

Synthesis and characterization of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes with new Schiff base derived from 6,7-dimethyl-quinoxaline-2,3(1*H*,4*H*)-dione and thiosemicarbazide

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ABSTRACT

New transition metal complexes of quinoxaline-2,3-dione-thiosemicarbazone ligand were prepared and characterized by elemental analysis, ¹H and ¹³C NMR spectroscopy. The ligand (LH) was obtained by the reaction of 6,7-dimethyl-quinoxaline-2,3(1*H*,4*H*)-dione with thiosemicarbazide. All the complexes are found to be monomer in nature and have tetrahedral geometry. The IR spectra data revealed that the new Schiff base behaved as monobasic tridentate ligand through deprotonation of thiol-SH group, oxygen atom of C=O of pyrazine moiety and nitrogen atom of azomethine -C=N- group. However, the molar conductivity measurements proved the neutral nature of all metal complexes in DMSO solution, as well as the magnetic moment measurements investigated the high spin properties of all complexes.

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1. Introduction

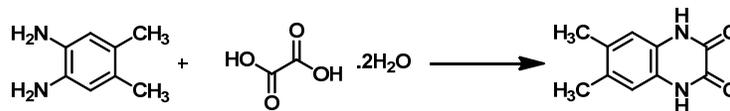
Schiff bases of quinoxalines and benzopyrazines have been extensively studied for biological applications, such as anti-microbial [1-3], insecticidal [4], anti-HIV [5], antitumor [6], and in vitro cytotoxic activities [7,8]. The quinoxaline-based Schiff bases were synthesized and characterized by several workers [9]. The synthesis and catalytic activity of metal complexes derived from quinoxalin-2-carboxaldehyde Schiff bases on the oxidation of cyclohexane was reported by Sebastian [10]. Two *bis*-azomethine derived from quinoxaline-2-carboxaldehyde were investigated on the basis of X-ray crystallography by Varghese D. and coworkers [11]. A new Schiff base derived from quinoxaline-2-carboxaldehyde and 2-aminocyclopent-1-ene-1-dithiocarboxylic acid and its Fe(III), Co(II), Ni(II), and Cu(II) complexes were synthesized and characterized by various spectral and analytical techniques [12]. Recently, new Co(III), Ni(II), and Cu(II) complexes of Schiff bases derived from 4-phenyl(-methyl)-thiosemicarbazone-bases quinoxaline(1*H*,2*H*)-2,3-dione have been prepared and antimicrobial studied. The ligands were a monobasic tridentate NNS donor in the Co(II) and Cu(II) complexes and neutral bi dentate nitrogen and sulphur donor

in the Ni(II) complex. The cytotoxicity of Co(III) complex was determined *in-vitro* as well as in tissue culture methods [13]. Al-Jibouri, M.N. has reported the synthesis, characterization and antimicrobial activity of template metal complexes derived from quinoxaline-2,3-dione [14]. Satish M.A. and coworkers have reported synthesis and spectroscopic of binuclear metal complexes with acyclic polydentate Schiff base derived from quinoxaline-2,3-dione [15]. The present work described the synthesis and characterization of new metal complexes of Mn(II), Co(II), Ni(II), Co(II) and Zn(II) with new Schiff base involving quinoxalin-2,3-dion-thiosemicarbazide.

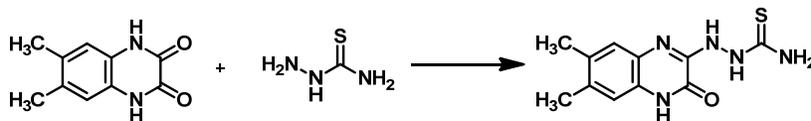
2. Experimental

2.1. Instrumentation

Elemental analyses (CHNS) of the new Schiff base HL and its metal(II) complexes were determined using EURO EA Elemental analyzer (Italy model). The electronic spectra of the prepared compounds were recorded using Cary Varian UV-Visible spectrometer in the range 200-800 nm in ethanol and *N,N*-dimethylformamide (DMF) solvents.



