

Synthesis, Characterization and Biological Activity of Chromium(III), Manganese(II), Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes with New Schiff Base Derived from 6-methylquinoxaline-2, 3(1H,4H)-dione and Diethylenetriamine

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Authors' contributions

This work was carried out in collaboration between both authors. Author MNAJ designed the study and wrote the protocol. Author SMH performed the synthesis, identification and biological study. Both authors read and approved the final manuscript.

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ABSTRACT

The new metal complexes of chromium(III), manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) were prepared by direct reactions of their metal chlorides with new Schiff base, ((3Z)-3,3'-((azanediyl-bis(ethane-2,1-diyl))bis(azanylylidene))bis(6-methyl-3,4-dihydroquinoxalin-2(1H)-one)) and fully characterized on the basis of GC-MS, ¹H, ¹³C NMR spectra and CHNM elemental analyses. The magnetic susceptibility of solid complexes and their molar conductance in DMSO solutions revealed the octahedral geometry for all complexes with [ML(H₂O)₂]Cl₂ (M: Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)) and [CrL(H₂O)Cl]Cl₂. Furthermore, the antimicrobial activity of the complexes were scanned against two bacteria and fungi and it is found that the cobalt(II), copper(II)

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and zinc(II) complexes showed the highest inhibition zone towards the selected microorganisms where as the other complexes exhibited medium activity with relative to standard antibiotic *Ciproflaxine* of 20 µg/ml. Furthermore, the nickel(II), copper(II) and zinc(II) complexes exhibited remarkable inhibition zones against *Candida albicans* and *Aspergillus flavus*.

Keywords: Schiff base; quinoxalines; benzopyrazine; polydentate ligands; biological activity; transition metal complexes.

1. INTRODUCTION

Heterocyclic compounds containing nitrogen atom attract a great deal of attention in coordination chemistry and homogeneous catalysis [1-3]. The combination of heterocyclic ring and azomethine moiety exerts potential biological and catalytic activities [4-6]. Although extensive studies have been made on the transition metal complexes of various nitrogen heterocyclic Schiff base ligands, comparatively less is reported on transition metal complexes derived from 2-oxo-1,2-dihydroquinoline-3-carbaldehyde [7-9]. Sahar, M. have reported the binuclear palladium(II) complexes with Schiff bases derived from 2-oxoquinoxaline-3-carboxaldehyde and investigated their main role in catalytic of imidazole synthesis [10]. As well as, the binuclear Co(II), Ni(II), Cu(II) and Zn(II) complexes with polydentate Schiff bases of quinoxaline-2,3-dione have investigated with their antimicrobial activity [11]. As well as Al-Jibouri has investigated the template Zn(II), Cd(II), Hg(II) and Zr(IV) chelates with Schiff bases of quinoxaline-2,3-(1*H*,4*H*)-dione [12]. The extensive studies of biological activity related to metal(II) chelates of benzopyrazine have been keeping by scientists especially DNA cleavage [13]. The synthetic quinoxaline nucleus is the part of a number of antibiotics which are known to inhibit the growth of gram positive bacteria and are also active agents to treat tuberculosis. Recent studies have shown that some quinoxaline derivatives inhibit selectively the platelet derived growth factor (PDGF) receptor kinase [14]. In the present work the Schiff base of benzopyrazine-2,3-dione with thiosemicarbazide was prepared and their metal complexes with 3d transition elements were approved by spectral methods [15]. The present work described the synthesis, characterization and antimicrobial study of chromium(III), manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes with novel Schiff base derived from 6-methyl-quinoxaline-2,3-(1*H*,4*H*)-dione and diethylenetriamine.

2. INSTRUMENTATION

Elemental analyses of the new Schiff base HL and its metal(II) complexes were determined using Carlo-Erba 1106 Elemental Analyzer. The electronic spectra of the prepared complexes were recorded on Carry UV-VIS. spectrometer in the range 200-1000 nm in ethanol and *N,N*-dimethylformamide (DMF) solutions. The ¹H and ¹³C NMR spectra were carried at AL-bait university, Amman, Jordan 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-Mustansiriya university, Baghdad, Iraq. The molar conductance measurements were made on WTW 750 conductivity bridge type CM-82 of cell constant of 1.00 cm⁻¹ in DMSO solutions. The percent of metal contents in the solid complexes were determined by flame atomic absorption on Shimadzu A.A-670 spectrometer at Instrumental analyses laboratory, chemistry department, Al-Mustansiriya university, Baghdad, Iraq.

3. MATERIALS AND METHODS

The hydrated metal chlorides CrCl₃·6H₂O, MnCl₂·4H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O and ZnCl₂·2H₂O were purchased from Sigma-Aldrich company and used without purification. The hydrated oxalic acid, 3,4-diamino-toluene and solvents were supplied from Sigma Aldrich company in 99% purity and used were of Analar grade.

3.1 Synthesis of 6-methyl- 2,3-quinoxaline-dione(A)

The 6-methyl-2,3-quinoxaline-dione was prepared according to the method published in literature [10], Scheme 1.

The characterization data and some physical properties of A compound are shown below:

Color: Pale grey.

Yield: 90%.

M.p.: 320-322°C.

FT-IR (KBr, ν , cm^{-1}): 3200-3270 (NH) (Quinoxalineamido), 1735-1683 (C=O) (Lactam), 1600 (-C=C-) (Ar-C=C), 1330(-C-N) (Pyrazine ring).

