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Synthesis And Spectral Study Of Cr(Iii), Mn(Ii), Ni(Ii) And Cu(Ii) Complexes Of Schiff Base Derived From Diacetylmonoxime With Thiourea

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Abstract Transition metal complexes of Cr(III), Mn(II), Ni(II) and Cu(II) of the Schiff base; 1-((2E,3E)-3-(hydroxyimino)butan-2-ylidene)thiourea were synthesized and characterized on the basis of physical characteristics, molar conductivity, micro-analytical data(CHN), magnetic moment measurements, Mass spectra, ^{1}HNMR, IR and UV-Vis spectrum data. The elemental analysis data showed the complexes are in 1:1 [M:L] ratio. The molar conductance values revealed the complexes of Cr(III), Mn(II), Ni(II) are electrolyte in nature while the Cu(II) complex is non-electrolyte. The results of magnetic moment measurements showed that, the complexes of Cr(III), Mn(II), Ni(II) and Cu(II) have unpaired electrons. The electronic spectral results of the Schiff base ligand and its complexes suggested that, the Cr(III), Ni(II), Mn(II) and Cu(II) complexes have an octahedral structure.
Keywords: Schiff base, Metal Complexes, 1-((2E,3E)-3-(hydroxyimino)butan-2-ylidene)thiourea.

تخليق ودراسة طيفية لمركبات الكروم الثلاثي والمنجنيز التنائي و النحاس التنائي من قاعدة شيف المشتقة من تنائي اسيتايل احادي الاوكسايم مع التيو يوريا

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الملخص مركبات العناصر الانتقالية للكروم الثلاثي والمنجنيز التنائي والنيكل التنائي والنحاس التنائي مع قاعدة شيف المشتقة من هيدروكسي امينو بيوتان يليدين – تيو يوريا تم تحضيرها وتشخيصها استنادا على خواصها الفيزيائية ونتائج التوصيل المولاري وتحليل العناصر و قياسات الخاصية المغناطيسية وطيف الكتلة وطيف الرنين النووي المغناطيسي و اطياف الاشعة تحت الحمراء وكذلك اطياف الامتصاص الالكتروني المرئية وفوق البنفسجية. اثبتت نتائج تحليل العناصر ان المركبات تكونت بنسبة 1:1 فلز : ليجاند، واثبتت نتائج التوصيل المولاري ان مركبات الكروم الثلاثي والمنجنيز التنائي والنيكل التنائي مركبات الكتروليتية في حين اثبتت النتائج ان مركب النحاس التنائي غير الكتروليتي ، كما اثبتت نتائج قياس الشدة المغناطيسية ان جميع المركبات تحتوي على الكترونات مفردة واثبتت نتائج تحليل اطياف الامتصاص الالكترونية لقاعدة شيف ومركباتها المحضرة ان جميع المركبات ذات تشكل هندسي ثماني السطوح.
الكلمات المفتاحية: قاعدة شيف، مركبات العناصر، تنائي اسيتايل احادي الاوكسايم مع التيو يوريا.

Introduction

Schiff base ligands are easily prepared by the condensation between aldehydes and imines, and were first reported by Hugo Schiff in 1864, also known as anils, imines or azomethines[1]. Metal complexes of Schiff bases have played a central role in the development of coordination chemistry. Schiff bases shows different properties including a broad range of biological activities antifungal, antibacterial, anti-malarial, antiviral, anti-allergic and anti-inflammatory, antitumor properties[2-4]. Schiff base oxime ligands and their complexes are widely known and studied, some oxime metal complexes are semiconducting and others have bioactive properties[5,6]. The first to identify the oxime ligands was Tschugaeff in his study of bidentate nature of vicinal dioximes, in the reaction between Ni(II) salts and dimethylglyoxime[7].

Several Schiff bases have been investigated as corrosion inhibitors for various metals and alloys in acidic media, due to the presence of the C=N group in the Schiff base molecules, they should be good corrosion inhibitors[8,9]. Some Schiff base compounds have recently been reported as effective corrosion inhibitors for mild steel, aluminum, copper, and zinc in acid media[10-12]. This study focuses on the synthesis of Co(II) and Cr(III) Schiff base complexes obtained from thiourea. The results showed that Co(II) complex has catalytic activity for oxidation of toluene, but Cr(III) complex did not show any catalytic activity[13] The present work aims to synthesize and characterize Cr(III), Mn(II), Ni(II and Cu(II) metal complexes of Schiff base derived from diacetylmonoxime with thiourea.

