INTRODUCTION

The five-membered nitrogen-containing heterocyclic compounds as pyrazolines have shown important antitumor, antitrypanosomal [1,2] and antileishmanial activity [3]. Pyrazole and coumarin derivatives are the ligand in chemical and biological systems as it appears as such in proteins, and together with its derivatives, has been extensively employed for modeling in a wide range of inorganic subject areas, from biological applications to electronic devices and materials [4].

Budzisz et al. [5] reported the anticancer activity of copper(II), palladium(II) and platinum(II) complexes derived from bidentate pyrazoline ligands. Furthermore, the investigation of transition metal complexes with 1,3,5-pyrazole ligands have interested wide ranges in bio-inorganic chemistry [6-8]. Over the years, the coordination chemistry of pyrazole has received considerable attention [6-8]. The DNA-cleavage of copper(II) complexes with mixed ligands involving pyrazoline moiety have assigned the high significances of pyrazoline complexes in the pharmaceutical industry [9]. The transition metals complexes of their quinoxaline-2-one have interested great attention due to their potential metal binding characteristics and promising extreme applications [10-12].

EXPERIMENTAL

Elemental analyses (CHNS) of ligand and its metal(II) complexes were determined using Carlo-Erba 1106 Elemental analyzer and Perkin-Elmer CHNS240 elemental analyzer. The electronic spectra were recorded using Shimadzu spectrometer in the range 200-800 nm in DMF solvent. The $^1$H and $^{13}$C NMR spectra were carried at Al-Yarmook University, Jordan on Bruker 400 MHz spectrometer in DMSO-$d_6$ solvent. The Fourier transform infrared spectra of the prepared complexes were recorded in KBr and CsI discs on Shimadzu model FT-IR8400 spectrometer at Laboratory of Chemistry Department, College of Science, university of Mustansiryah, Baghdad, Iraq. The molar conduc-
tance measurements were made on Hanna conductivity meter with a cell constant of 1.0 cm⁻¹. The atomic absorption measurements were performed using the Analytik Jena/A Spect LSFL 1.3.0.0, Ibn Sina Center, Ministry of Industry, Iraq.

All the reagents and solvents used were of laboratory grade. The synthesis of new ligand was monitored by TLC using silica gel-G plates (Ranbaxy) for TLC. The hydrated metal chlorides MnCl₂·4H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O and ZnCl₂ were purchased from Sigma-Aldrich company and used without further purification. The oxalic acid, hydrated hydrazine 99 % and 1,2-phenylenediamine and solvents were supplied by Fluka company with 99 % purity. 3-Acetyl coumarin was prepared according to the method assigned in literature [15].

**Synthesis of 3-hydrazino-quinoxalin-2(1H)-one:** This compound was prepared in two steps according to the reported method [16]. Yield: 88 %, m.p. 250-252 °C, Rf = 0.82 (ethyl acetate:cyclohexane, v:v, 3:1). FT-IR (KBr, ν_{max}, cm⁻¹): 3400 (-NH-NH₂), 1683 (C=O), 1588 (-C=N), 2930-2855 (-NH- pyrazoline ring). ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 4.60 (s, 2H, J = 8.22 Hz, H₂N-N=C-), 7.22-7.59 (m, 4H, Ar-H), 9.86 (s, 1H, J = 6.33 Hz, Ar-H), 8.90 (s, 1H, HN-N), 10.89 (s, 1H, J = 6.35 Hz, HN-C=O), 12.22 (s, 1H, J = 4.90 Hz, HN-C=O). MS (m/z %): 176 (100) [M⁺].