MS (EI, m/z (%): 177.05 (M^+ , 100), 176 (M^+ , 70).

UV/Vis (Methanol, λ_{max} , nm, (ϵ): 310 (2.88), 225 (3.49).

Anal.calcd. for $\text{C}_9\text{H}_8\text{N}_2\text{O}_2$: C, 61.36; H, 4.58; N, 15.90. Found: C, 62.67; H, 4.99; N, 13.67%.

3.2 Synthesis of Schiff base L, (3Z)-3,3'-((azanediybis(ethane-2,1-diyl))bis(azanylylidene))bis(6-methyl-3,4-dihydroquinoxalin-2(1H)-one)

0.011 mole of diethylenetriamine (0.162 g) in 20 mL ethanol was added gradually to a 6-methylquinoxaline-2,3(1*H*,4*H*)-dione (A) (3.52 g, 0.02 mole) in 30 mL of hot methanol. The reaction mixture was refluxed for 8 hours and the completing of the reaction was followed by thin layer chromatography (TLC). The pale yellow solid separated up on cooling the mixture at room temperature for 30 minutes, filtered, washed several times with ethanol and dried in oven, Scheme 2.

The characterization data and some physical properties of L compound are shown below:

Color: Pale yellow.

Yield: 78%.

M.p.: 250-252°C.

FT-IR (KBr, ν , cm^{-1}): 3196-3450 (NH) (Quinoxaline amide), 1741-1676 (C=O) (Lactam), 1653-1599 (-C=N-, Imine), 1354 (C-N) (Pyrazine ring), 2973 (C-H, CH_3 , CH_2 -).

^1H NMR (300 MHz, $\text{DMSO}-d_6$, δ , ppm): 1.23 (s, 6H, CH_3), 2.10-3.35 (m, 8H, $-\text{CH}_2-\text{N}^+\text{HN}-\text{CH}_2-$), 7.20-7.60 (m, 6H, Ar-H), 12.20 (s, 2H, NH-pyrazine).

^{13}C NMR (75 MHz, $\text{DMSO}-d_6$, δ , ppm): 161.20 (C, C=O Amide pyrazine), 154.71 (C=N), 139.20 (C, C-NH-), 127.70 (C, C-N- Pyrazine), 31.60-131.50 (C, -C-C-NH), 130.60-129.80 (C, C=N-Ar), 127.70 (C, C=C-Ar), 124.29 (C, C-Ar), 114.82 (Ar-C=C- CH_3), 25.90 (C, CH_2 -NH), 21.1 (C, CH_2 -N=C-), 10.50 (C, CH_3).

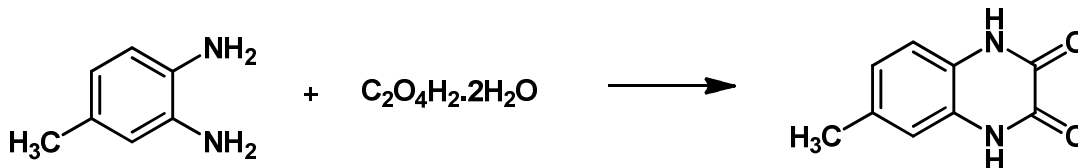
MS (EI, m/z (%): 420.035 (M^{+1} , 5), 405 (M- CH_3 , 9), 370 (M-2OH, -2 CH_3 , 12), 388 (M-2OH, 10).

UV/Vis (methanol, λ_{max} , nm, (ϵ): 250 (2.77), 320 (3.111).

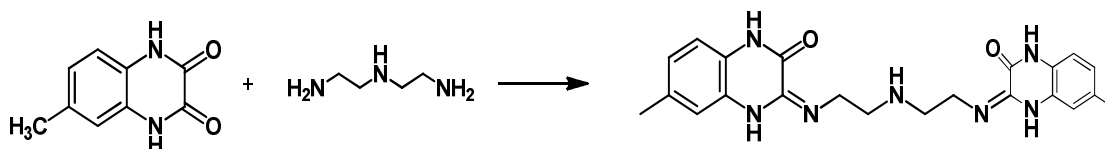
Anal.calcd. for $\text{C}_9\text{H}_8\text{N}_2\text{O}_2$: C, 62.99; H, 6.01; N, 23.37. Found: C, 61.90; H, 5.88; N, 22.28%.

