

**Complex formation of Cr³⁺, Mn²⁺, Ni²⁺ and Cu²⁺ ions using 1-((2E,3E)-3-(hydroxyimino)butan-2-ylidene)urea**

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Abstract Metal complexes of Cr(III), Mn(II), Ni(II), and Cu(II) of the Schiff base derived from 1-((2E,3E)-3-(hydroxyimino)butan-2-ylidene)urea have been prepared and characterized on the basis of physical characteristics, micro-analytical data(CHN), molar conductivity, magnetic moment measurements, Mass spectra, ¹HNMR, IR and UV-Vis spectrum data. The elemental analysis data showed the isolated complexes are in 1:1 [M:L] ratio. The obtained molar conductance values revealed the complexes are electrolyte in nature. The results of magnetic moment measurements showed that, the complexes of Cr(III), Mn(II), Ni(II), and Cu(II) have unpaired electrons. The infrared spectral data displayed the main coordination sites of 1-((2E,3E)-3-(hydroxyimino)butan-2-ylidene)urea towards Cr(III), Mn(II), Ni(II) and Cu(II) ions. The electronic spectral results of the Schiff base ligand and its complexes suggest that, the Cr(III), Ni(II), Mn(II) and Cu(II) complexes have octahedral structure.

Keywords: Schiff base, Complexes, 1-((2E,3E)-3-(hydroxyimino)butan-2-ylidene)urea, Diacetylmonoxime, Urea.

تحضير معقدات Cr(III), Mn(II), Ni(II), Cu(II) مع مرتبط 1-((2E,3E))-3-(هيدروكسي**إمينو) بيوتان-2-إيل دين) يوريا**

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المخلص تم تحضير مرتبط قاعدة شيف من تكثيف داي اسيتايل مونوكساييم مع اليوريا وتمت دراسته بواسطة التقنيات مثل التحليل العنصري والأشعة فوق بنفسجية والأشعة تحت الحمراء والرنين النووي المغناطيسي ومطياف الكتلة، وحضر منها مترابكات لقواعد شيف بتكثيفها مع أيونات Cr(III)، Mn(II)، Ni(II)، Cu(II). وتم تحديد الاشكال الفراغية للمترابكات بواسطة الطرق الطيفية والمغناطيسية، وإقترحت جميع المترابكات ثمانية السطوح.

الكلمات المفتاحية: قاعدة شيف، معقدات، 1-((2E,3E))-3-(هيدروكسي إمينو)بيوتان-2-إيل دين)يوريا، داي اسيتايل مونوكساييم، يوريا.

Introduction:

Schiff bases are the compounds that contain azomethine group (-HC=N-). and were first reported by Hugo Schiff in 1864^[1]. These compounds are also known as anils, imines or azomethines. It is usually formed by condensation of an aldehyde or ketone with a primary amine^[2]. Schiff bases have been studied extensively due to their different properties such as, easy to synthesize, exhibit excellent characterizations and structural similarity with biological substances, exhibit a broad range of biological activities, including antifungal, antibacterial, anti-malarial, anti-inflammatory, antiviral, anti-allergic and antitumor properties^[3-5]. Metal complexes of Schiff base oxime ligands are widely known. It has been reported that some oxime metal complexes are semiconducting and others bioactive^[6,7]. Tschugaeff was the first one to identify the bidentate nature of vicinal dioximes in his study of the reaction between Ni(II) salts and dimethylglyoxime (DMGH₂), where square planar structures occur^[8]. The oxime ligands can exhibit three coordination modes: coordination through N, coordination through O after deprotonation and

coordination through N after deprotonation^[9]. Schiff bases and their metal complexes play an important role in the development of coordination chemistry, resulting in an enormous number of publications and has been studied extensively and have gained much importance recently due to their chelating ability, antimicrobial, anti-inflammatory activities and anticorrosion properties^[10-13]. Schiff bases used in the fields of medicine, industry, and organic synthesis, inorganic and analytical chemistry, they used in optical and electrochemical sensors, transition metal complexes of Schiff bases are used in dyes industry for food, leathers, wood etc^[13-15].

Experimental

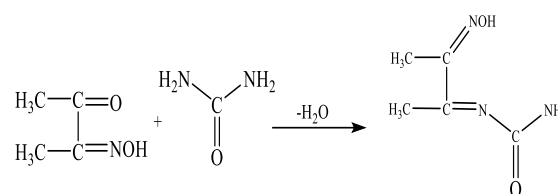
Materials: All chemicals used in this investigation were reagent of BDH or Aldrich including, diacetylmonoxime, urea, EtOH, DMF, ether.

