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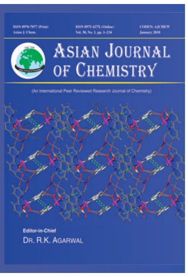

Synthesis and Spectroscopic Study of Some Transition Metal Complexes with New Pyrazolinone Ligand Derived from 2-Hydrazino Quinoxaline-3-one

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New transition metal complexes of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) with (*E*)-3-[4-(hydroxy(phenyl)methylene)-3-methyl-5-oxo-4,5-dihydro-1*H*-pyrazol-1-yl]quinoxalin-2(1*H*)one were synthesized and characterized by elemental analysis, FT-IR, NMR and mass spectra. The ligand was synthesized by the reaction of 2-hydrazinoquinoxaline-3(1*H*,4*H*)-one with 3-acetylcoumarin. All the metal complexes are found to be monomer in nature and have tetrahedral geometry. The IR spectra data revealed that the ligand behaves as neutral bidentate Lewis base through two nitrogen atoms of pyrazole and pyrazine moiety forming six-membered ring. The molar conductivity measurements suggested the neutral nature of all metal complexes in DMF solution. The magnetic moment measurements investigated the high spin properties of all the metal complexes.

Keywords: Transition metal(II) complexes, Pyrazole, Pyrazolinone.

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 pyrazoline 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]. The complexes of cadmium(II) with di-sigma pyrazoles have studied with X-ray crystallography [13,14]. In view of the importance of such quinoxaline and pyrazoles ligands, we report here the synthesis and characterization of pyrazoline-quinoxaline based ligand and its manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) metal ion complexes. The structure of (*E*)-3-[4-(2-hydroxybenzylidene)-3-methyl-5-oxo-4,5-dihydro-pyrazol-1-yl]-1*H*-quinoxalin-2-one and its metal complexes have elucidated by NMR, FT-IR, mass spectra and elemental analyses.

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 conductance 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 $MnCl_2·4H_2O$, $CoCl_2·6H_2O$, $NiCl_2·6H_2O$, $CuCl_2·2H_2O$ and $ZnCl_2$ 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 from Fluka company with 99 % purity. 3-Acetyl coumarin was prepared according to the method assigned in literature [15].

Synthesis of 3-hydrazino-quinoxalin-2(1*H*)-one: This compound was prepared in two steps according to the reported method [16]. Yield: 88 %, m.p. 250-252 ºC, R_f = 0.82 (ethyl acetate:cyclohexane, v:v, 3:1). FT-IR (KBr, ν_{max}, cm^{-1}): 3400 (-NH-NH_2), 1683 (C=O), 1588 (-C=N), 2930-2855 (-NH- pyrazoline ring). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 4.60 (s, 2H, *J* = 8.22 Hz, H_2N-N=C-), 7.22-7.59 (m, 4H, *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^+].

