



## Preparation, Spectral Characterization and Antibacterial Activity of some Divalent and Trivalent Metal Ion Schiff Base Complexes

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**ABSTRACT:** The Schiff base formed from the reaction of hydrazine and 2-hydroxyacetophenone was synthesized and investigated by using several physical techniques, in particular; CHN elemental analysis, infrared, ultraviolet and mass spectra. Only one product was formed from the reaction of the carbonyl and primary amine. The purity of the isolated Schiff base was confirmed by its melting points and by TLC technique. The Schiff base under investigation forms complexes with Co(II), Ni(II), Cu(II), Cr(III) and La(III) ions. The synthesized complexes were confirmed by elemental analysis, molar conductivity, thermogravimetric analysis (TGA) analysis and spectral (IR, electronic and ESR) measurements. The analytical data show the formation of 1:1 (M:L) complexes. The molar conductance measurements of the complexes reveal a non-electrolytic nature. The thermogravimetric analysis data of some complexes show the presence of coordinated and hydrated molecules water. The infrared spectral data display the chelation behavior of the Schiff base towards the metal ions. The electronic spectral results of the Schiff base and its complexes show  $\pi \rightarrow \pi^*$  (phenyl ring),  $n \rightarrow \pi^*$  (HC=N) and the expected geometrical structures for the synthesized complexes. Basis on the electron paramagnetic resonance spectral data, an octahedral structure was suggested for all complexes. The synthesized Schiff base and its complexes were tested against some pathogenic bacteria [*Escherichia coli*, *Proteus Sp*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*].

**Keywords:** Schiff base; Complexes; Physiochemical tools; Antibacterial activity.

**INTRODUCTION:** The family of Schiff bases derived from diamines (especially ethylene-diamine), phenolic aldehydes and salen has proved to be the source of versatile ligands for many transition metals, including vanadium(IV) <sup>1-4</sup>. Compounds containing an azomethine group (-CH=N-) are known as Schiff bases. Schiff bases are generally bi, tri, tetra-dentate ligands capable of forming very stable complexes with transition metals. Tetradentate Schiff bases with a N<sub>2</sub>O<sub>2</sub> donor atom set are well known to coordinate with various metal ions and this has attracted many author Schiff base complexes have been studied for their dioxygen uptake<sup>5</sup> and oxidative catalysis<sup>6</sup>, insertion of oxygen into organic substrate<sup>7 & 8</sup>. This review article deals the complexation behavior of Schiff base ligands with first series of transition metal ions. The coordination behavior of various ligands and their structures formed after complexation with first series transition metal ions and its applications in various fields have been studied. The review mainly discusses

the literature of last ten years. This review article is especially useful for inorganic as well as bio-inorganic chemists<sup>9</sup>.

### MATERIAL AND METHODS:

**Chemicals and reagents:** All chemicals and solvents used in this investigation were of analar Grade (BDH, Aldrich). They included 2-hydroxyacetophenone, hydrazine, 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, LaCl<sub>3</sub>.7H<sub>2</sub>O, absolute ethanol, ammonia solution, ether and dimethylformamide. These solvents were either spectroscopically pure or purified by the recommended methods, and then tested for their spectral purity.

**Physical measurements:** 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 Pascial's Constan. The infrared spectra were recorded as KBr disc on a Perkin-Elmer 1430 IR Spectrophotometer. The electronic 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.

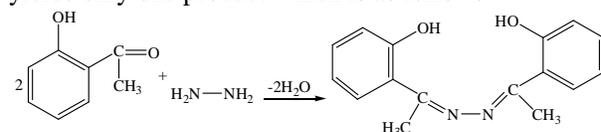
**Preparation of Schiff base:** The Schiff base under investigation was synthesized by adding (6.02 cm<sup>3</sup>, 0.05mmole) of 2-hydroxy- acetophenone dropwise to hydrazine (1.58 cm<sup>3</sup>, 0.05 mmole) in 50 cm<sup>3</sup> of absolute ethanol. The mixture reaction was refluxed for three hours, and then allowed to cool at ambient temperature, filtered and recrystallized from ethanol. The resulted product was dried under vacuum to get yellow precipitate. (m.p. 202°C; yield 87%). By measuring the melting point and TLC technique, the purity of this compound is confirmed

**Preparation of complexes:** The synthesis of the complexes was formed by adding Schiff base (2.68 gm; 0.01 mole) in 50 cm<sup>3</sup> 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 salts (2.3793 gm), (2.3769 gm), (2.4968 gm) , (2.6650 gm) and (3.7137 gm) in same amount of ethanol. The mixtures were stirred for 3hours, and the separated complexes were filtered, recrystallized from suitable solvents and finally kept in a desiccator over silica gel, (yield 55-75% and melting points >250°C).