3.3 Synthesis of Metal Complexes

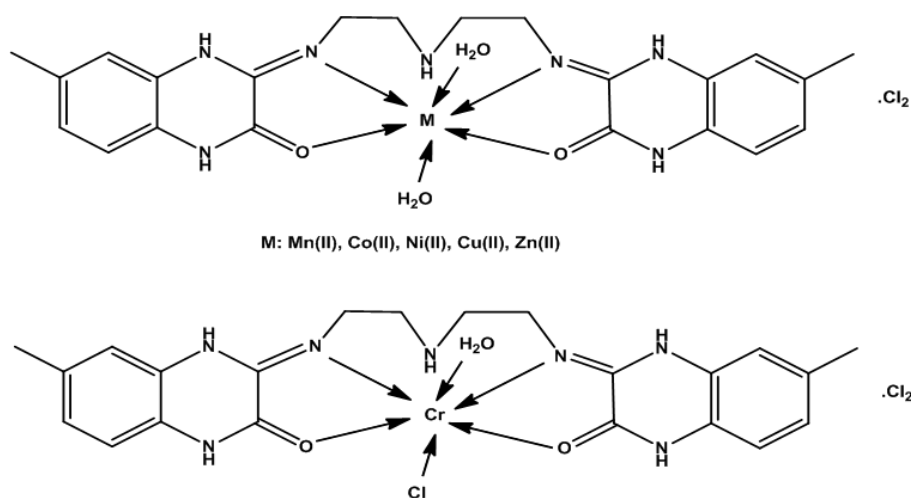
An ethanol solution (20 mL) of 1.0 mmole of $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ was added to a solution of the ligand (0.419 g, 1.0 mmole) in 50 mL of hot methanol then refluxed with constant stirring for 6 hours. The crude dark yellow precipitate was separated by filtration under suction, washed with hot ethanol several times and dried in vacuum, scheme (3).



Scheme 1. Synthesis of A compound



Scheme 2. Synthesis of the Schiff base L



Scheme 3. Octahedral structure of metal complexes of Schiff base L

3.4 Antibacterial Activity

3.4.1 Primary screening

The antibacterial activities of the newly synthesized complexes were evaluated by the Agar Well Diffusion Assay Technique against two bacteria, gram-positive was *Staphylococcus aureus* and gram-negative was *Escherichia Coli*. The tested fungi were *Aspergillus flavus* and *Candida albicans*. The bacterial cultures were maintained on the nutrient agar media by sub-culturing them on fresh slants after every 4-6 weeks and incubating them at the appropriate temperature for 24 h. All stock cultures were stored at 5°C. For the evaluation of antimicrobial activity of the synthesized complexes, a suspension of each test microorganism was prepared. The turbidity of each suspension was adjusted to 0.5 McFarland units by suspending the cultures in sterile distilled water. The size of final inoculums was adjusted to 6×120 CFU/mL. Volume of 20 mL of agar media was poured into each Petri plate and the plates were swabbed with broth cultures of the respective microorganisms and kept for 15 min for adsorption to occur. Using a punch, ~8 mm diameter wells were bored in the seeded agar plates and a 100 μ L volume of each test compound reconstituted in DMSO was added into the wells. DMSO was used as the control for all the test complexes. After holding the plates at room temperature for 2 h to allow diffusion of the compounds into the agar, the plates were incubated at 37°C for 24 hours [16]. The antibacterial activity was determined by measuring the diameter of the inhibition zone. The entire tests were performed

in triplicate and the mean of the diameter of inhibition was calculated. The antimicrobial activities of the complexes were compared against standard drugs.

3.4.2 Antifungal study

Potato dextrose medium (PDA) was prepared in a flask and sterilized. To check the growth of bacterial culture in the medium, the requisite quantity of the standard antibiotic (*Ketoconazole*) was added to obtain the desired final concentration of 100 μ g/mL of the medium. Test samples were prepared in different concentrations (10 and 50 μ g/mL) in dimethyl sulphoxide and 100 μ L of each sample was spread on the PDA media contained in sterilized Petri plates. Mycelial discs taken from the standard cultures of fungi (*Aspergillus flavus* and *Candida albicans*) were grown on the PDA medium for 2-4 days. These cultures were used for the aseptic inoculation in the sterilized Petri dish. Standard cultures inoculated at $25 \pm 1^\circ\text{C}$ were also used as the control. The efficacy of each sample was determined by measuring the radial mycelia growth. The radial growth of the colony was measured in two directions at right angle to each other and the average of two replicates was recorded in each case. The data are expressed as percent inhibition over the control obtained from the size of colonies. The percent inhibition (ϕ) was calculated using the formula:

$$\phi = 100 \frac{C - T}{C} \quad (1)$$

Where C is the diameter of fungus colony in the control plate after incubation for 48 hours and T is the diameter of the fungus colony in the tested plate after the same incubation period [13,16].

4. 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.

4.1 GC-Mass Spectra

Fig. 1 shows the absorption that ascribes molecular weight of A compound with $M^+ = 177$ of 100% intensity due to formation of base peak of $C_9H_8N_2O_2$ formula. As well as the peaks at 176, 161 and 131 may be assigned to fragments of M-H, M-CH₃, M-CH₃, 2OH respectively [17].

Fig. 2 shows the mass spectra of the Schiff base L. The molecular ion peak at 420 indicate the molecular weight of $C_{22}H_{25}N_7O_2$ formula with effect of deuterium and carbon isotopes. The fragments at 405 (M-CH₃), 388 (M-2OH) and 370 (M-2OH, 2CH₃) [17,18] may support the proposed structure of the Schiff base due to presence of fragments of (M-OH, M-2OH, M-CH₃ and M-NH-CH₂-CH₂-) peaks as shown in scheme (4).

4.2 Molar Conductivity Measurements

The molar conductance values of the complexes measured at room temperature in DMF solution with 0.001 M concentration fall in the range 74-84 $\text{ohm}^{-1} \cdot \text{cm}^2/\text{mol}$ indicating the electrolytic nature of the complexes [19], due to presence of chloride ions as a counter ions thus supports the $[M(L)(H_2O)_2]Cl_2$ formula. The nature of complexes solutions are electrolytic in 1:2 ratios due to presence of chloride ions in the outer sphere of complexes and then confirm the neutral donating N₂O₂ of the Schiff base towards the empty orbital's of the metal ions, Table 4.