Synthesis of Schiff base: The Schiff base 1-((2E,3E)-3-(hydroxyimino)butan-2-ylidene)urea was synthesized by refluxing 50ml ethanolic solution of (1.01g, 0.01mmol) of diacetylmonoxime with 50ml ethanolic solution of

urea (0.60 g, 0.01mmol) for three hours. The obtained product was allowed to cool at room temperature, filtered and washed with ether and recrystallized from ethanol, and kept in a desiccator over silica gel to get white precipitate (m.p. 145 °C; yield 70%).

Synthesis of Complexes: The Schiff base complexes under investigation were synthesized by adding 1-((2E,3E)-3-(hydroxyimino)butan-2-ylidene)urea (1.43g; 0.01mmole) in 30ml absolute EtOH to 0.01 mmole of the salts of CrCl₃.6H₂O (2.66 g), MnCl₂.4H₂O (1.97 g), NiCl₂.6H₂O (2.37 g) and CuCl₂.2H₂O (1.70 g) in the same amount of the absolute EtOH. The reaction mixtures were heated under reflux for 3 hours. The complexes were filtered off, recrystallized from the suitable solvent and finally kept in a desiccator over silica gel.

RESULTS AND DISCUSSION: The reaction between the diacetylmonoxime and urea yields only one product which is as follows:



Microanalysis and molar conductance measurements: The elemental analysis data and some physical properties of the Schiff base and its complexes are summarized in Table 1 where the results confirm the proposed composition. The synthesized complexes were formed in 1:1 (M:L) ratio. The obtained molar conductance values of the complexes in DMF solvent lie in the range of 93.8 - 150.4 ohm⁻¹ cm² mol⁻¹ indicating their complexes of Cr³⁺, Mn²⁺, Ni²⁺, Cu²⁺ are electrolytic^[16].

Table (1): Elemental analysis and some physical properties of the Schiff base(L) and its complexes

Compound	Colour	M. wt.	M.P. °C	%Calc.(Found)			Λ (μs)	BM
				C%	H%	N%		
L C ₅ H ₉ N ₃ O ₂	White	143.14	145	41.95(41.53)	6.34(5.96)	23.87(22.90)	-	-
[CrL(H ₂ O) ₂ Cl]Cl ₂ .H ₂ O	Black-green	355.54	>250	16.89(16.32)	4.25(4.07)	11.82(11.34)	106.6	3.84
[MnL(H ₂ O) ₃]Cl ₂ .H ₂ O	Grey	341.05	245	17.61(17.25)	5.02(4.78)	12.32(12.07)	95.4	5.65
[NiL(H ₂ O) ₃]Cl ₂ .2H ₂ O	Brown	362.82	130	16.55(16.11)	5.28(4.71)	11.58(10.99)	150.4	2.73
[CuL(H ₂ O) ₃]Cl ₂	Light green	331.64	>250	18.11(17.75)	4.56(4.04)	12.67(12.11)	93.8	1.79

Mass spectrum of the Schiff base: The mass spectral data of the Schiff base ligand shown in figure 1. Mass spectrum of the ligand showed molecular ion peaks, which were in good agreement with the expected values^[17]. The mass spectrum of ligand gives a peak at 143m/z.

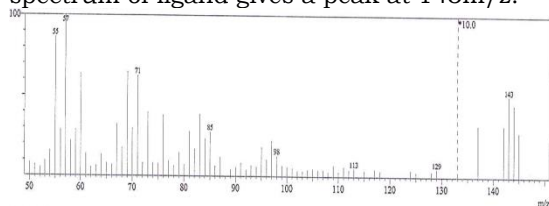


Fig.(1): Mass spectrum of Schiff base

Proton nuclear magnetic resonance spectrum of ligand: The ¹H-NMR spectrum recorded in d⁶ DMSO solvent on a Jeol-90 Fourier Transform (200 MHz). 1-((2E,3E)-3-(hydroxyimino)butan-2-ylidene)urea shows three singlet signals figure 2 at 2.495, 3.383, 5.454, and 11.344 ppm, downfield of TMS, attributed to the protons of CH₃, CH₃, NH₂, and OH respectively^[18,19].