Scheme 1



Scheme 2

The ^1H and ^{13}C NMR spectra were carried at Al-Yarmouk University, Amman on Bruker 300 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-IR-8400 Spectrometer at the Laboratories of Chemistry Department, College of Science, Al-Mustansirya University, Iraq. The molar conductance measurements were made on Philips conductivity bridge type CM-82 with a cell having a cell constant of 1.1 cm^{-1} in DMSO solutions. The percent of metal contents of the complexes were determined by flame atomic absorption on Shimadzu A.A-670 spectrometer at Instrumental Analyses Laboratory, Chemistry Department, Al-Mustansirya University, Baghdad, Iraq. The magnetic susceptibility of the solid metal complexes was measured on Sherwood Magnetic Balance apparatus at Inorganic Chemistry Laboratory for post graduate students via Farady's method at 303 K.

2.2. Materials

The hydrated metal chlorides $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 were provided from Sigma-Aldrich Company and used without purification. The oxalic acid, 4,5-dimethyl-1,2-phenylenediamine and solvents were supplied from Fluka company in 99% purity. All other chemicals used were of Analar grade.

2.3. Methods

2.3.1. Synthesis of 6,7-dimethyl-quinoxaline-2,3(1H,4H)-dione (DMQ)

The 6,7-dimethyl-quinoxaline-2,3(1H,4H)-dione was prepared according to the published method in literature [14], Scheme 1. Color: White off. Yield: 95%. M.p.: 289-291 °C. FT-IR (KBr, ν , cm^{-1}): 3200-3100 (NH) (Quinoxalineamido), 1734, (C=O) (Lactam), 1610 (C=N) (Amide pyrazine), 1320 (C-N) (Pyrazine ring). UV/Vis (Methanol, λ_{max} , nm, (ϵ)): 330 (4.77), 290 (4.42). ^1H NMR (300 MHz, DMSO- d_6 , δ , ppm): 3.09 (s, 6H, 2CH₃), 7.66-8.05 (m, 4H, Ar-H + NH-CO). ^{13}C NMR (300 MHz, DMSO- d_6 , δ , ppm): 160.32 (2C, C=O), 130.50 (2C, C-N-pyrazine), 125.60 (2C, -C=C-), 118.55 (2C, C=C-CH₃), 19.22 (2C, Ar-CH₃). Anal. calcd. for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 62.67; H, 4.99; N, 13.67%.

2.3.2. Synthesis of 2-(6,7-dimethyl-3-oxo-3,4-dihydroquinoxalin-2(1H)-ylidene)hydrazinecarbothioamide (HL)

0.01 mole of thiosemicarbazide (0.91 g) in 100 mL ethanol was added gradually to 6,7-dimethyl-quinoxaline-2,3(1H,4H)-dione (DMQ) (1.90 g). The reaction mixture was refluxed for 6 hrs on water bath and the pale yellow solid separated was filtered, washed several times with ethanol and dried in oven, Scheme 2. Color: Pale yellow. Yield: 80%. M.p.: 233-235 °C. FT-IR (KBr, ν , cm^{-1}): 3250 (NH) (Amide and lactam), 1680 (C=O)

(Amide), 1610 (C=N) (Imine of pyrazine ring), 2972 (C-H) (Aliphatic-CH₃). ^1H NMR (300 MHz, DMSO- d_6 , δ , ppm): 3.40 (s, 6H, CH₃), 5.62 (s, 1H, NH), 6.21 (s, 1H, Ar-H), 6.78 (s, 1H, Ar-H) 7.89 (s, 1H, HN), 8.01 (s, 1H, HN), 8.61 (s, 2H, H₂N). ^{13}C NMR (300 MHz, DMSO- d_6 , δ , ppm): 155.2 (C, C=S thioamide), 131.91 (C, Amide-C=O), 128.9 (C, C=N-imine), 127.7 (C, C-N-Pyrazine), 126.7 (C, -C-N-Pyrazine), 123.90 (C, C=C-Ar), 122.04 (C, C=C-Ar), 115.61 (9C, C-Ar), 110.79 (C=C-Ar), 51.4 (C, CH₃), 25.2 (C, CH₃). UV/Vis (Ethanol, λ_{max} , nm, (ϵ)): 350 (3.82), 222 (5.401). MS (EI, m/z (%)): 264 (M⁺, 100). Anal. calcd. for $\text{C}_{11}\text{H}_{13}\text{N}_5\text{OS}$: C, 50.17; H, 4.98; N, 26.60. Found: C, 49.07; H, 3.99; N, 25.22%.