4.3 IR Spectra

The IR spectra of metal complexes are presented in (Table 2). The appearance of strong absorption band in the region 1741-1676 cm^{-1} corresponds to $\nu C=O$ stretching frequency that may be attributed to carbonyl at position 3 of pyrazine ring [18,20]. A broad absorption

recorded in the region 3196-3450 cm^{-1} may be ascribed to hydrogen bonded of $\nu N-H$ of amide -HN-C=O and HN-CH₂- [15, 20-23]. As well as, the shoulder band at 1653 cm^{-1} could be attributed to the -C=N- bond of Schiff base. Up on comparison the FTIR spectra of all metal complexes, the lowering in the values of wave numbers of $\nu(C=N)$ and $\nu(C=O)$ may be explained on the basis of drift of lone pair density of imine nitrogen and carbonyl oxygen towards metal atoms [21]. The broad absorptions in the spectra of all complexes in the regions 3443-3640 cm^{-1} assigning to $\nu(O-H)$ of coordinated water molecules in the inner sphere of metal complexes. The bands present in the range ~1299-1356 cm^{-1} are assigned to $\nu(C-N)$ vibration. Furthermore, the weak to medium bands of M-O and M-N are shown in the 422-528 and 461-593 cm^{-1} [15,20]. The chromium (III) complex exhibits very weak bands in the far-infrared region 277-370 cm^{-1} confirming Cr-Cl bond [20,21]. Furthermore the vibrational modes of N-H of pyrazine ring have increases in the metal complexes in the regions 2930-2850 cm^{-1} due to cleavage of hydrogen bonding [14].

4.4 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 233 and 350 nm, (Table 3) which are assigned to electronic transitions for chromophores -C=N and C=C, respectively [13,24]. The green solution of Cr(III) complex in DMF shows two weak absorptions at 430 and 290 nm assigning to ${}^4A_2g(F) \rightarrow {}^4T_2g$ and ${}^4A_2g(F) \rightarrow {}^4T_1g(P)$, respectively [25]. The disappearance of third transition in the visible region may be attributed to the overlapping by the high intensity MLCT transition with it, thus confirms the octahedral environment around chromium (III) ion [22]. The electronic transitions from the 6A_1 ground term of Mn(II) to higher energy terms are spin-forbidden [23]. However, the band appearing in the region 430-350 nm in the electronic spectrum of Mn(II) complex is assigned to ${}^6A_1g \rightarrow {}^4T_1g(G)$ and is consistent with octahedral geometry. Furthermore, the olive solution of cobalt(II) complex, the peaks at 650 and 360 nm are assigned to the ${}^4T_1g \rightarrow {}^4T_2g(F)$ and ${}^4T_1g \rightarrow {}^4T_1g(P)$, respectively, which is a typical of octahedral cobalt(II) complexes. The nickel(II) complex solution in DMF exhibits two weak bands in the region 485 nm and 330 nm that are related to ${}^3A_2g \rightarrow {}^3T_2g(F)$ and ${}^3A_2g \rightarrow {}^3T_1g(F)$ transitions respectively [23,24]. The

green solution of copper(II) complex in DMF shows two distinct peaks at 404 and 390 nm which are remarkably assigned to ${}^2A_{1g} \rightarrow {}^2B_{1g}$ and ${}^2A_{1g} \rightarrow {}^2B_{2g}$, this splitting in the d-d transitions of copper(II) complex confirms the elongated distortion on z-axis [25]. The magnetic moments of Cr(III) complex is 3.60 BM is consistent with expected high spin of d^3

configuration[24]. However, the manganese(II), cobalt(II), nickel(II) and copper(II) complexes recorded expected values of magnetic moments at 5.62, 3.97, 3.02 and 1.50 BM respectively [26-27]. The communication of UV-visible spectra of the prepared complexes with their obtained magnetic properties helped us to adopt the octahedral geometry.