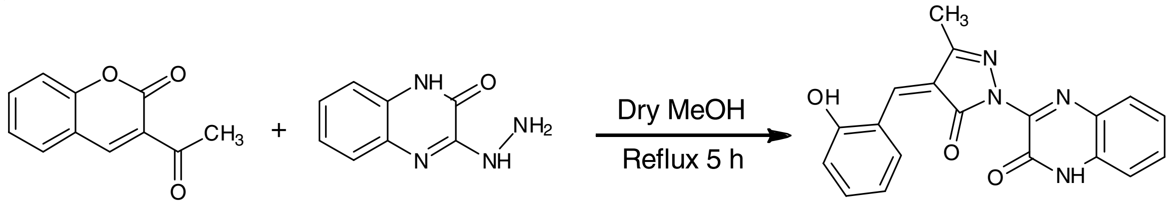
Synthesis of (*E*)-3-[4-(2-hydroxybenzylidene)-3-methyl -5-oxo-4,5-dihydropyrazol-1-yl]-1*H*-quinoxalin-2-one: 2-Hydrazinopyridine (0.176 g, 10 mmol) in methanol (15 mL) was added to a solution of 3-acetylcoumarin (1.88 g, 10 mmol) in methanol (20 mL) and the mixture was refluxed for 5 h. The solid crude 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. $C_{19}H_{14}N_4O_3$; m.p. 200-202 ºC; R_f: 0.63 (methanol:dichloromethane, v:v, 4:1). FT-IR (KBr, ν_{max}, cm^{-1}): 3300 (OH), 1738 (C=O), 1638, 1610 (C=N), 1460 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 2.5 (s, 3H, CH_3), 6.5 (t, 1H, *J* = 6.15 Hz, HC=C-), 6.99-7.22 (m, 4H, *J* = 3 Hz, Ar-H), 7.49-7.83 (m, 4H, Ar-H), 9.86 (s, 1H, *J* = 6.35 Hz, HO-C=C), 10.22 (s, 1H, *J* = 5.33 Hz, HN-C=O pyrazole). ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm): 45.45, 75.18, 100.05, 115.33, 133.91, 122.05, 125.77, 135.11, 146.88, 150.01, 170.00, 180.11, 198.10, 194.44, 196.65, 197.98. MS (*m/z* %): 347 (70) [M^+], 332 (50) [M-CH_3], 316 (33) [M-OH,-CH_3].

Synthesis of metal complexes: A methanolic solution (50 mL) of corresponding metal(II) chloride *e.g.*, [$MnCl_2·4H_2O$ (0.221 g), $CoCl_2$· $6H_2O$ (0.237 g), $NiCl_2·6H_2O$ (0.237 g), $CuCl_2·2H_2O$ (0.170 g) and $ZnCl_2$ (0.135 g)] was added with constant stirring to ethanolic solution of ligand (1 mmol, 0.347 g) in 25 mL ethanol and refluxed on water bath for 3-5 h depending on the nature of metal ion. The obtained solid complex was separated by filtration under suction, washed with hot ethanol and dried in vacuum.

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-1. 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.cm^2/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 pyrazolinone ligand mainly proceeds by an attack of -NH- 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**).

IR studies: The key IR spectral bands of ligand and its corresponding metal complexes along with assignments are shown in Table-2.The absence of a band in the region 1710 cm^{-1} [15] which is characteristic of H_3C-C=O group in chromone-2-one derivative indicates the condensation with H_2N-NH-moiety 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-,