2.4. Synthesis of the metal complexes

A methanolic solution (100 mL) of metal(II) chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.221g), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237 g), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237 g), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.170 g) and ZnCl_2 (0.135 g)) was added with stirring to an ethanol solution of the ligand (LH (0.264 g) and refluxed on water bath for 6-8 hours. So, the obtained solid complex was separated by filtration under suction, washed with hot ethanol and dried in vacuum. The characterization data of all metal complexes were shown in Tables 1-3.

3. Results and discussion

The new metal complexes prepared in this course were non-hygroscopic (stable at the room temperature) and in the form of amorphous solids. These are soluble easily in DMSO, DMF and sparingly in ethanol and methanol whereas they are insoluble in chlorinated hydrocarbons. The elemental analysis data of the ligand and its metal complexes along with their physical properties are shown in Table 1. However, the continuous variation method was adopted to deduce the mole ratio of ligand to metal ion at maximum wavelength of absorption [16].

3.1. Molar conductivity measurements

The molar conductance values of the complexes measured at room temperature in DMSO solution with 0.001 mol/dm³ concentration fall in the range 10-22 ohm.cm²/mol indicating the non-electrolytic nature of the complexes [17]. Comparatively high values are due to the interaction of solvent molecules of DMSO on the vacant orbital's of metal ions.

3.2. IR spectral study

The important IR spectral bands of ligand and corresponding complexes along with assignments are presented in Table 2.

Table 1. The physical properties and elemental analysis of the prepared metal complexes.

Compound	Color	M.p. (°C) ^a	C%		H%		N%		S%		M% ^b
			Calculated	(Found)	Calculated	(Found)	Calculated	(Found)	Calculated	(Found)	
HL	Pale yellow	233-235	50.17	(49.07)	4.98	(3.99)	26.60	(25.22)	12.18	(11.88)	-
[MnLCl]	Yellow	298 (Dec.)	37.46	(36.55)	3.43	(3.22)	19.87	(20.09)	9.10	(8.48)	15.58 (14.72)
[CoLCl]	Brown	312 (Dec.)	37.04	(36.44)	3.39	(2.88)	19.63	(19.77)	8.99	(8.76)	16.55 (15.77)
[NiLCl]	Red	319 (Dec.)	36.59	(35.39)	3.15	(2.00)	19.39	(20.11)	8.82	(8.11)	17.11 (16.17)
[CuLCl]	Dark brown	315 (Dec.)	36.60	(35.63)	3.35	(3.12)	19.39	(20.11)	8.82	(9.90)	17.59 (16.66)
[ZnLCl]	White off	322 (Dec.)	36.38	(35.00)	3.34	(2.80)	19.29	(19.79)	8.92	(7.97)	18.22 (17.55)

^a Dec: Decomposed.^b Content of metal was done by flame atomic absorption spectroscopy.**Table 2.** FT-IR absorptions of the Schiff base HL and its template metal complexes in cm⁻¹.*

Compound	ν NH	ν C=O	ν C=N	ν C=S	ν C-N	ν M-N	ν M-O	ν M-S	ν M-Cl	Other bands
DMQ	3250(m)	1689(s)	1622(s)	-	1189(m)	-	-	-	-	2964(m), 3020(w)
HL	3320(m)	1680(s)	1610 (s)	890(s)	1150(m)	-	-	-	-	2976(m), 3050(w)
[MnLCl]	3180(m)	1666(sh)	1589(s)	833(m)	1160(m)	500(m)	400(m)	522(m)	288(w)	2984(m), 3020(w)
[CoLCl]	3180(br)	1677(s)	1569(s)	780(m)	1144(m)	490(m)	430(m)	540(m)	280(w)	2976(s), 3050(w)
[NiLCl]	3235(br)	1666(sh)	1577(s)	835(m)	1140(m)	480(m)	430(w)	533(m)	370(w)	2933(m), 3080(w)
[CuLCl]	3169(m)	1640(s)	1580(s)	740(m)	1180(m)	485(m)	433(w)	525(m)	280(w), 344(w)	2890(m), 3060(w)
[ZnLCl]	3300(m)	1655(sh)	1575(s)	826 (m)	1060(m)	500(w)	444(w)	518(m)	375(w)	2980(s), 3013(w)