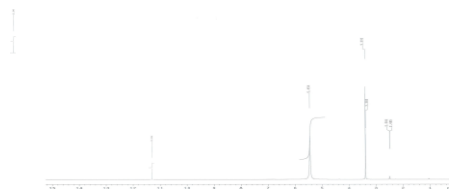


Fig.(2): ¹H-NMR spectrum of Schiff base

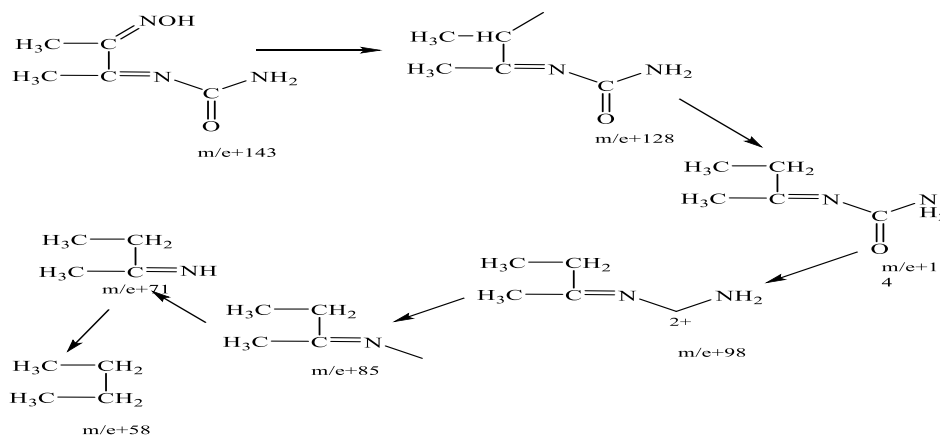
Electronic spectra
The electronic absorption spectra of the complexes under investigation were recorded using in Nujol mull on a Unicam model UV2 spectrophotometer (Figs. 3-7). The Schiff base ligand spectrum exhibits two absorption bands at 40733 cm⁻¹, 39138 cm⁻¹, attributed to π→π* and n→π* transitions respectively^[20]. The spectrum of Cr³⁺ exhibits absorptions at 41810 cm⁻¹ and 38610 cm⁻¹ attributed to π→π* and n→π* transition, and show two bands at 23539 cm⁻¹ and at 17094 cm⁻¹ which is due to ⁴A_{2g}→⁴T_{1g}(F) and ⁴A_{2g}→⁴T_{2g}(F) (d-d) transitions for an octahedral geometry^[21]. The electronic absorption spectrum of Mn²⁺ complex show two bands at 48899 cm⁻¹, 39062 cm⁻¹ attributed to π→π* and n→π* transitions, and show a band at 15974 cm⁻¹, which is due to ⁶A_{1g}→⁴T_{1g}(P) transition for octahedral geometry^[22].

The electronic absorption spectrum of Ni²⁺ show a band at 38986 cm⁻¹ attributed to $\pi \rightarrow \pi^*$ transitions and two bands at 19607 cm⁻¹ and at 16260 cm⁻¹ due to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (d-d) transitions which suggest an octahedral geometry^[23]. Cu(II) complex spectrum exhibits two absorption bands at 47505 cm⁻¹ and 39138 cm⁻¹ attributed $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$

transitions, and show bands at 24390 cm⁻¹ and at 16129 cm⁻¹ mainly due to ${}^2E_g \rightarrow {}^2T_{2g}$ transition suggesting octahedral geometry^[24].

Table (2): IR and electronic spectral data of the Schiff base and its complexes

Ligand/ Complexes	IR (cm ⁻¹)						UV - Vis λ_{\max} (cm ⁻¹)
	ν OH	ν NH ₂	ν C=O	ν C=N	ν M-N	ν M-O	
L (C ₅ H ₉ N ₃ O ₂)	3443	3348	1675	1619	-	-	39138,40733
[CrL(H ₂ O) ₂ Cl]Cl ₂ .H ₂ O	3420	3328	-	1622	623	582	41810,38610, 23539,17094
[MnL(H ₂ O) ₃]Cl ₂ .H ₂ O	3476	3416	-	1630	595	531	48899,39062 15974
[NiL(H ₂ O) ₃]Cl ₂ .2H ₂ O	3474	3412	-	1624	623	585	38986,19607 16260
[CuL(H ₂ O) ₃]Cl ₂	3413	3326	-	1615	602	538	47505,39138 24390,16129