**Synthesis of 3-[4-(2-hydroxybenzylidene)-3-methyl-5-oxo-4,5-dihydropyrazol-1-yl]-1H-quinoxalin-2-one:** This compound was prepared according to the method assigned in literature [15]. Synthesis of 3-[4-(2-hydroxybenzylidene)-3-methyl-5-oxo-4,5-dihydropyrazol-1-yl]-1H-quinoxalin-2-one: 2-Hydradnopyridine (0.176 g, 10 mmol) in methanol (15 mL) was added to a solution of 3-acetylcoumarin (1.88 g, 10 mmol) in methanol (20 mL) and the mixture was refluxed for 5 h. The solid crude product formed was filtered off, dried in air and recrystallized from hot absolute ethanol as a deep yellow solid (Scheme-I). Yield: 0.247 g, 70 %; m.f. C₁₉H₁₄N₄O₃; m.p. 200-202 °C; Rf: 0.63 (methanol:dichloromethane, v:v, 4:1). FT-IR (KBr, ν_{max}, cm⁻¹): 3400 (OH), 1738 (C=O), 1638, 1610 (C=N), 1590, 1450 and 1650 cm⁻¹ could be assigned to lactone -C=O, -N=C-, form imine -C=N- group [13,14]. The strong absorptions at 1735, 1683, 1638 cm⁻¹ which is characteristic of H₃C-C=O group in chromone-moiety of hydrazinoquinoxaline-2-one and give evidence to condensation with H₂N-NH₂. The key IR spectral bands of ligand and its metal complexes along with molar conductivity values are shown in Table-I. The molar conductance values of the complexes measured at room temperature in DMF solution with 0.001 mol/L concentration fall in the range 18-30 ohm.cm²/mol indicating the non-electrolytic nature of the complexes [17] assigning to absence of chloride ions as counter ion in the structure of complexes. The formation of pyrazolinoine ligand mainly proceeds by an attack of -NH₂group of intermediate formed up on condensation in the first step on carbonyl group (C=3 lactone), followed by ring closure to afford the pyrazole ring, which contains keto group that stabilizes the compound with inductive effect with neighboring benzopyrazine annulated ring [11,13] (Scheme-II).

**IR studies:** The key IR spectral bands of ligand and its corresponding metal complexes along with assignments are shown in Table-II. The absence of a band in the region 1710 cm⁻¹ [15] which is characteristic of H₂C-C=O group in chromone-2-one derivative indicates the condensation with H₂N-NH₂moiety of hydrazinoquinoxaline-2-one and give evidence to form imine -C≡N group [13,14]. The strong absorptions at 1735, 1590, 1450 and 1650 cm⁻¹ could be assigned to lactone -C≡O, -N≡C-

![Chemical structure](image)

**Scheme-I**

**TABLE-I**

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.w. (g/mol)</th>
<th>Colour</th>
<th>m.p. (°C)²</th>
<th>Elemental analysis (%): Calcd. (found)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>347.05</td>
<td>Pale yellow</td>
<td>200-202</td>
<td>C 65.98 (65.33) H 4.09 (3.55) N 16.20 (15.88) M –</td>
</tr>
<tr>
<td>[NiCl₂]</td>
<td>495.11</td>
<td>Orange</td>
<td>310-312 (Dec.)</td>
<td>C 46.99 (46.81) H 3.00 (2.90) N 12.00 (12.81) M 12.34 (12.66)</td>
</tr>
<tr>
<td>[CuCl₂]</td>
<td>515.00</td>
<td>Beige</td>
<td>290-292 (Dec.)</td>
<td>C 47.20 (46.05) H 2.95 (2.49) N 12.00 (12.22) M 13.30 (13.00)</td>
</tr>
<tr>
<td>[ZnCl₂]</td>
<td>480.00</td>
<td>White off</td>
<td>278-280 (Dec.)</td>
<td>C 46.05 (45.95) H 2.66 (2.09) N 11.44 (11.80) M 15.09 (14.76)</td>
</tr>
</tbody>
</table>

¹Dec: Decomposed, ²Content of metal was estimated by flame atomic absorption spectroscopy.

