

# Preparation, Spectroscopic Characterization and Antibacterial Activity of New Schiff Base Complexes

MM. El-ajaily<sup>1\*</sup>, M. Abdelkarem<sup>2</sup>, M. Himmet,<sup>3</sup> AM. Hamil<sup>3</sup> and HA. Boghdadi<sup>4</sup>

<sup>1</sup>Chemistry Department, Faculty of Science, Benghazi University, Benghazi, Libya.

<sup>2</sup>Chemistry Department, Faculty of Science, Sudan University of Science and Technology, Sudan.

<sup>3</sup>Chemistry Department, Faculty of Science, Omdorman Islamic University, Sudan.

<sup>4</sup>Botany Department, Faculty of Science, Sebha University, Sebha, Libya.

## ABSTRACT

Some new transition metal ion complexes of 2-1-[(*E*)-6-[(*E*)-1-(2-hydroxyphenyl) ethylidene] amino-hexylidene)amino]ethylphenol were synthesized and characterized by physicochemical studies. The IR spectral results reveal the involvement of azomethine nitrogen atom and hydroxyl groups in coordination to the central metal ion. According to the electronic and electron paramagnetic resonance spectral studies, an octahedral structure was proposed for all complexes. The Schiff base and its complexes were screened against some pathogenic bacteria.

**Key Words:** Schiff base, Metal salts, Physicochemical techniques and Antibacterial activity.

## INTRODUCTION

More focus in Schiff base compounds were done via the treatment of 2-Chloro-1-(2, 3-dihydro-perimidin-1-yl) ethanone with 5-amino-8-hydroxyquinoline afford a 2-(8-Hydroxy-quinolin-5-ylamino)-1-(5-methyl-4-methylene-1,4-dihydro-2H-quinazolin-3-yl)-ethanone(PEHQ), the transition metal complexes of PEHQ with Mn<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> metal ions have been prepared and characterized by elemental analyses, spectral studies, magnetic moment determination, molar conductivity and antimicrobial activity<sup>1</sup>. A range of Schiff base compounds such (E)-3-(phenylimino)petan-2-one {ArN(CH<sub>2</sub>(C-Me)<sub>2</sub>O} (Ar = C<sub>6</sub>H<sub>5</sub>) contain the chelating imino and oxygen in position  $\alpha$ - has been prepared, and structurally characterized in several cases, well-defined (E)-3-(phenylimino)petan-2-one ArN(CH<sub>2</sub>(C-Me)<sub>2</sub>O} (Ar = C<sub>6</sub>H<sub>5</sub>) was obtained by stoichiometric addition of {ArNH<sub>2</sub>} (Ar = C<sub>6</sub>H<sub>5</sub>) and {CO(CH(CH<sub>3</sub>))<sub>2</sub>CH<sub>2</sub>CO} in n-propanol at reflux temperature. IR, NMR and X-ray studies have been obtained for this compound<sup>2</sup>. The Synthesis and biological evaluation of the Schiff bases derived from the condensation of 4,4'-diaminodiphenylsulphone and various aromatic or heterocyclic aldehydes in ethanol in the presence of concentrated sulphuric acid as a catalyst were reported<sup>3</sup>. The divalent metal ions Mn, Co, Ni, Cu, Zn and Cd complexes of ethylenediamine condensation with 4-(benzeazo)salicylaldehyde

(1:2) [H<sub>2</sub>L were prepared and characterized by CHN elemental analyses, molar conductivity measurements, infrared and electronic spectra, the ligand and their Ni(II), Zn(II) and Cd(II) complexes were further identified using <sup>1</sup>HNMR spectra. The results that metal ion is bonded to the ligand through the phenolic oxygen and the imino nitrogen<sup>4</sup>.

The aim of this work is to synthesize, characterize and study the antibacterial activity of some new M(II) and M(III) Schiff base complexes.

## Experimental

### Materials and Methods

#### Materials

Analytical grade reagents (BDH) were used. The molar conductance measurements were performed on a BC 3020 Professional Benchtop Conductivity Meter. Magnetic susceptibility was determined using a Johnson Matthey instrument at room temperature (25 °C) with Hg[Co(SCN)<sub>4</sub>] as blank. Diamagnetic corrections for the ligands and metal atoms were reduced using Pascal's Constan. The infrared spectra were recorded as KBr disc on a Perkin – Elmer 1430 IR Spectrophotometer. The UV spectra were recorded on a Unicam Model UV-2 Spectrophotometer. The EPR spectra were recorded by using EMX ESR spectrometer (Bruker) 1998 Y. All analyses were done at Microanalytical center, Cairo University, Giza, Egypt.