**Bacteria assay:** The Schiff base complexes with Co(II), Ni(II), Cu(II), Cr(III) and La(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. Then stock solutions of extracts were sterilized by filtration using a Millipore membrane filter of 0.2

µm pore-size. The sterile mixtures resulted from compounds were stored at 40°C for further uses, 5, 6 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. The assessment of antibacterial activity was based on measurement of the diameter of inhibition formed around the well.

**RESULTS AND DISCUSSION:** The reaction between the 2-hydroxyacetophenone and hydrazine yields only one product which is as follows:



**Microanalysis and molar conductance measurements:** The CHN and some physical properties of the Co(II), Ni(II), Cu(II), Cr(III) and La(III) complexes are listed in Table 1. The obtained data are consistent with the calculated values indicating that the complexes are formed in 1:1[M:L] ratio. The elemental analysis data exhibit that the most of the complexes have more than one water molecule associated with the complex formation. The molar conductance measurements of all complexes were carried out in DMF solvent (10<sup>-3</sup> M) using conductivity meter model BC 3020 Professional Benchtop Conductivity meter, Sebha university, Libya. The molar conductance values (Table 1) reveal that all the complexes are non electrolytes [10]. These data confirm that no inorganic anions are present outside the complexes.

**Table 1: CHN and some physical characters of the Schiff base and its complexes.**

Complexes	Color	M.Wt.	M.P., °C	Found (calc.) %				Λ
				C%	H%	N%	Cl%	
[CoL (H <sub>2</sub> O) <sub>2</sub> ]	voilet	361.29	278	53.76(53.19)	5.22(5.02)	6.95(7.75)	-	24.10
[NiL (H <sub>2</sub> O) <sub>2</sub> ]	Pale green	361.02	266.8	53.56(53.22)	5.56(5.03)	6.82(7.76)	-	23.9
[CrLClH <sub>2</sub> O] 2H <sub>2</sub> O	green	409.81	279.6	47.32(46.89)	4.53((5.41)	6.63(6.84)	8.67(8.65)	55.4
[CuL (H <sub>2</sub> O) <sub>2</sub> ]4H <sub>2</sub> O	Pale blue	437.93	284.4	43.84(43.88)	5.02((5.89)	6.39(6.40)	-	3.08
[LaLClH <sub>2</sub> O] H <sub>2</sub> O	Pale yellow	476.69	294.6	40.28(40.31)	3.65(3.81)	5.07(5.88)	7.72(7.44)	3.8

**Infrared spectra:** The IR spectra of the complexes exhibit broad bands in the range of 3340 – 3563  $\text{cm}^{-1}$  which are attributed to  $\nu\text{OH}$  vibration of water molecules associated with complex formation<sup>11</sup>. The change of phenolic OH groups positions in the spectra of the complexes supports the participation of OH groups in chelation with metal ion, this confirmed by the existence of new bands at 521 – 589  $\text{cm}^{-1}$  due to  $\nu\text{M-O}$  vibration which are absent in the IR spectrum of free Schiff base<sup>12</sup>. The  $\nu\text{C=N}$  band observed at 1604  $\text{cm}^{-1}$  in free Schiff base is shifted to lower frequency in the IR spectra of all complexes confirming the complexation of the azomethine group via nitrogen atom. Whereas, a new band at 527  $\text{cm}^{-1}$  which is assigned to  $\nu\text{M-N}$  bands supports the complexation process<sup>13</sup>.

**Thermogravimetric analysis of Co(II) and Cr(III) complexes:** The Thermogravimetric analysis data (Table 3) show the weight-losses for both complexes in the range of 5.04 – 10.64% which are in a good agreement with the theoretical values, indicating the existence of one or two hydrated water molecules at 39-159 $^{\circ}\text{C}$ . Meanwhile, at the temperatures of 159–296 $^{\circ}\text{C}$ , the values in the range of 5.04–10.64% which are closed to the theoretical values corresponding to the presence of 1 or 2 coordinated water molecules in the complexes. At temperatures of 296 – 655  $^{\circ}\text{C}$ , the Schiff base (free ligand) decomposes as carbonate or oxalate ion<sup>14</sup>. The metal oxides (CoO and  $\text{Cr}_2\text{O}_3$ , appeared at the end of the curves as stable states > 641  $^{\circ}\text{C}$ .

**Electronic spectra:** Complex  $[\text{CoL}(\text{H}_2\text{O})_2]$ , has one shoulder band at 560 nm which is assigned to  ${}^4\text{T}_{1g}(\text{F})$

$\rightarrow {}^4\text{A}_{2g}(\text{F})$  transition within an octahedral structure<sup>15</sup>. A  $[\text{NiL}(\text{H}_2\text{O})_2]$  complex displays two bands at 570 and 590 nm attributed to  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$  and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  transitions suggesting an octahedral geometry around Ni(II) ion. The electronic spectrum of Cr(III) complex  $[\text{CrLCIH}_2\text{O}].2\text{H}_2\text{O}$  exhibits two bands at 570 and 580 nm. These bands can be assigned  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$  and  ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$  transitions. The intensity of the bands suggesting an octahedral geometry around Cr(III) ion. The Cu(II) complex shows a band situated at 550 nm which can be assigned to  ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$  transition. An octahedral geometry around Cu(II) ion was proposed<sup>16</sup>. For La(III) complex, the electronic spectrum shows charge transfer transition suggesting the existence of an octahedral structure around La(III) ion<sup>17</sup>.

