ₂ Cl ₂)	[Cu(C ₁₈ H ₁₈ Br ₄ N ₄ Cl ₂)	744.433	248-250 d*	Umber	65	14	-	-	-

The solution are stirred and warmed at 50°C. The color of the mixture change instantly. The mixtures are refluxed for 2Hrs. The complexes are precipitated which upon cooling. The precipitated are filtered, washed with cold methanol and recrystallized from hot methanol Table 1.

RESULTS AND DISCUSSION: The L₁, L₂ are synthesized in a good yield as follows Scheme1, 2 .



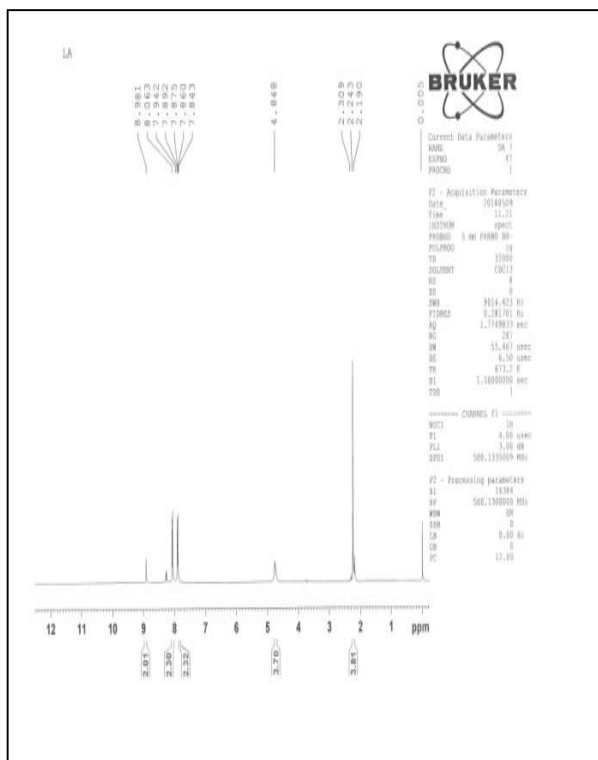
Scheme 1: Synthesis of L₁



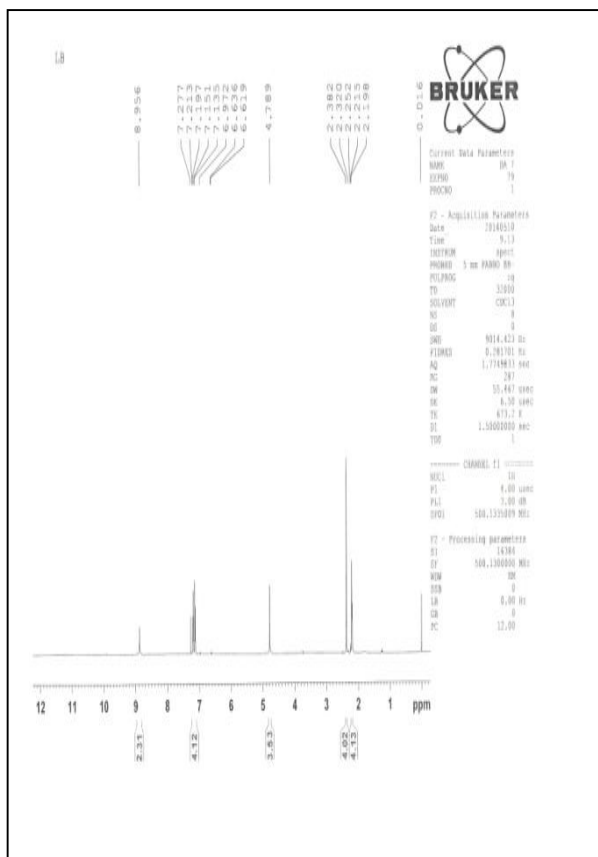
Scheme 2: Synthesis of L₂

¹H-NMR spectra for the L₁, L₂: ¹H-NMR spectra of the ligands L₁, L₂ figures 1, 2 in CDCl₃ exhibited singlet at 2.20 ppm and broad singlet at 4.7-4.9 ppm are assigned to proton of CH₂NH₂, NH₂ phenyl groups. The (CH=N) has chemical shift at 8.98 ppm. Multi singlet's in the 7.84-8.06 ppm are assigned of the aromatic ring (Figures 1& 2).

FT-IR analysis: Tentative assignments of the observed bands for the compounds are made by comparing spectra of the metal complexes with those of the Schiff bases. Due to the unsymmetrical nature of the ligands and the complexes, two bands are observed for each of the following bands, (C=N), (M-N) ^{5 & 6}. The ligands exhibited characteristic (C=N) stretching frequency at 1627-1631 and 1593cm⁻¹ which shift to higher frequency at 1629-1670 and 1597-1612 cm⁻¹, respectively, upon coordination. This indicates participation of the azomethane nitrogen in bonding ^{7 & 8} the corresponding phenyl amine NH₂ occurs at 3433-3250 cm⁻¹ while in the complexes appeared as multi bands at 3371, 3340, 3250 cm⁻¹. This confirms participation of the pHNH₂ in H₂N-M bond formation. These (M-N) bands showed at 421-467 cm⁻¹.thus , it can be concluded that the Schiff base are tetradentate, coordinating via the azomethine N and phenyl NH₂ ⁹.