### Synthesis of Schiff base

The present compound was synthesized by adding (6.02 cm<sup>3</sup>, 0.05 mmole) of 2-hydroxyacetophenone dropwise to 1,6-hexanediamine ( 5.80 g, 0.05 mmole) in 50 cm<sup>3</sup> of absolute ethanol. The obtained mixture was refluxed for three hours, and then allowed to cool at ambient temperature, filtered and recrystallized from ethanol. The product was dried under vacuum to get yellow precipitate (m.p. 166°C ; yield 81% ).

### preparation of complexes

The present complexes were synthesized by adding L3 (3.53 gm; 0.01 mole) in 50 cm<sup>3</sup> absolute ethanol to CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CuSO<sub>4</sub>.5H<sub>2</sub>O, CrCl<sub>3</sub>.6H<sub>2</sub>O and LaCl<sub>3</sub>.7H<sub>2</sub>O (2.3793 gm), (2.3769 gm), (2.4968 gm) , (2.6650 gm) and (3.7137 gm) in 50 cm<sup>3</sup> of the same solvent ethanol. The mixtures were refluxed for three hours. The colored complexes were filtered, recrystallized and finally kept in a desiccator over silica gel.

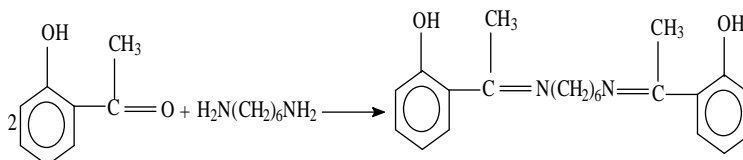
### Bacteria assay

The Schiff base complexes with Co(II), Ni(II), Cu(II) and Cr(III) ions were added separately to the mixtures of DMF and H<sub>2</sub>O solvent (1:1). The obtained mixtures were further purified and

filtrated by using Whatman filter paper No 1. The stock solutions of extracts were sterilized by filtration using a Millipore membrane filter of 0.2 μm pore-size. The sterile mixtures resulted from each compounds were stored at 4°C for further uses,<sup>5,6</sup> and the stock mixtures of the compounds were tested against four pathogenic bacteria species (*Escherichia coli* , *Proteus Sp*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*). Antibacterial activity was determined by the well (6 mm diameter) diffusion method. Petridishes containing Mueller Hinton agar medium were seeded with a 24 hrs culture of the bacterial species were growth on nutrient agar. Each well was filed with 50μl of the compound. Solvents were used as a negative control. Inoculated plates were Incubated at 37 °C for 24 hr.<sup>7</sup> The assessment of antibacterial activity was based on measurement of the diameter of inhibition formed around the well.

### RESULTS AND DISCUSSION

The reaction of 2-hydroxyacetophenone with 1,6-diaminehexane in ethanol showed a new spot after refluxing the mixture for two workup a yellow product, the reaction represented as follows:



### Microanalysis and molar conductivity

The CHN elemental analysis data agree with the proposed composition of the formed complexes. The molar conductance values of the complexes in DMF solvent are in the range of 3.87 – 33.6 ohm<sup>-1</sup>

cm<sup>2</sup> mol<sup>-1</sup> indicating their non electrolytic nature<sup>8</sup>. These values reveal that there is no inorganic anions outside the coordination sphere. Thus, the complexes may be formulated as [M(L)X<sub>n</sub>(H<sub>2</sub>O)<sub>n</sub>]nH<sub>2</sub>O.

**Table1: CHN elemental analysis and some physical data of the Schiff base(L) and its complexes**

Schiff base / Complexes	Color	M.wt.	M.P. °C	Found ( calc. ) %			(μs)Δ	BM
				C%	H%	N%		
L; C <sub>22</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub>	Yellow	352		(75.00)	(7.95)	(7.95)	-	-
[Co <sub>2</sub> LCl <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ]	Pale green	647.32	260.90	40.98 (40.82)	5.34 (5.92)	4.52 (4.33)	16.95	4.70
[Ni <sub>2</sub> LCl <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ]	green	646.84	259.90	40.77 (40.85)	5.76 (5.92)	4.09 (4.33)	33.60	2.05
[Cr <sub>2</sub> LCl <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ] 2H <sub>2</sub> O	green	704.33	2640	37.35 (37.51)	5.76 (5.44)	4.11 (3.98)	11.65	4.40
[Cu <sub>2</sub> LCl <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ] 3H <sub>2</sub> O	Pale blue	710.59	278.90	37.83 (37.19)	5.74 (6.24)	4.24 (3.94)	3.87	0.00