**Electron paramagnetic resonance spectra:** The observed  $e\text{pr}$  values of the complexes (Table 2) are deviated from the ideal value (2.0023), this difference is in agreement with the covalent character of the metal- ligand bond<sup>18</sup>. The deviation of these values compared to the ideal value supports the existence of an octahedral geometry around the metal ions.

**Antibacterial activity:** The free Schiff base shows inhibitory activity on *Proteus Sp* bacteria, and the synthesized complexes were screened for antibacterial activity on some pathogenic bacteria. The  $[\text{CuL}(\text{H}_2\text{O})_2].4\text{H}_2\text{O}$  complex shows inhibitory activity against all bacteria specie (9 mm).Whereas, the Co(II), Ni(II) and Cr(III) complexes did not show any inhibitory activity against *Escherichia coli* and *Proteus Sp*.

**Table 2: Infrared, electronic and paramagnetic resonance spectral data of some complexes.**

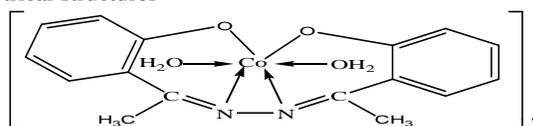
Complexes	$\nu\text{OH}(\text{H}_2\text{O})$	$\nu\text{C=N}$	$\nu\text{M-O}$	$\nu\text{M-N}$	$\lambda_{\text{max}} \text{ nm } (\text{cm}^{-1})$	g- values
$[\text{CoL}(\text{H}_2\text{O})_2]$	3557	1599	580	413	<b>560</b> (17857), <b>575</b> (17391)	2.00363
$[\text{NiL}(\text{H}_2\text{O})_2]$	3407	1600	589	413	<b>570</b> (17543), <b>590</b> (16949)	2.09272
$[\text{CrLCIH}_2\text{O}] 2 \text{H}_2\text{O}$	3340	1603	573	527	<b>570</b> (17543), <b>580</b> (17241)	2.9919
$[\text{CuL}(\text{H}_2\text{O})_2].4\text{H}_2\text{O}$	3391	1599	521	431	<b>550</b> (18182)- <b>580</b> (17241)	1.98662
$[\text{LaLCIH}_2\text{O}] \text{H}_2\text{O}$	3563	1600	531	433	<b>570</b> (17543)	0.00

Table 3: Thermogravimetric analysis data of some complexes.

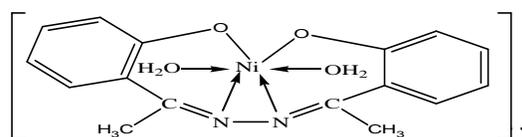
Complexes	Hyd. Water weight loss%	No. of water molecules	Temp °C	Coord. Water weight loss%	No. of water molecules	Temp °C	Temp. °C of Schiff base decomposition	Metal oxide weight loss%	Temp °C
[CoL (H <sub>2</sub> O) <sub>2</sub> ]	-	-	-	10.64 (9.96)	2	182-295	296-641	21.99 (20.74)	> 641
[CrLCIH <sub>2</sub> O] 2H <sub>2</sub> O	9.54 (8.78)	2	39-159	5.04 (4.41)	1	159-255	256-655	38.06(37.34)	>655

### CONCLUSION:

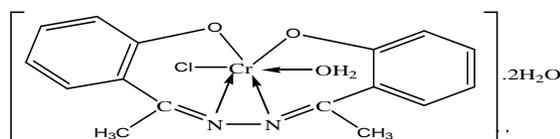
From the above results, we can suggest the following geometrical structures



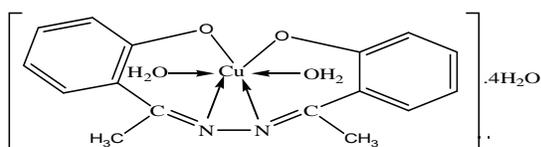
[CoL (H<sub>2</sub>O)<sub>2</sub>]



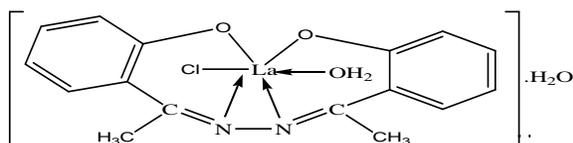
[NiL (H<sub>2</sub>O)<sub>2</sub>]



[CrLCIH<sub>2</sub>O] 2H<sub>2</sub>O



[CuL (H<sub>2</sub>O)<sub>2</sub>] 4H<sub>2</sub>O



[LaLCIH<sub>2</sub>O] H<sub>2</sub>O

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