Scheme 1: Mass fragmentation of the Schiff base

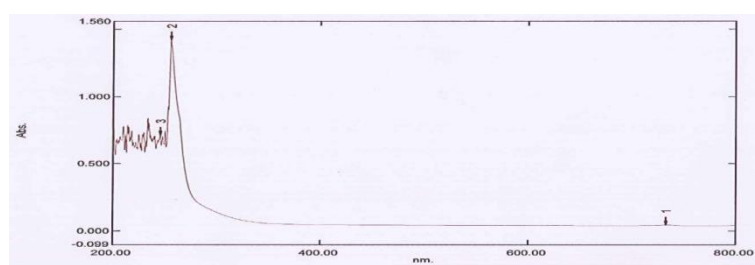


Fig.(3): UV spectrum of the free ligand L

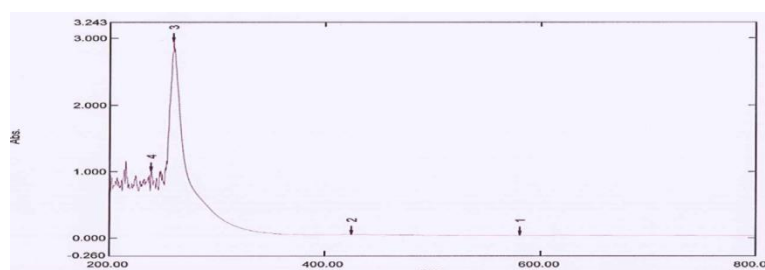


Fig.(4): Electronic spectrum of Cr(III) complex

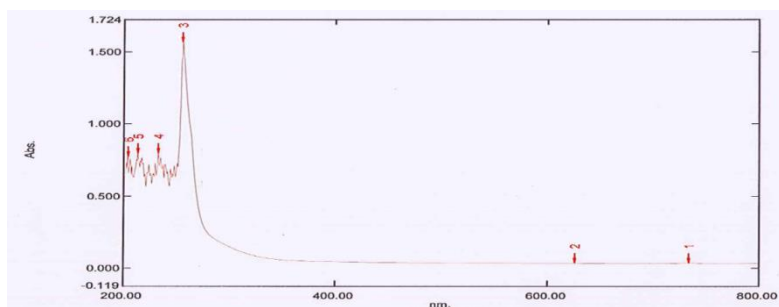


Fig.(5): Electronic spectrum of Mn(II) complex

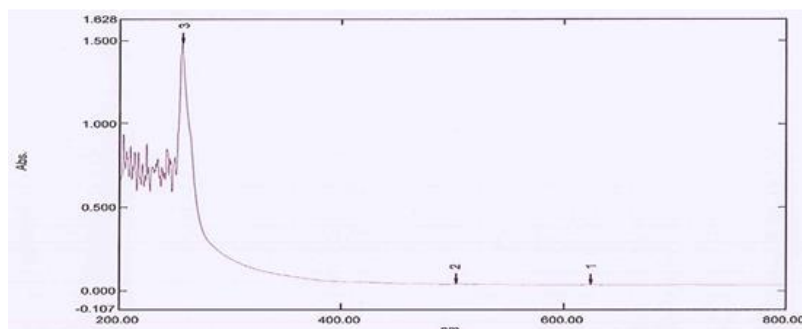


Fig.(6): Electronic spectrum of Ni(II) complex

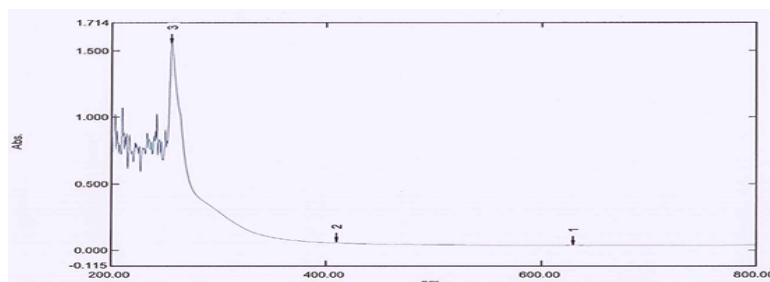


Fig.(7): Electronic spectrum

of Cu(II) complex

Magnetic susceptibility measurements: The magnetic moment value of Cr(III) complex is 3.84 BM which suggests an octahedral geometry^[25]. The magnetic moment of Mn(II) complex is 5.65 BM which suggests the high spin six-coordinated octahedral arrangement of the ligand around the metal ion^[26]. The Ni(II) complex has magnetic moment value of 2.73 BM indicating a spin-free octahedral configuration^[27]. The magnetic moment value of Cu(II) complex is 1.79 BM which suggests a distorted octahedral geometry around the metal ion^[28].