### Infrared spectra

The assignments of the significant IR bands of the Schiff base and its complexes are listed in Table 2. In principle the Schiff base can exhibit a band at 1645cm<sup>-1</sup> due to νC=N vibration which is shifted towards lower wave number in the complexes indicating chelation through the azomethine

nitrogen atom<sup>9</sup>. This is also confirmed by the appearance of new band which is absent in the free Schiff base in the range of 422-458 cm<sup>-1</sup>, this has been attributed to the νM-N vibration<sup>10</sup>. Broad band found in the range of 3029-3593 cm<sup>-1</sup> are due to the existence of the water molecules in the complexes. The position of the hydroxyl group of

the Schiff base overlapped with the position of water molecules<sup>11</sup>. The involvement of the oxygen atom of the hydroxyl group is confirmed by the

appearance of new band in the range of 488-667  $\text{cm}^{-1}$  assigned to the  $\nu\text{M-O}$  vibration<sup>12</sup>.

**Table 2: Infrared and electronic spectral data of the Schiff base and its complexes**

L/ complexes	IR bands ( $\text{cm}^{-1}$ )				Uv-Vis, nm ( $\text{cm}^{-1}$ )
	$\nu\text{OH}(\text{H}_2\text{O})$	$\nu\text{C=N}$	$\nu\text{M-O}$	$\nu\text{M-N}$	
L: $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2$	3446	1645	-	-	
$[\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6]$	3029	1609	502	447	<b>530(18867), 560(17857)</b>
$[\text{Ni}_2\text{LCl}_2(\text{H}_2\text{O})_6]$	3593	1612	667	458	<b>590(16949), 620(16129)</b>
$[\text{Cr}_2\text{LCl}_4(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$	3394	1598	525	444	<b>580(17241), 610(16393)</b>
$[\text{Cu}_2\text{LCl}_2(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O}$	3574	1592	488	422	<b>620(16129), 630(15873)</b>

### Electronic spectra and magnetic moments

The ultraviolet absorption spectrum of the Schiff base shows two bands located at 300 and 430 nm ( $33333$  and  $23255 \text{ cm}^{-1}$ ) assigned to  $\pi \rightarrow \pi^*$  (phenyl ring) and  $n \rightarrow \pi^*$  ( $-\text{C}=\text{N}$ ) group<sup>13</sup>. The electronic spectrum of Co(II) complex displays two bands at  $\lambda_{\text{max}}$  530 nm and  $\lambda_{\text{max}}$  560 nm. These bands correspond to the  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  transitions. The intensity of the bands and the magnetic moment value (Table 1) confirmed the presence of an octahedral structure around Co(II) ion<sup>14</sup>. It is well known that Ni(II) ions form large number of complexes whose their coordination number varies from 4 to 6<sup>15</sup>. The electronic spectral data of Ni(II) complex exhibit two bands (Table 2) attributed to  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$  and  ${}^3\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$  transitions. The diamagnetic phenomena and the nature of the bands support the existence of an octahedral geometry<sup>16</sup>. The spectrum of Cr(III) complex shows two bands at  $\lambda_{\text{max}}$  580 nm and  $\lambda_{\text{max}}$  610 nm, these bands can be due to  ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  and  ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$  transitions including an octahedral geometry around the Cr(III) ion.<sup>(17)</sup> The magnetic moment value of the complex (4.40 BM) reveals the presence of three odd electrons in its 3d orbital of Cr (III) ion. The Cu(II) complex shows bands (Table 2) which can be assigned to  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$  transition and the paramagnetic behavior of the complex supports the octahedral structure around Cu(II) ion<sup>18</sup>.

### Electron paramagnetic resonance spectra of the complexes

The spectra of the powdered samples of Co(II), Ni(II), Cr(III) and Cu(II) complexes were recorded at room temperature. The g values are 2.09242, 1.97734, 2.00779 and 2.16274, respectively. The observed values deviated from the ideal value (2.0023), this deviation is in agreement with the covalent character of the metal-ligand bond<sup>19</sup>. This deviation supports the presence of an octahedral geometry around the metal ions<sup>20</sup>.