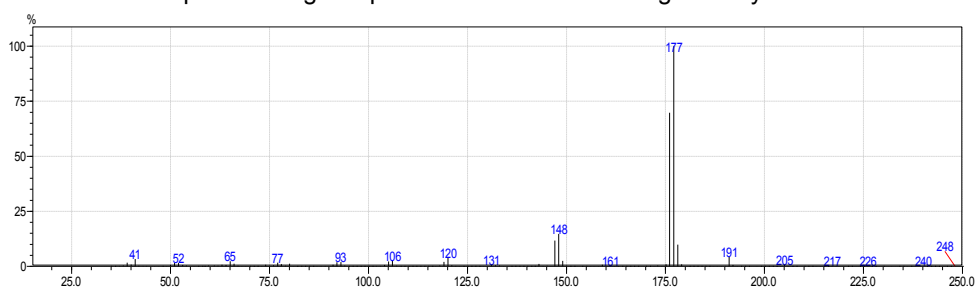


Fig. 1. Mass spectrum of A compound

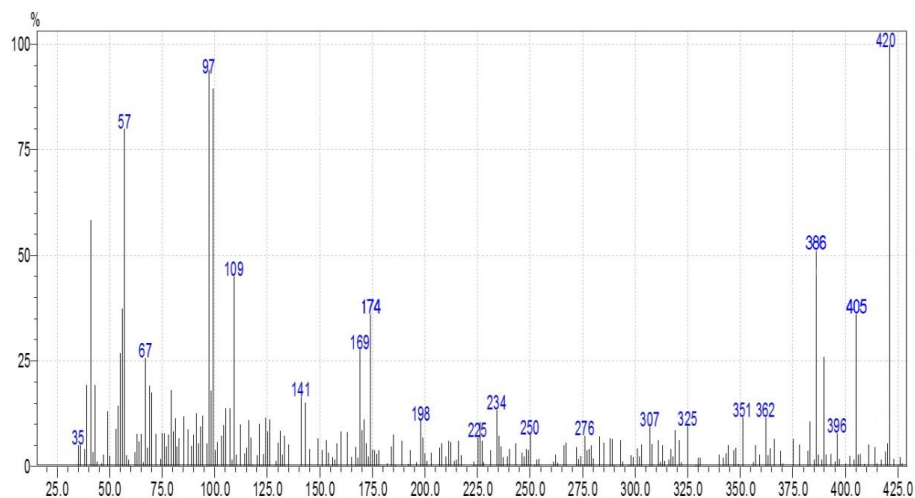
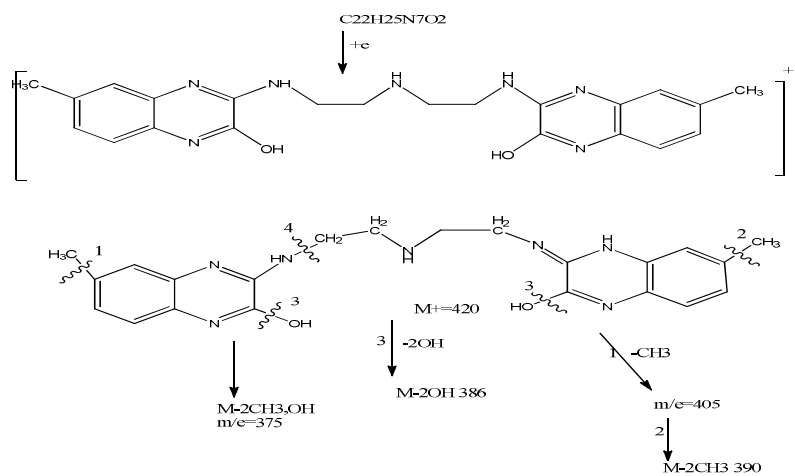


Fig. 2. Mass spectrum of Schiff base L



Scheme 4. Proposed mechanism of L fragmentations via mass spectra.

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

Compound	Color	M.p. (°C) *	Molecular formula	C%	H%	N%	M%
				Calcd. (found)	Calcd. (found)	Calcd. (found)	Calcd. (found)
[CrL(H ₂ O)Cl]Cl ₂	Pale green	309 ^D	595.52	44.33	4.54	16.45	8.75
			CrC ₂₂ H ₂₇ Cl ₃ N ₇ O ₃	(44.00)	(3.92)	(16.12)	(8.26)
[MnL(H ₂ O) ₂]Cl ₂	Pink	326 ^D	580.68	45.51	5.10	16.87	9.47
			C ₂₂ H ₂₉ Cl ₂ N ₇ O ₄ Mn	(44.80)	(4.62)	(16.98)	(8.87)
[CoL(H ₂ O) ₂]Cl ₂	Olive	317 ^D	582.89	45.29	4.97	17.01	9.88
			C ₂₂ H ₂₉ Cl ₂ N ₇ O ₄ Co	(44.72)	(4.11)	(17.12)	(9.00)
[NiL(H ₂ O) ₂]Cl ₂	Green	322 ^D	583.09	45.16	5.14	16.75	10.03
			C ₂₂ H ₂₉ Cl ₂ N ₇ O ₄ Ni	(44.81)	(4.65)	(17.53)	(9.56)
[CuL(H ₂ O) ₂]Cl ₂	Dark green	370 ^D	589.04	44.83	4.63	16.64	10.77
			C ₂₂ H ₂₉ Cl ₂ N ₇ O ₄ Cu	(43.90)	(3.90)	(17.09)	(9.84)
[ZnL(H ₂ O) ₂]Cl ₂	Off white	360 ^D	590.20	45.15	4.88	16.72	11.06
			C ₂₂ H ₂₉ Cl ₂ N ₇ O ₄ Zn	(44.84)	(4.00)	(17.02)	(10.86)

*D: Decomposed

Table 2. FT-IR absorptions of the quinoxalin-2,3-dione and its template metal complexes in cm⁻¹.*