IR spectra: The IR spectra of the ligand and its complexes with Cr^{3+} , Mn^{2+} , Ni^{2+} and Cu^{2+} were recorded in the solid state in the range 400-4000 cm^{-1} using KBr disc on a Perkin-Elmer 1430 ratio recording infrared spectrophotometer (Figs. 8-12). The IR spectral data are present in Table 2. A verification of the structures of the metal complexes can be easily achieved by comparing the IR spectrum of the free ligand with those of complexes^[29]. When a Schiff base ligand is

coordinated to metal ion at least one additional atom is introduced into the ligand vibrating system. It is thus expected that bond lengths, angles and interacting forces within the ligand would be altered even at least slightly. The IR spectrum of the Schiff base display three bands at 3443 cm^{-1} attributed to νOH group, and a band at 1675 cm^{-1} attributed to $C=O$, and show a band at 1619 cm^{-1} attributed to $C=N$ group^[30-32]. The shifting of $\nu(C=N)$ group vibration in all complexes indicates the participation of nitrogen atom during chelates^[33,34]. Complexes IR spectrum display broad bands in the range of 3413 – 3476 cm^{-1} which is attributed to stretching vibration νOH of coordinated water molecules banding with complexes formation^[35]. The disappearance of the $C=O$ group indicates its involvement in coordination with the metal ions and the bands in the range of 3221-3016 cm^{-1} indicates that the NH_2 group is not participating in coordination^[36]. New bands observed at 538-585 cm^{-1} and at 595-623 cm^{-1} which could be attributed $\nu(M-O)$ and $\nu(M-N)$ vibrations respectively^[37,38].