Experimental

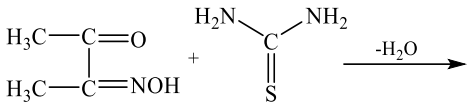
Materials and Methods: All chemicals used were reagent of BDH or Aldrich including, Diacetylmonoxime, Thiourea, EtOH, DMF, Ether.

Synthesis of Schiff base:

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

absolute ethanol with 50ml ethanolic solution of thiourea (0.76g, 0.01mmol) for three hours. The obtained product 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. 195 ^{o}C; yield 75%).

The reaction between the diacetylmonoxime and thiourea yields only one product as outlined in **scheme I**



Scheme 1: Synthesis of Schiff base

Synthesis of Complexes:

The Schiff base complexes were synthesized by adding 1-((2E,3E)-3-(hydroxyimino)butan-2-ylidene)thiourea (1.59g; 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 kept in a desiccator over silica gel.

RESULTS AND DISCUSSION:

Microanalysis and molar conductance measurements:

The elemental analysis data and some physical properties of the Schiff base and its complexes are presented in Table1 where the results confirm the proposed composition. The 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 77.6-112.4 ohm^{-1} cm^{2} mol^{-1} indicating complexes of Cr^{3+}, Mn^{2+}, and Ni^{2+} are electrolytic while Cu^{+2} have a molar conductance value of 23.37 Ω^{-1} mol^{-1} cm^{2} which indicate its non-electrolyte nature [14].

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

Compound	Colour	M. wt.	M.P. ^{0}C	%(Calc.) **(Found)**				Λ (μs)	BM
				C%	H%	N%	S%		
$C_5H_9N_3OS$	white	159.21	195	37.72**(37.41)**	5.70**(5.34)**	26.39**(26.06)**	20.14**(19.65)**	-	-
$[CrL(H_2O)Cl_2]Cl.H_2O$	Black	353.59	225	16.98**(16.62)**	3.71**(3.52)**	11.88**(11.52)**	9.07**(8.82)**	101.2	3.79
$[MnL(H_2O)_2Cl]Cl$	Grey	321.08	232	18.70**(18.44)**	4.08**(3.81)**	13.09**(12.87)**	9.99**(9.78)**	77.6	5.70
$[NiL(H_2O)_2Cl]Cl.2H_2O$	Brown	360.87	233	16.64**(16.45)**	4.75**(4.50)**	11.64**(11.49)**	8.89**(8.62)**	112.4	2.76
$[CuL(H_2O)Cl_2]2H_2O$	Grey	347.70	177	17.27**(16.92)**	4.35**(4.05)**	12.08**(11.79)**	9.22**(8.89)**	23.37	1.82

Mass spectrum of the Schiff base:

Mass spectra of the ligand showed molecular ion peaks, which were in good agreement with the expected values, shown in figure 1.and the mass fragmentation of the Schiff illustrated in **scheme 2.** The mass spectrum of the ligand gives a peak at 159m/z[15].