### Antibacterial activity

No effect was observed for the Schiff base under investigation on the used bacteria. Three different inhibition zones were observed for *E. coli*, *Proteus Sp* and *S.aureus* (Table 3) were reported by the Co(II) complex. Whereas, the same complex does not give any indication on *P.aeruginosa*.  $[\text{Ni}_2\text{LCl}_2(\text{H}_2\text{O})_6]$  complex shows inhibitory activity against *E. coli*, *Proteus Sp* and *S.aureus* (9, 11 and 9 mm), and no any inhibitory activity was recorded against *P.aeruginosa*. The *E. coli*, *Proteus Sp* and *S.aureus* were affected by  $[\text{Cr}_2\text{L3Cl}_4(\text{H}_2\text{O})_4] \cdot 5\text{H}_2\text{O}$  complex (Table 3). No inhibitory activity against *P.aeruginosa*. The same effect was observed against *P.aeruginosa* and *S.aureus* species (9 mm). There is no effect against *E. coli* and *Proteus Sp* species. The inhibition zones vary depending on bacteria species and type of compound. The largest zone of inhibition was observed from  $[\text{Co}_2\text{LCl}_4(\text{H}_2\text{O})_4]$  and  $[\text{Cr}_2\text{LCl}_4(\text{H}_2\text{O})_4] \cdot 5\text{H}_2\text{O}$  complexes.

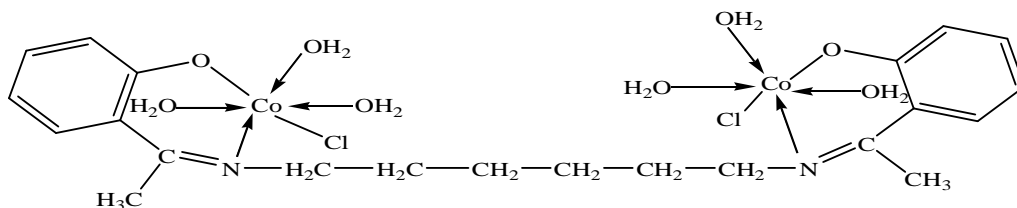
**Table 3: Antibacterial activity of the Schiff base and its complexes**

Schiff base/ complexes	Bacteria species			
	<i>E. coli</i>	<i>Proteus Sp</i>	<i>P.aeruginosa</i>	<i>S.aureus</i>
L: ( $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2$ )	-	-	-	-
$[\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6]$	11	12	-	9
$[\text{Ni}_2\text{LCl}_2(\text{H}_2\text{O})_6]$	9	11	-	9
$[\text{Cr}_2\text{LCl}_4(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$	10	12	-	9
$[\text{Cu}_2\text{LCl}_2(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O}$	-	-	9	9

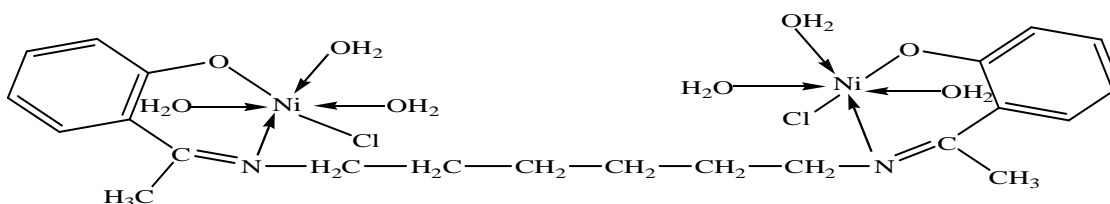
-: not active.

**CONCLUSION**

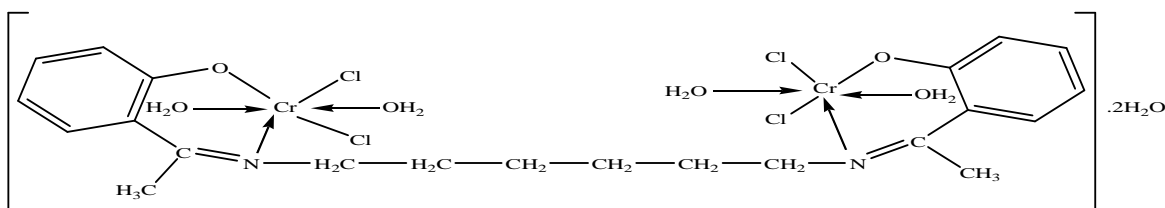
From the previous results, one can suggest the chemical structures for the prepared complexes as follows