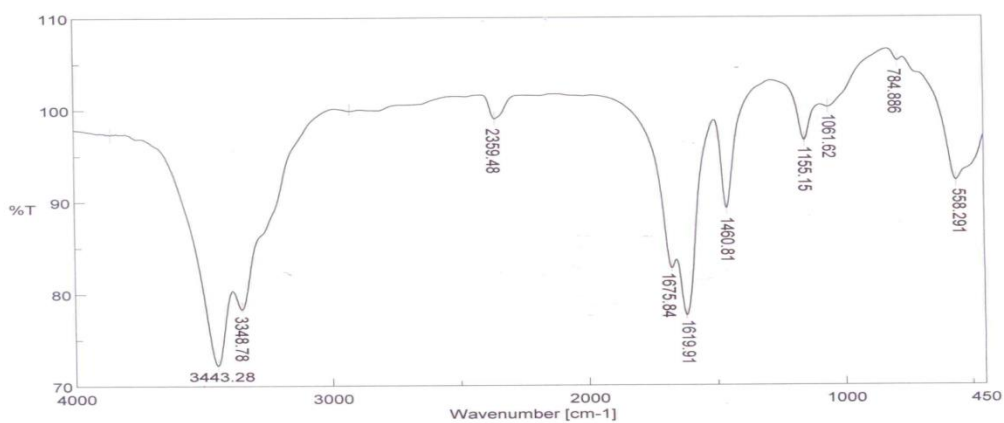


Fig.(8): IR spectrum of the Schiff base

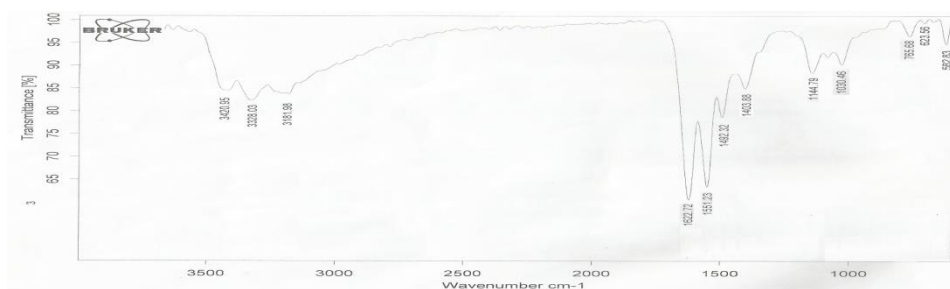


Fig.(9): IR spectrum of Cr(III) complex

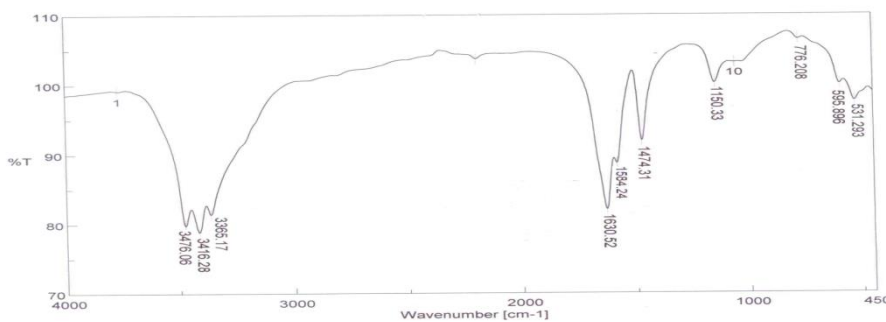


Fig.(10): IR spectrum of Mn(II) complex

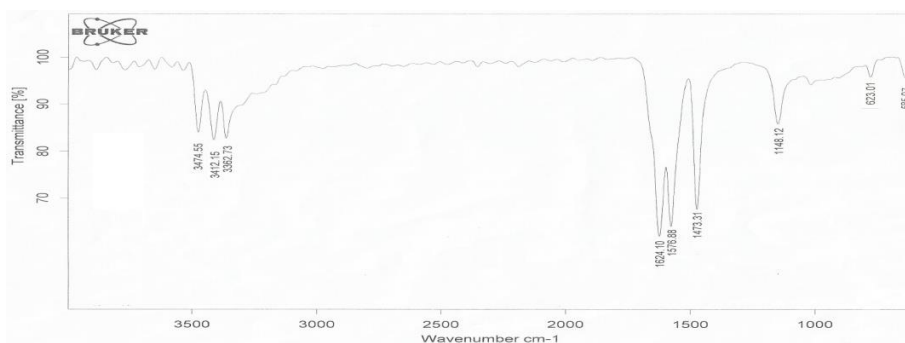


Fig.(11): IR spectrum of Ni(II) complex

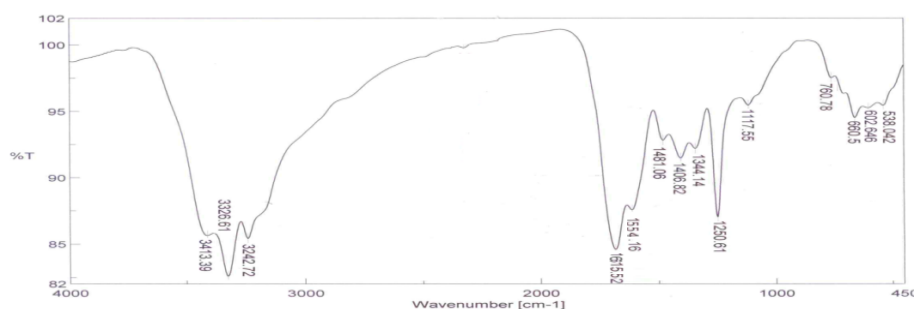
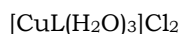
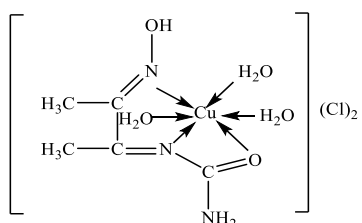
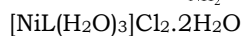
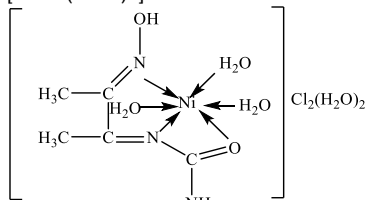
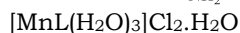
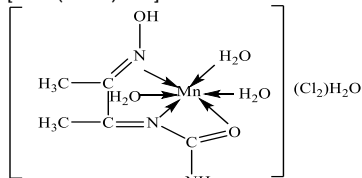
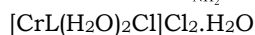
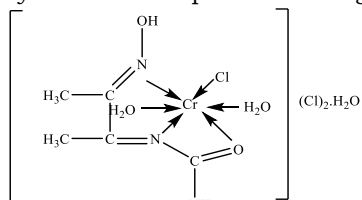


Fig.(12): IR spectrum of Cu(II) complex

Conclusion: On the basis of the analytical and spectral data, the synthesized chromium(III), manganese(II), nickel(II) and copper(II) Schiff base (L) complexes suggests 1:1 [ML] metal to ligand stoichiometry and exhibit octahedral structures and the ligand is coordinated to the metal ions as a tridentate, the following geometrical structures of the synthesized complexes were suggested.



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