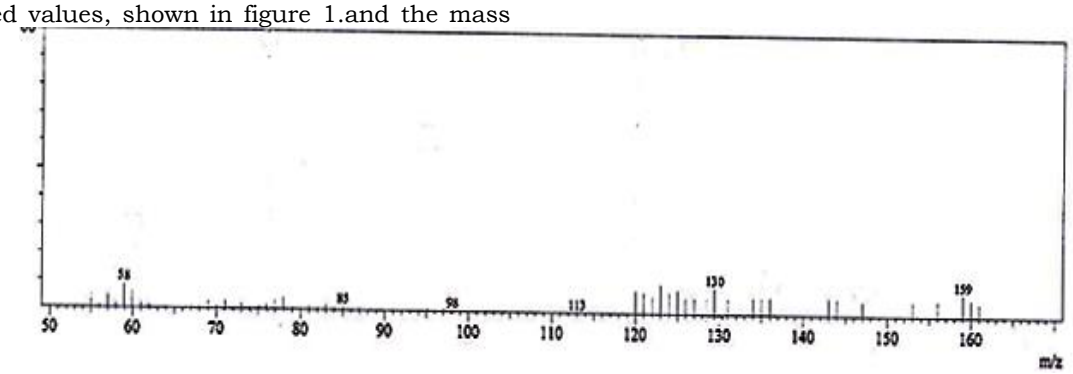
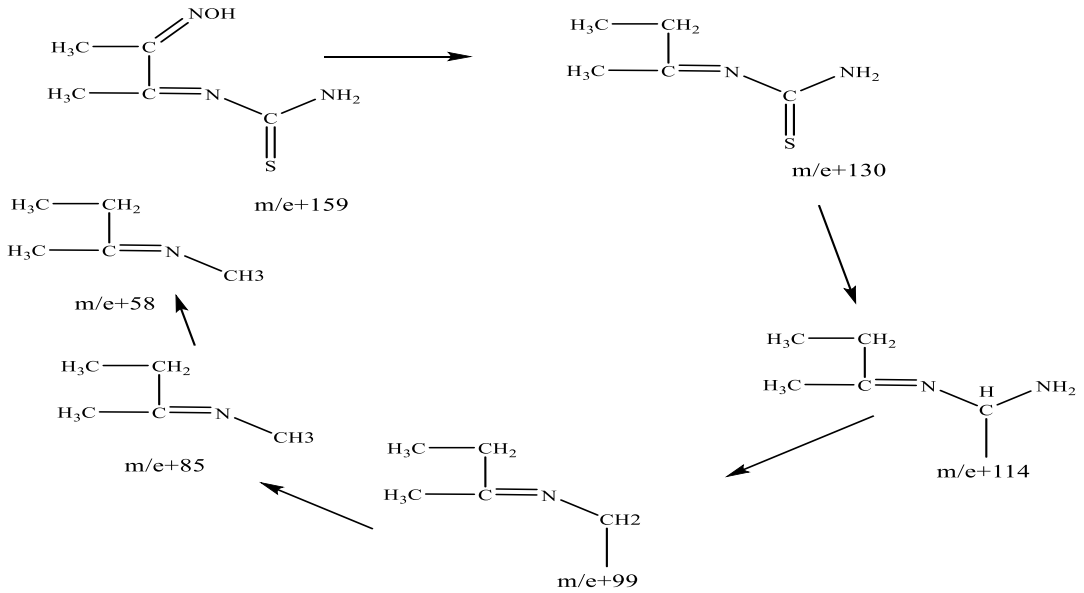


Fig. (1): Mass spectrum of Schiff base



Scheme 2: Mass fragmentation of the Schiff base

Proton nuclear magnetic resonance spectrum of ligand:

The Schiff base ligand shows four singlet signals at 2.50, 3.385, 7.027, and at 9.979 ppm (Fig. 2), downfield of TMS, attributed to the protons of CH_3, CH_3, NH_2, and OH respectively[16].