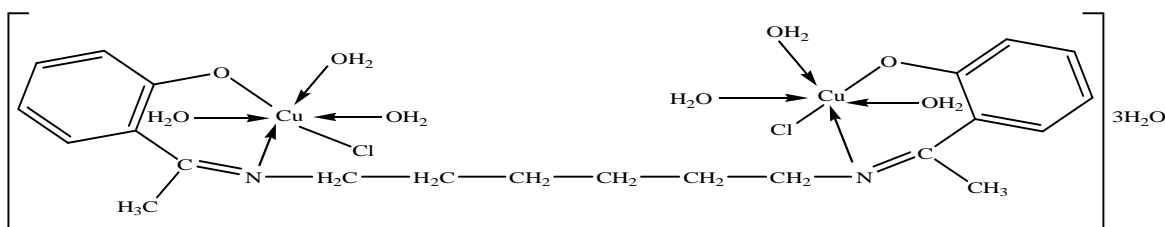
Structure of  $[\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6]$  complex



Structure of  $[\text{Ni}_2\text{LCl}_2(\text{H}_2\text{O})_6]$  complex



Structure of  $[\text{Cr}_2\text{LCl}_4(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$  complex



Structure of  $[\text{Cu}_2\text{LCl}_2(\text{H}_2\text{O})_6].3\text{H}_2\text{O}$  complex

**REFERENCES**

1. P.S. Ashwinbha, F. B. Bux and A. Singh, *Rasayan J. Chem.*, 3 (2) , 240-245 (2010).
2. S. E. Ashoor, H. M. Abosadiya and A. Algaed, *Rasayan J. Chem.*, 2 (3), 562-565 (2009).
3. S. J. Wadher\*, M. P. Puranik, N. A. Karande and P. G. Yeole, *International Journal of PharmTech Research*, 1 (1) , 22-33(2009).
4. A. M. Hamil, K. M. Khalifa, A. Al-Houni, and M. M. El-ajaily, *Rasayan J. Chem.*, 2 (2), 261-266(2009).
5. H. A. A. Bogdadi, L. Kokoska, J. Havlik, P. Kloucek, V. Rada and K. Vorisek, *Phar. Bio.* 45 ( 5), 386- 391(2007).
6. I. O. Sule and T. O. Agbabiaka, *Ethno. Leaf.*, 12, 1035-1042 (2008).
7. A. M. A. Hamil, M. M. El-ajaily and H. A. A. Bogdadi, *International Journal of Chem.Tec. Research*, 1(4), 1714- 1717 (2009).

8. W.G. Greay, *Coord. Chem. Rev.*, 7, 81 (1971).
9. M.M. EL- ajaily, A . A. Maihub, S. S. Hudere and S. M. Ben-Saber , *Asian Journal of Chemistry* , 18 (4) , 2427-2430 (2006).
10. K.V. Pate and P. K Bhattachaiy, *J .Chem. Soc.*, 21 A, 1110 (1982).
11. F.A. Abdlseed1, M. M. El-ajaily , *International Journal of Pharm.Tech. Research.*,1 (4) 1097-1103, (2009).
12. F.M. Morad, M. M. EL-ajaily, S. F. Ben-Gweirif, Garyounis University Press *Journal of Science and Its Applications*, 1(1), 72-78 (2007).
13. R. M. Silverstein, G. C. Bassler and T.C. Morrill, "Spectrometric Identification of Organic Compounds", John Wiley and Sons, 4<sup>th</sup> ed., London (1981).
14. Y. M. Issa, A. L. Al-ansary, O. E. Sharif and M.M. El-ajaily, *Transition Metal Chemistry*, 22, 441-446 (1997).
15. C. R. Hammond "The Elements, in *Handbook of Chemistry and Physics*", 1<sup>st</sup> ed. New York (2000).
16. G. Budige, M.R. Puchakayala, S.R.Kongara, A.Hu and R. Vadde, *Chem. Pharm. Bull (Japan)*, 59(2), 166-167 (2011).
17. S. Chadra and U. Kumar, *Spectrochimica Acta, A* 61, 219 (2005).
18. M. El-Behery and H. El-twigry, *Spectrochimica Acta*, 66(1), 28-36 (2006).
19. Z. A.Taha, A.M. Ajtouni, W. Momani and A.A. Al-Ghzawi, *Spectrochimica Acta*,71, 570-577 (2011)
20. N. V. Thakkar and S. Z. Bootwala, *Indian J. Chem.*, 34(A), 370-374(1995).