Complex	vNH ₂	vC=N	vC=O	vAr-H	vC-N	vM-N	vM-O	Other bands
L	3196-3450(br.)	1653-1599 (s)	1741-1676 (s)	3050, 2962 (m)	1354(s)	-	-	707-750 ^a
[CrL(H ₂ O)Cl]Cl ₂	3640 (br.)	1588-1570 (s)	1683-1664 (s)	3060 (w) 2870 (m)	1325 (m)	533 (w)	466(w)	780-810 (w) ^a , 277-370 ^b
[MnL(H ₂ O) ₂]Cl ₂	3600 (br.)	1590 (s)	1699 (s)	3080	1299 (m)	550 (m)	452 (m)	766 (m)
[CoL(H ₂ O) ₂]Cl ₂	3443 (br)	1624-1591 (s)	1691 (s)	3060 (w), 2870 (m)	1326 (s)	461 (m)	429(w)	727 (w)
[NiL(H ₂ O) ₂]Cl ₂	3462 (br)	1608-1527(s.)	1694(s)	3010 (w)	1350(m)	594 (w)	528 (m)	770-790 (w) ^a
[CuL(H ₂ O) ₂]Cl ₂	3425 (br)	1581(s)	1691(s.)	3064(w)	1356 (s)	593 (m)	491 (m)	755-810(w.) ^a
[ZnL(H ₂ O) ₂]Cl ₂	3562-3471 (br)	1580(s)	1691(s)	3090(w)	1340 (m)	501 (m)	422 (w)	722 (w) ^a

* s: strong, m: medium, br: broad, w: weak, a: rocking of methylene -CH₂ moiety and b: far IR of Cr-Cl bond

4.5 ^1H and ^{13}C NMR Study

The proton and carbon-13 nuclear magnetic spectra for L ligand in DMSO- d_6 solution were performed by using tetramethylsilane as internal reference. Fig. 3 shows different peaks at 12.20, 7.20-7.60, 3.35, 2.10-3.35 and 1.30 ppm assigning to resonance of HN-C=O(2H), Ar-H(6H), -CH₂-CH₂-NH(9H) and -CH₃(6H, H₃C-Ar) respectively [22]. The inexact values of area under peaks for some peaks may be reasoned for exchange of acidic HN-C=N- or HN-C=O with water molecules in DMSO solvent [25]. As well as, the Fig. 4 exhibits the absorptions of ^{13}C NMR spectra of L in DMSO- d_6 solution where the eleven peaks entirely investigates the presence of 161.20(C, C=O Amide pyrazine), 154.71 (C, =N Imine), 139.20(C, C-NH-), 127.70 (C, C-N-Pyrazine), 31.60-131.50 (C, -C-C-NH), 130.60-129.80 (C, C=N-Ar), 127.70 (C, C=C-Ar), 124.29(C, C-Ar), 114.82(Ar-C=C-CH₃), 25.90(C, CH₂-NH), 21.1 (C, CH₂-N=C-), 10.50(C, CH₃-). The data of carbon-13 NMR reveals the expected numbers of carbon atoms in the structure of L Schiff base, then agree well with ^1H NMR, FT-IR, CHN and GC-Mass spectra data [13,17].

4.6 Antimicrobial Study

In this study, all the chemically synthesized complexes were evaluated against gram-positive (*Staphylococcus aureus*) and gram-negative bacteria (*E. coli*). The MIC values of the synthetic

complexes were determined by the method given by Andrews [26]. Standard antibiotic, *Ciproflaxine* was used as standard drug in order to make. The solution of free ligand in DMSO (20 $\mu\text{g}/\text{ml}$.) shows no activity towards the tested *fungi*, and shows low inhibition zone in the range 10-16 mm against *Staphylococcus aureus* and *E. Coli* bacteria respectively. The nickel(II) and zinc(II) complexes exhibited antifungal activity in their solutions in the range 17-20 and 20-22 mm against *Aspergillus flavus* and *Candida albicans* respectively, this may be interoperated on the lipophilicity of nickel(II) and zinc(II) complexes [27]. However, the rest complexes do not show any antifungal activity toward the two studied *fungi*. The cobalt(II), copper and zinc(II) complexes have the maximum values of inhibition zone in the regions 17-19 and 20-22 mm against *Staphylococcus aureus* and *E. coli* respectively. This result may be related to possibility of these complexes to pass the bacteria wall via hydrogen bonding causing the damage in synthesis of the proteins that are necessary for growth of bacteria [28]. Furthermore, the Fig. 5 shows the relative inhibition zones of the tested compounds in 20 g/ml. concentration toward *Staphylococcus a. and E. coli* bacteria. The height in columns of Cu(II) and Zn(II) complexes revealed the high lipophilicity of such complexes that might facilitate their passing across the peptidoglycans layers of bacteria wall [12,29-30].

Table 3. The electronic spectra ν (cm⁻¹) and molar conductance of the prepared complexes

Complex	UV-visible λ , nm	$\nu(\text{cm}^{-1})$	Λ_m , S mol ⁻¹ cm ² *	μ , B.M.	Geometry
L	320	31250	12	-	-
	250	40000			
[CrL(H ₂ O)Cl]Cl	430	23255	81	3.60	Octahedral
	290	34482			
[MnL(H ₂ O) ₂]Cl ₂	410	24390	80	5.62	Octahedral
	350	28571			
[CoL(H ₂ O) ₂]Cl ₂	650	15384	79	3.97	Octahedral
	360	27777			
[NiL(H ₂ O) ₂]Cl ₂	485	20618	82	3.02	Octahedral
	330	30303			
[CuL(H ₂ O) ₂]Cl ₂	404	24752	84	1.50	Octahedral
	390	25641			
[ZnL(H ₂ O) ₂]Cl ₂	370	27027	74	Diamagnetic	Octahedral
	210	46619			