**RESULTS AND DISCUSSION**

All the metal complexes prepared are non-hygroscopic (stable at room temperature) and amorphous solids. These are soluble easily in DMSO, DMF and sparingly in ethanol and methanol whereas insoluble in chlorinated hydrocarbons. The elemental analyses data of the ligand and its metal complexes along with molar conductivity values are shown in Table-I. The molar conductance values of the complexes measured at room temperature in DMF solution with 0.001 mol/L concentration fall in the range 18-30 ohm.cm²/mol indicating the non-electrolytic nature of the complexes [17] assigning to absence of chloride ions as counter ion in the structure of complexes. The formation of pyrazolinoine ligand mainly proceeds by an attack of -NH₂ group of intermediate formed up on condensation in the first step on carbonyl group (C=3 lactone), followed by ring closure to afford the pyrazole ring, which contains keto group that stabilizes the compound with inductive effect with neighboring benzopyrazine annulated ring [11,13] (Scheme-II).

**TABLE-II**

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</tr>
</tbody>
</table>

¹Dec: Decomposed, ²Content of metal was estimated by flame atomic absorption spectroscopy.
C-N and -C=O of pyranopyrazole [16]. The absorption of \(\nu(NH)\) related to quinoxaline ring and hydravine \(\nu(NH_2)\) were observed around 2955-2855 cm\(^{-1}\) for pyrazine ring. -NH- as broad band was discovered by reaction of hydrazine group -HN-NH\(_2\) with acetyl group of coumarin thus indicates the formation of pyrazole ring [13]. However, the appearance of strong absorption in the free ligand at 1020-950 cm\(^{-1}\) reveals the pyrazole group attached to phenyl group that mainly belonged to coumarin ring [12,13]. How- 1\(\text{H}\) and \(\text{13C}\) NMR studies: The ligand displays two sharp singlet at \(\delta 11.70\) ppm attributed to the resonance of deshielded protons of pyrazine ring \(\text{NH-C}=\text{O}\). As well as the proton of \(-\text{OH}\) group attached to phenyl group that mainly belonged to coumarin derivative was appeared at \(\delta 9.11\) ppm, which support the ring closure occurred by attaching of lone pair of \(-\text{OH}\)- on the carbon atom \text{C-O} of lacton moiety [17]. However, the absorption of aliphatic \(-\text{CH}_3\) was observed in the region 3.88 ppm as singlet peak which is strong evidence for the keto-enol forms of the free ligand in solution. The nuclear resonance of aromatic protons \text{Ar-H} and pyrazine \text{H} were recorded about \(6.90-7.11\) and \(7.90-8.22\) ppm, respectively. Furthermore, \(\text{13C}\) NMR showed distinct absorptions of \(-\text{C}=\text{N}\)- at 190 and 220 ppm indicating the ring closure of pyrazolinone ring [12,13]. However, the other peaks belonged to aromatic \(-\text{C}=\text{C}\)- of pyrazine and phenyl rings were measured around (88.2-137) ppm. The aliphatic \(-\text{CH}_3\) was resonated at 38.70 ppm indicating the effect of withdrawing groups and resonance effect on the positions of the functional groups in the ligand [15,16].
The metal/ligand ratio was found to be 1:1 estimated by determining the metal and ligand content of the metal complexes. The data obtained from IR spectra suggested the participation of carbonyl and imine moiety of pyrazoline and pyrazine rings with the metal ions. According to the molar conductance, magnetic susceptibility and spectral data, the tetrahedral geometry of the prepared complexes is shown in Scheme-III. However, the interesting work of pyrazolinone complexes may have led to novel work in future that would enclose thermal analysis and antimicrobial studies.

**Conclusion**

The authors thank Department of Chemistry, College of Science, University of Mustansiriya, Baghdad, Iraq for providing spectral and analytical facility. Recording of magnetic susceptibility and elemental analyses are also gratefully acknowledged. Thanks are also due to Al-Yarmook University (Jordan) for facilitating the NMR analyses.

**CONFLICT OF INTEREST**

The authors declare that no conflict of interest regarding the publishing of the article.

**REFERENCES**