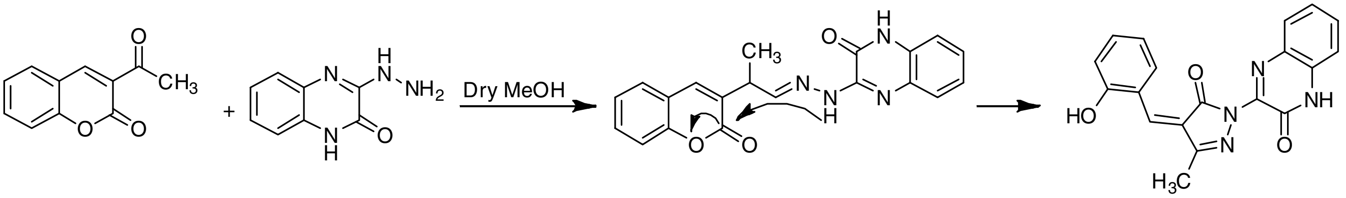


Scheme-I

TABLE-1
PHYSICO-CHEMICAL ANALYTICAL DATA OF SYNTHESIZED LIGAND AND ITS METAL(II) COMPLEXES

Compound	m.w. (g/mol)	Colour	m.p. (°C)^a	Elemental analysis (%): Calcd. (found) C	H	N	M^b
L	347.05	Pale yellow	200-202	65.98 (65.33)	4.09 (3.55)	16.20 (15.88)	–
[$MnLCl_2$]	472.25	Reddish brown	300-302 (Dec.)	48.86 (46.99)	4.00 (3.99)	13.11 (13.59)	12.22 (11.53)
[$CoLCl_2$]·H_2O	493.80	Brown	305-307 (Dec.)	47.90 (46.93)	3.39 (2.88)	14.55 (15.00)	12.88 (12.11)
[$NiLCl_2$]·H_2O	495.11	Orange	310-312 (Dec.)	46.99 (46.81)	3.00 (2.90)	12.00 (12.81)	12.34 (12.66)
[$CuLCl_2$]·$2H_2O$	515.00	Beige	290-292 (Dec.)	47.20 (46.05)	2.95 (2.49)	12.00 (12.22)	13.30 (13.00)
[$ZnLCl_2$]	480.00	White off	278-280 (Dec.)	46.05 (45.95)	2.66 (2.09)	11.44 (11.80)	15.09 (14.76)

^{a}Dec: Decomposed, ^{b}Content of metal was estimated by flame atomic absorption spectroscopy.



Scheme-II: Proposed steps wise of ligand formation

TABLE-2
FT-IR KEY ABSORPTIONS OF LIGAND AND ITS METAL COMPLEXES (cm^{-1})

Compound	ν(NH)	ν(C=O)	ν(C=N)	ν(C-H)	ν(C-N)	ν(M–N)	ν(M–O)	ν(M-Cl)
QHZ	3350(m)	1680(s)	1610,1 590(s)	3010 (w)	1420(m)	–	–	–
Ligand	3380	1735, 1650(s)	1630(sh)	3090(w), 2970(m)	1433(m)	–	–	–
[$MnLCl_2$]	3180	1740, 1640	1610 (s)	3050(w), 2964(m)	1410(s)	520(m)	436(m)	355(w)
[$CoLCl_2$]·H_2O	3300	1733(s), 1642(sh)	1560 (s)	3010(w), 2987(m)	1433(s)	530(w)	430(m)	380(w)
[$NiLCl_2$]·H_2O	3235	1738, 1641(sh)	1570 (s)	3010(w), 2967(m)	1390(s)	522(w)	477(m)	370(w)
[$CuLCl_2$]·$2H_2O$	3369(br)	1735(s), 1640(s)	1585 (s)	3010(m), 2977(m)	1398(m)	500(w)	480(m)	390(w)
[$ZnLCl_2$]	3300	1739(s), 1642(sh)	1575 (s)	3010(w), 3000(w)	1422(m)	515(w)	450(w)	359(w)

C-N and -C=O of pyranopyrazole [16]. The absorption of ν(NH) related to quinoxaline ring and hydrazine ν(NH_2) were observed around 2955-2855 cm^{-1} for pyrazine ring -NH- as broad band was disappeared 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 based ligand. In the complexes, it is remarkable shifts to lower frequency region (1645-1640 cm^{-1}) and (1610-1560 cm^{-1}) due to the formation of M-O and M-N bonds since the drift of lone pairs on oxygen and nitrogen atoms moved to vacant orbitals of the metal ions [18]. In the spectra of all the metal complexes, a weak bands were appeared in the far-infrared regions 390-355 cm^{-1}, this may be attributed to M-Cl bonds and support the participation of chloride ions in inner sphere of metal complexes structures [15,16].The bands due to ν(NH) are broadened in all the complexes due to the overlapping of ν(OH) bands of enol form of ligand to H-N-of pyrazoline ring. The non-ligand bands in the region 530-500 and 480-430 cm^{-1} were assigned to ν(M-N) and ν(M-O), respectively [16,17].