* Λ_m = molar conductances were measured in DMSO solutions

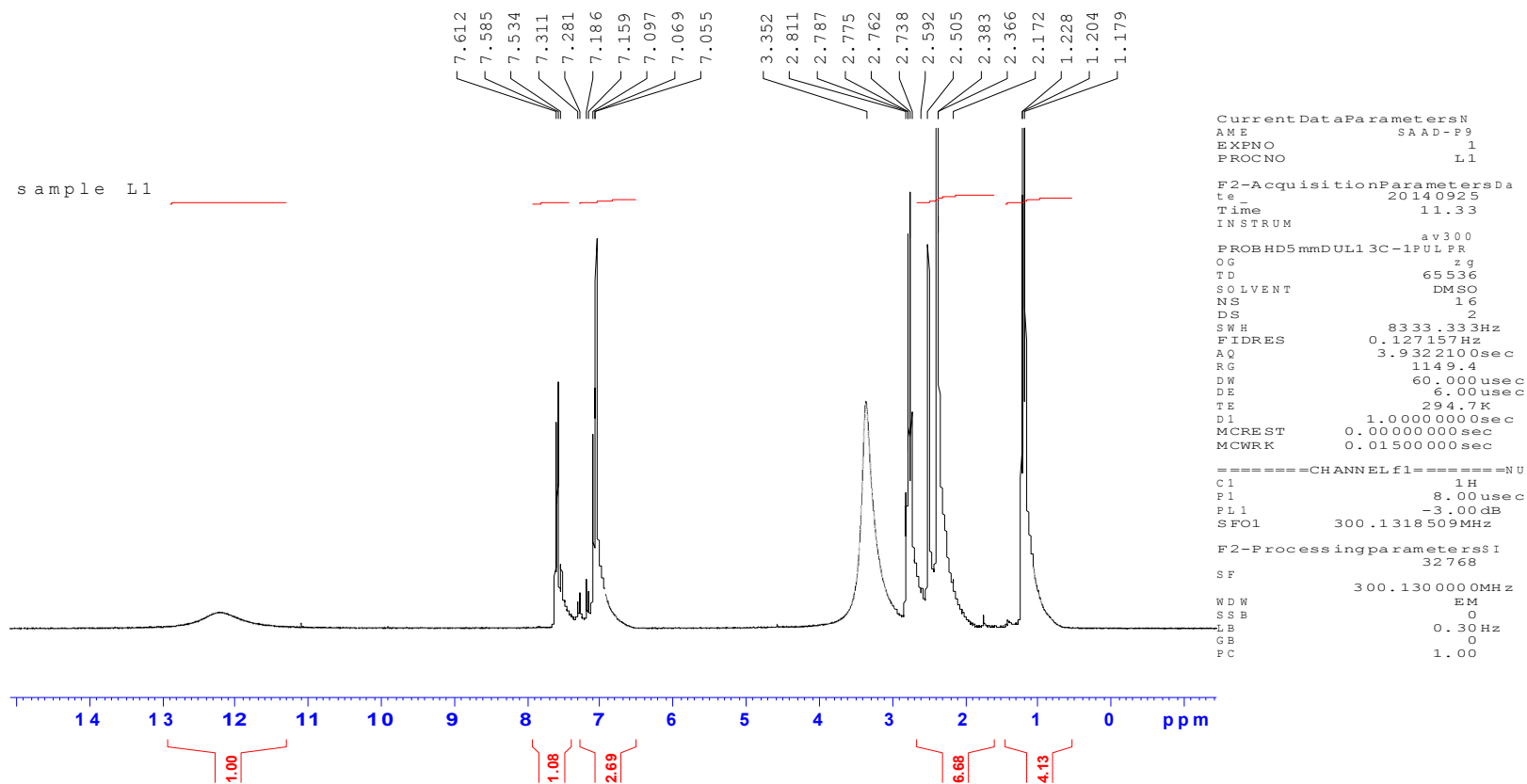


Fig. 3. ¹H NMR spectra of L Schiff base in DMSO-d₆ solution.