Figures 1: NMR-spectra for L₁



Figures 2: NMR-spectral for L₂

Spectral studies and the molar conductivity: The UV-visible spectrum of the ligands (L₁, L₂) showed two absorption at (270 nm), (280 nm) are due to $\pi-\pi^*$ and $n-\pi^*$ transition⁷. The visible spectra of Co complexes in DMSO exhibited two bands appeared in the range (18883 cm⁻¹) and (15454 cm⁻¹) are assigned to the $^4T_{1g} \rightarrow ^4A_{2g}(v_2)$ and $^4T_{1g} \rightarrow ^4T_{1g}(p)$ (v_3) transitions respectively of octahedral geometry. Visible spectra of Cr. complexes showed bands at (16667 cm⁻¹) are due to $^4T_{2g} \rightarrow ^4T_{2g}$ transition of octahedral geometry¹⁰. While Cu complexes showed broad band (11363 cm⁻¹) assigned to $^2E_g \rightarrow ^2T_{2g}$ transition which refers to Jahn-Teller distortion of octahedral geometry^{11 & 12} the molar conductance of Cu(II), Co(II) complexes in DMSO solvent are found to be low which suggested coordination of anion to the metal . The Cr complexes are found electrolyte within range (1:1) ratio.

Mass spectra for two Schiff bases and their complexes: The mass spectra of two ligands and their complexes are recorded at room temperature table 2. The two ligands L₁, L₂ shows a molecular ion peak with relative abundance (RA) at m/z 582(12.5), 610 (18.18). The mass spectra of Cr(III) complexes (L₁, L₂) shows a molecular ion peak with relative abundance (RA) at m/z=740.28(25.86), 768.33 (11.36) , Co (II) complexes shows a peak at m/z = 712(9.5), 704.81 (5.68), Cu(II) complexes shows a peak with relative abundance (RA) at m/z=716.38(17.85), 477.97 (10.56) which correspond s to molecular weight of the respective compounds (Table 2 and Figures 3).

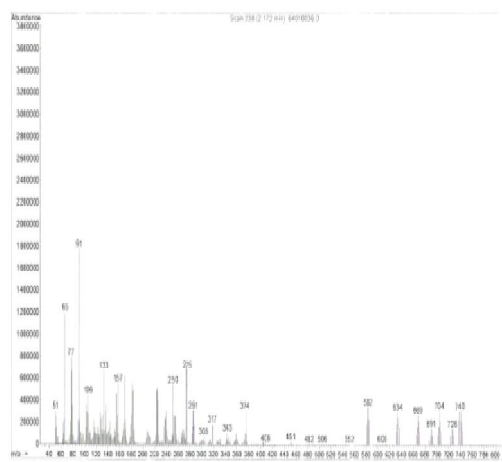
Biological Activity: The antimicrobial activity of ligands and its metal complexes were tested *in vitro* against bacteria¹³ such as *Staphylococcus aureus*, *Escherichia coli*, Bacillus and Pseudomons earuginosa by paper disc plate method. The compounds were tested at the concentration 1000ppm in DMSO and compared with known antibiotics Ciprofloxacin it is clear that the inhibition by metal chelates is higher than that of a ligand and metal salts. The results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes¹⁴⁻¹⁶. The metal chelates showed various activation toward antibacterial activity than the corresponding free ligand and control against the same microorganism under identical experimental conditions¹⁷⁻¹⁸. The increase in activity with concentration is due to the effect of metal ions on the normal process. In case of antibacterial studies it was observed that. Comparison of activities of the ligand and its metal chelates showed that the copper complex is approximately found to be all times more active as the ligands, The cobalt complex show the activity comparable to

Cu(II) and Cr(III) complexes. The activity of these complexes follow the order Co > Cu > Cr. Inhibition was found to increase with increasing the concentration of metal complex^{19,20}. Table 3 Figure 3.

Table 2: Mass Spectral data of the L₁ and L₂.