^{1}H and ^{13}C NMR studies: The ligand displays two sharp singlet at δ 11.70 ppm attributed to the resonance of deshielded protons of pyrazine ring NH-C=O. As well as the proton of -OH group attached to phenyl group that mainly belonged to coumarin derivative was appeared at δ 9.11 ppm, which support the ring closure occurred by attaching of lone pair of -NH- on the carbon atom C-O of lacton moiety [17]. However, the absorption of aliphatic -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 Ar-H and pyrazine H were recorded about (6.90-7.11) and (7.90-8.22) ppm, respectively. Furthermore, ^{13}C NMR showed distinct absorptions of -C=N- at 190 and 220 ppm indicating the ring closure of pyrazolinone ring [12,13]. However, the other peaks belonged to aromatic -C=C- of pyrazine and phenyl rings were measured around (88.2-137) ppm. The aliphatic -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].

Mass spectral studies: The mass spectra of starting materials, 3-hydrazinoquinoxaline-2-one, 3-acetylcoumarin and free ligand with its metal complexes with Co(II) and Cu(II) were carried out in order to elucidate the proposed structure of complexes. The molecular ion at $M^+ = 188$ of 100 % intensity support the proposed formula of 3-acetylcumarine $C_{11}H_8O_3^+$ whereas the molecular ion M+1 at 176, supporting the proper formula of 3-hydrazino-quinoxaline-2-one. The EIMS spectrum of the free ligand (LH) exhibits the nuclear resonance of molecular ion related to free pyrazoline-quinoxaline based ligand which is remarkably observed from the base peak at $M^+ = 347$ gives strong evidence for ring closure of Schiff base intermediate, formed *via* condensation of acetyl moiety of coumarin with 2-hydrazinoquinoxaline. The mass spectra of cobalt(II) complex displayed absorptions around *m/e* = 474 and 442 due to molecular ions of $MnLCl_2^+$ and $MnLCl^+$, respectively confirming the isotope effect of manganese(II). As shown in Fig. 1, the cleavages of -Cl and -OH in addition to substraction of hydrated water molecules confirm the right suggested molecular structure of the prepared complex. In the same way, the low intensity peak at 477 in the mass spectrum of zinc(II) complex (Fig. 2) may be associated with the molecular ion $[ZnCl_2]^+$ whereas the fragmentations at 436, 298 and 167 are belonged to the

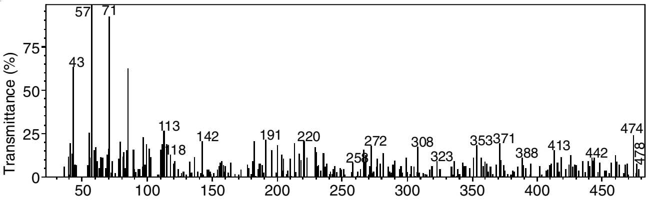


Fig. 1. Mass spectra of [$MnLCl_2$] complex

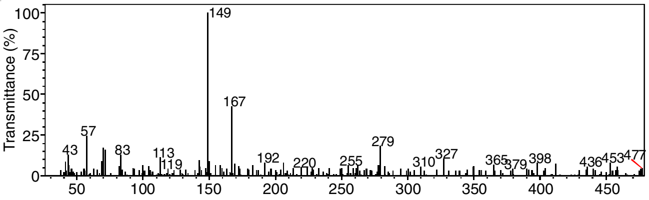


Fig. 2. Mass spectra of [$ZnLCl_2$] complex

TABLE-3
ELECTRONIC SPECTRA, MOLAR CONDUCTANCE AND THE MAGNETIC MOMENTS OF SYNTHESIZED LIGAND AND ITS METAL(II) COMPLEXES

Compound	UV-visible (λ_{max})	μ (BM)	Λ_m (S mol^{-1} cm^2)*	Geometry
Ligand (L)	260, 360	–	–	–
[MnLCl$_2$]	340, 455	5.80	20	Tetrahedral
[CoLCl$_2$]·H$_2$O	370, 690, 875	3.90	27	Tetrahedral
[NiLCl$_2$]·H$_2$O	378, 600, 744	3.04	30	Tetrahedral
[CuLCl$_2$]·2H$_2$O	333, 690	1.70	22	Tetrahedral
[ZnLCl$_2$]	280, 390	0	25	Tetrahedral