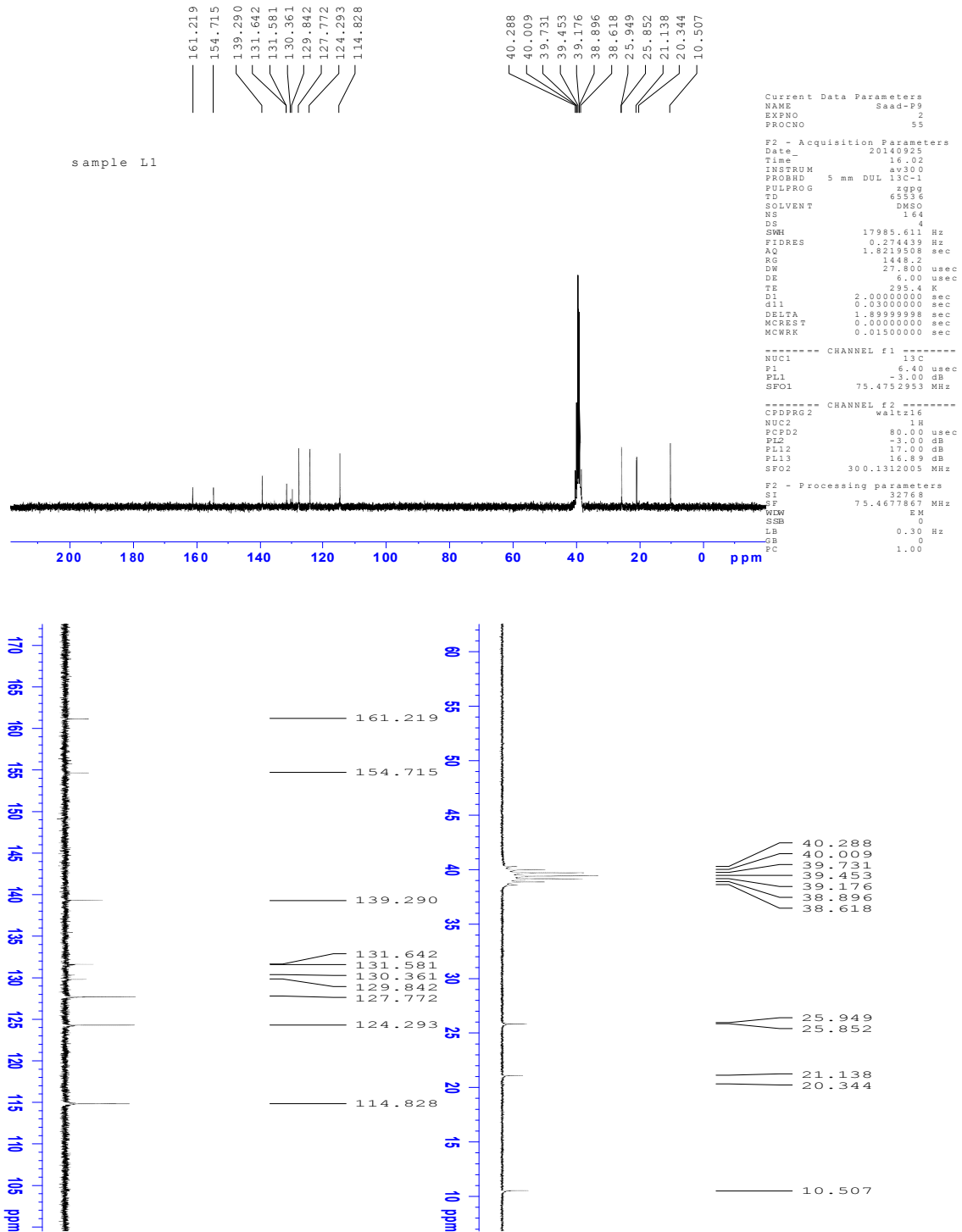


Fig. 4. ¹³C NMR spectra of Schiff base (L) in DMSO-d₆ solution

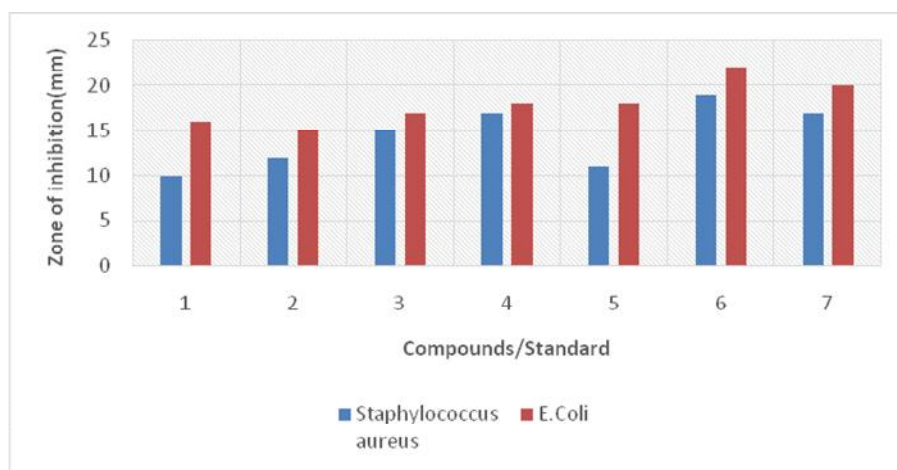


Fig. 5. Inhibition of growth bacteria by Schiff base L and its metal complexes
1=L, 2=Cr(III), 3=Mn, 4=Co, 5=Ni, 6=Cu and 7=Zn(II) complexes in 20 µg/ml. solution in relative to control DMSO=0 mm

5. CONCLUSION

The chromium(III), manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes with tetra dentate Schiff base of the N_2O_2 donor system were prepared and fully characterized with the help of GC-Mass, NMR, FT-IR, UV-Visible spectra and elemental analyses. The data of molar conductivity in dimethyl sulphoxide(DMSO) solutions investigate the electrolytic behavior of all metal complexes in 1:2 ratios suggesting the presence of chloride ions in the outer sphere of complex structures. The downshift in the carbonyl of pyrazine moiety and terminal imine in the IR spectra for all the metal complexes suggest the participation of oxygen and nitrogen atoms of such functional groups in coordination with the central metal ions. The octahedral geometry with $[ML(H_2O)_2]Cl_2$, (M:Mn(II), Co(II), Ni(II), Cu(II), Zn(II) ions) and $[CrL(H_2O)Cl]Cl_2$ formula were proposed according to the data obtained from elemental, spectral and magnetic susceptibility analyses.. As well as the antimicrobial activity of the prepared complexes were screened against two bacteria and two fungal and the obtained inhibition zones data investigated the possibility of their applications in treatment of diseases reasoned by these micro-organisms.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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