* s: Strong, m: Medium, br: Broad, w: Weak, sh: Shoulder.

Table 3. The electronic spectra and molar conductance of the prepared complexes*.

Complex	UV-visible, λ (nm)	μ (B.M.)	Λ_m (S.mol ⁻¹ .cm ²)	Geometry
DMQ	290,330	-	-	-
HL	222,350	-	-	-
[MnLCl]	340,470	5.45	12	Tetrahedral
[CoLCl]	390,550,670	4.22	67	Tetrahedral
[NiLCl]	388,650,700	2.84	22	Tetrahedral
[CuLCl]	370,690	1.56	10	Tetrahedral
[ZnLCl]	344,365(CT)	0	13	Tetrahedral

* Λ_m = Molar conductance's were measured in DMF solutions and CT: Charge transfer.

The absence of a band in the region 2500-2600 cm⁻¹, which is characteristic of thiol group ν (SH), suggests the stable of the thione amide form in the solid state, hence decline the thione-thiol tautomerism (H-N-C=S, C=N-SH) in the present set of thiosemicarbazone ligand [18,19]. The thioamidic coupled vibrations, I [ν (CN) and ν (NH) + δ (CH)], II [ν (CN) and ν (CS)], III [ν (CS) and ν (CS) + ν (CN)] and IV ν (CS) were observed around 1600, 1545, 1460 and 940 cm⁻¹ confirm the *thio-keto* form of ligand [15,16]. The ν (C=O) of pyrazine ring was observed as a sharp, intense band at 1683 cm⁻¹ and the stretching vibrations of azomethine functionality ν (C=N) were observed near 1620 cm⁻¹. The absorption of ν (NH) related to quinoxaline ring and hydrazine ν (NH₂) were observed around 3400 cm⁻¹ as double intense band [20]. For the free Schiff base HL, a sharp band at 1689 cm⁻¹ is assigned to ν (C=O) [19]. In the complexes, it shifts to lower frequency region (1680-1644 cm⁻¹) due to the carbonyl oxygen coordination [19]. In the spectra of all metal complexes, weak bands appeared in the far-infrared regions 270-375 cm⁻¹, this may be attributed to M-Cl bonds and support the participation of chloride ions in inner sphere of metal complexes structures [14,16]. A new band was appeared around 1230-1200 cm⁻¹ attributable to ν (C-O) confirms the same oxygen after deprotonation. The band due to ν (C=N) has been shifted to the lower frequency side in all the complexes, owing to the coordination of nitrogen atom of azomethine C=N- moiety [20-22]. The thioamide bands having major contribution from the ν (C=S) group in the regions 890cm⁻¹ which were disappeared in the IR spectra of all complexes, thus indicates the transformation to thiol form up on coordination with central metal ions. It is further supported by the weak absorption at 770-835 cm⁻¹ attributable to ν (C-S). The absence of ν (S-H) in the complexes suggests the coordination of sulfur through deprotonation. The bands due to ν (NH) are broadened in all the complexes due to the overlapping of ν (OH) bands of coordinated water molecule. The new bands in the Far-IR spectra for all metal complexes in the 500-480 cm⁻¹, 400-440 and 518-544 cm⁻¹ regions are assigned to ν (M-N), ν (M-O) and ν (M-S) bonds, respectively [20,22].