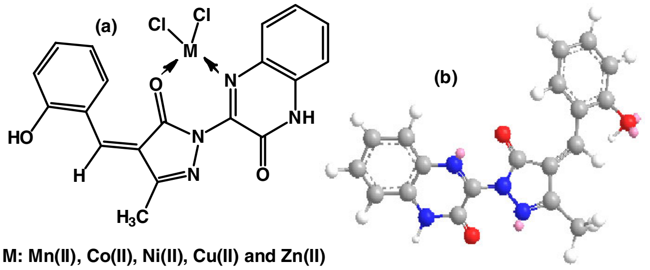
*Λ_m = molar conductance was measured in DMF solutions, μ = magnetic moment in Bohr Magneton unit.

breaking of weak points of methyl and hydroxyl groups in the organic moiety of pyrazolinone ring [18,19].

Electronic spectra and magnetic properties: The electronic absorptions of the ligand and its metal complexes solutions in DMF and ethanol are shown in Table-3. The solution of ligand in ethanol displays two spin-allowed transitions in the regions 260 and 360 nm which is characteristic of -C=N-, -C=C- and -C=O functional groups incorporated in pyrazole and pyrazine rings, respectively [12,15]. The pale coloured solution of Mn(II) complex showed weak peak at 455 nm and other of high intensity at 340 nm, these may be assigned to *d-d* and MLCT, respectively [13,20]. The cobalt(II) complex exhibited spin-allowed *d-d* transitions at 870 and 690 nm that are assigned to $^4A_2 \rightarrow {}^4T_1$ (P) and $^4A_2 \rightarrow {}^4T_1$ (F), respectively, which is typical for tetrahedral Co(II) complexes [21]. At the same way, the electronic spectra of nickel(II) complex in DMF at 730 and 550 nm are assigned to $^3T_1$ (F) $\rightarrow {}^3T_1$ (P) and $^3T_1$ (F) $\rightarrow {}^3A_1$ (F), respectively [22] thus ascribing the tetrahedral structure around Ni(II) ion. Due to the distorted tetrahedral configuration, Cu(II) complex showed a broad band at 690 nm for $^2T_2 \rightarrow 2E$ transition supporting the distorted tetrahedral geometry. The values of magnetic moments for solid complexes displayed increasing for cobalt and nickel(II) complexes due to orbital contribution and high spin state for tetrahedral symmetry [16,18,22]. The magnetic susceptibility measurements thus help to predict the possible geometry of the metal complexes. In paramagnetic Mn(II), Co(II) and Cu(II) complexes, often the magnetic moment (μ_{eff}) gives the spin value corresponding to the number of unpaired electron, while tetrahedral nickel(II) complex showed little increasing in magnetic moment due to spin-orbital coupling effect [23]. The expected magnetic values of Cu(II) and Mn(II) complexes are 1.77 and 5.80 B.M., respectively [23,24]. Thus the value of magnetic moment of a complex would give valuable insights into its constitution and structure. The magnetic susceptibility measurements obtained at room temperature for Ni(II) complex can be associated with its configurations, stereochemistry, hybrid orbital and number of unpaired electrons, spin-only and expected magnetic values at 3.04 B.M.

Conclusion

The synthesis of (*E*)-3-[4-(2-hydroxybenzylidene)-3-methyl-5-oxo-4,5-dihydropyrazol-1-yl]-1*H*-quinoxalin-2-one was done by ring closure of of 3-acetyl-coumarin with 2-hydrazinoquinoxaline-2-one in an equimolar ratio in dry methanol. The geometry of newly synthesized compounds were elucidated based on their elemental analysis, magnetic susceptibility measurements and spectral data. The stoichiometry of free ligand and its metal complexes were confirmed by elemental analyses. 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.



Scheme-III: The tentative structure of the complexes (a) and 3D structure of ligand (b)

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CONFLICT OF INTEREST

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

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