compound	Expected m/z	Found m/z	Relative abundance
L ₁ [C ₁₆ H ₁₄ Br ₄ N ₄] ⁺		582	12.5
[C ₈ H ₇ Br ₂ N ₂] ⁺	581.92	290.69	14.7
[C ₆ H ₄ BrN] ⁺		294.94	8.33
[C ₂ H ₃ N] ⁺		41.05	6.7
[Cu (L ₁) Cl ₂] ⁺		716	17.85
[Cu (L ₁) Cl] ⁺	716.38	680.80	5.36
[Cu (L ₁)] ⁺		645.38	5.36
[C ₁₆ H ₁₄ N ₄ Br ₄] ⁺		581.96	5.36
(L ₁)Cl ₂ ⁺ Co [711.76	9.5
(L ₁)Cl] ⁺ Co [712	676.81	6.7
[Co (L ₁)] ⁺		640.85	6.7
[(L ₁)] ⁺		581.92	22.85
[Cr (L ₁) Cl ₃] ⁺		740	25.86
[Cr (L ₁) Cl ₂] ⁺	740.28	704	17.24
[Cr (L ₁) Cl] ⁺		669.73	17.42
[Cr (L ₁)] ⁺		633.92	18.96
[(L ₁)] ⁺		581.92	8.62
[C ₁₈ H ₈ Br ₄ N ₄] ⁺		609.96	18.18
[C ₉ H ₅ Br ₂ N ₂] ⁺	609.97	304.98	30.90
[C ₇ H ₅ Br ₂ N ₂] ⁺		267.93	3.63
[C ₆ H ₅ Br ₂ N] ⁺		249.91	20.0
[Cu (L ₂)Cl ₂] ⁺		477	10.65
[Cu(L ₂)Cl] ⁺	744.43	708.97	10.65
[Cu (L ₂)] ⁺		673.28	10.65
[L ₂] ⁺		609.97	13.11
[Co (L ₂) Cl ₂] ⁺	739.81	763.39	5.68
[Co (L ₂) Cl] ⁺		704.36	5.68
[Co (L ₂)] ⁺		668.91	5.68
[L ₂] ⁺		609.97	1.14
[Cr (L ₂) Cl ₃] ⁺		786.33	11.36
[Cr (L ₂) Cl ₂] ⁺	768.33	732.88	11.36
[Cr (L ₂) Cl] ⁺		697.42	9.09
[Cr (L ₂)] ⁺		667.97	21.59
[L ₂] ⁺		609.95	

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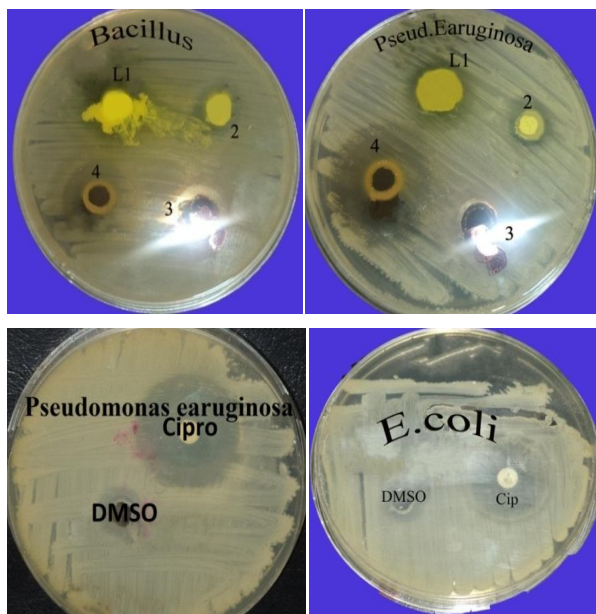
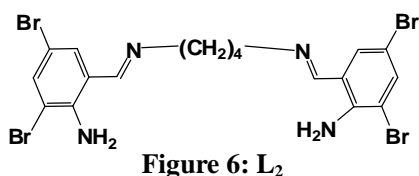
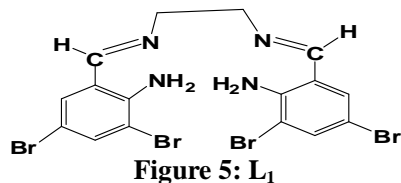
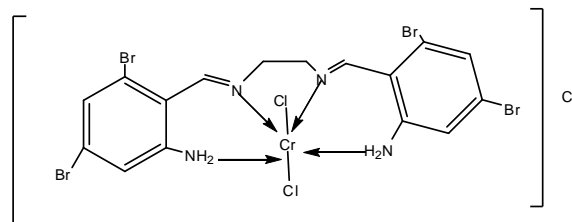
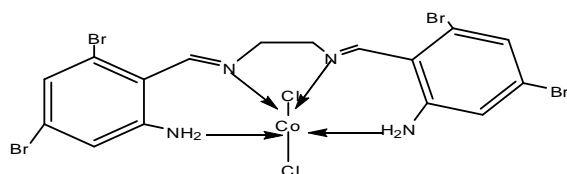
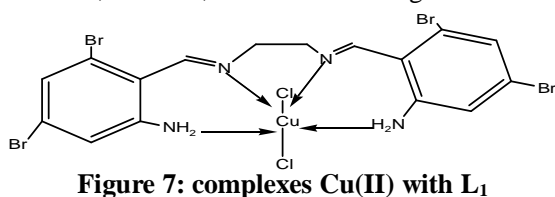


Figure 10: The antimicrobial activity of chemical compounds (ligand (L₁) and complexes 1,2,3) appear the inhibition zones against somepathogenic bacteria and compared inhibition this bacterial with Ciprofloxacin.

CONCLUSION: The two new Schiff bases are synthesized by microwave irradiation with good yields and short time (two minutes). They are behaved as tetradentate with metal ions coordinate with tow azomethene and two amine group in octahedral geometry.



The two Schiff bases and their complexes showed varieties effect towards Escherichia coli, Staphylococcus aureus, Bacillus, Pseudomonas earuginosa.



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