3.3. Electronic spectra and magnetic moments

The magnetic and electronic spectral data is in relevance with proposed geometry of complexes. The free ligand solution displays high intensity peaks in the UV regions at 290-330 nm which are assigned to ligand field of C=N and C=C chromophores [23]. The electronic transitions from the ⁶A₁ ground term of Mn(II) to higher energy terms are spin-forbidden. However, the band appearing in the region 570-340 nm in the electronic spectrum of Mn(II) complex is assigned to ⁶A₁ → ⁴T₁(G) and is consistent with tetrahedral geometry. For the cobalt(II) complex, the band at 670 and 550 nm are assigned to the ⁴A₂ → ⁴T₁(P) and ⁴A₂ → ⁴T₁(F), respectively, which is typical for tetrahedral Co(II) complexes. The bands at 735-650 nm in the Ni(II) complex are assigned to the forbidden transition ³T₁(F) → ³T₁(P), due to the tetrahedral structure around Ni(II). Due to the distorted tetrahedral configuration, the copper(II) complex shows a broad band at 690 nm for ²T₂ → ²E transition [24]. The low energy bands in the visible region for all complexes solutions confirms the tetrahedral geometry of metal(II) complexes [18,24], respectively. The room temperature magnetic moment values of nickel and cobalt complexes were found to be 2.84 and 4.22 BM for [NiLCl] and [CoLCl], respectively, suggesting the four coordinated, tetrahedral geometry [25]. Whereas copper complex [CuLCl] exhibit the magnetic moment value 1.56 BM. Fairly lower magnetic moment value of copper complex is attributed to the higher covalence of S-Cu bond and lower orbital contribution of sulphur [25,26].

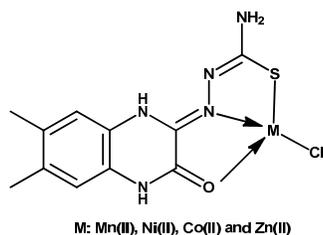
3.4. ¹H and ¹³C NMR study

The ¹H NMR spectra study of the free Schiff base HL is recorded in DMSO-*d*₆ solution using tetramethylsilane as internal standard. The chemical shifts of the different types of protons found in the ¹H and ¹³C NMR spectra of DMQ and LH compounds are listed in the experimental section. The ¹H NMR spectrum of DMQ compound exhibits absorption at 3.09 ppm that belongs to resonance of 6H of -CH₃ groups linked to phenyl moiety at 6 and 7 positions [15,27]. As well as the

peaks at 7.66-8.05 ppm may be assigned to aromatic Ar-H and amide NH-CO, respectively [27]. The ^1H NMR spectrum of LH Schiff base shows signal observed at 8.61 ppm that is assigned to 2H of $\text{H}_2\text{N}-\text{C}=\text{S}$ moiety [14,15,27]. The resonance of -NH protons of pyrazine ring are showed at 7.89 and 8.01 ppm, respectively [13,14]. The peaks that are showed in 6.21, 6.78 and 7.89 ppm could be attributed to aromatic Ar-H and $-\text{C}=\text{N}-\text{NH}-$ protons, respectively [15]. However, the shielded protons of $-\text{CH}_3$ groups are recorded at 3.40 ppm as singlet peak. In addition, ^{13}C NMR spectra data of LH also entirely agree with the data of ^1H NMR spectra [27-29].

4. Conclusions

The Mn(II), Co(II), Ni(II), Co(II) and Zn(II) complexes with tridentate monobasic LH ligand synthesized in this study have a monomer structure as suggested by elemental analysis, NMR, FT-IR, UV-Visible spectra and magnetic moments data. The values of infrared stretching frequencies corresponding to the C=S and M-Cl bands are in good agreement with four-coordinated metal(II) complexes and the electronic spectra of these complexes also exhibit spectral bands corresponding to the electronic transitions characteristic of tetrahedral complex. The four coordinated metal complexes with the novel Schiff base LH is again confirmed by the molar conductance measurements that assigned the non-electrolytes species with $[\text{MLCl}]$ formula. According to the obtained results from molar conductance, magnetic susceptibility and spectra data, the tetrahedral geometry of the prepared complexes was shown in Scheme 3.



Scheme 3

Acknowledgements

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