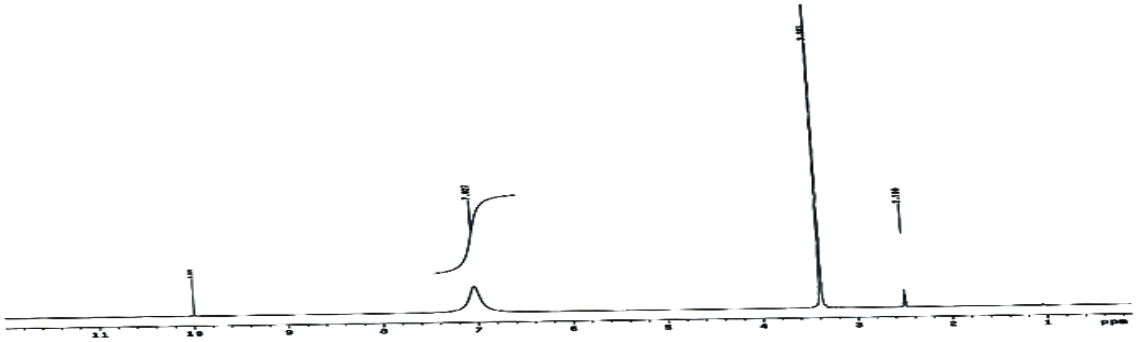


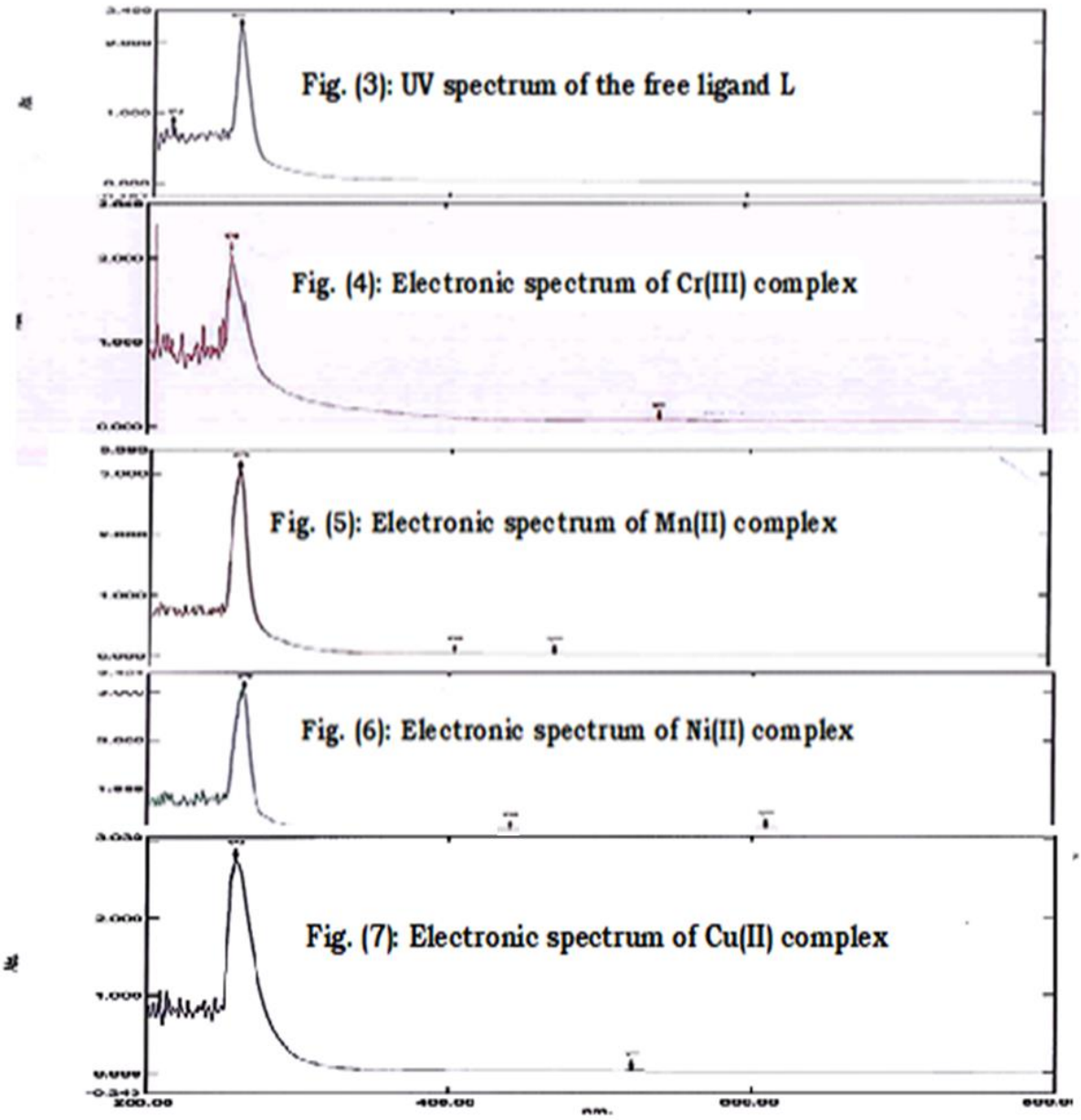
Fig. (2): ^{1}H-NMR spectrum of Schiff base

Electronic spectra:

UV-Vis spectral data of the ligand and its synthesized complexes are presented in table 2 and Figs.3-7 The ligand spectrum exhibits two absorption bands at 47058 cm^{-1} and 38833 cm^{-1}, attributed to π→π* and n→π* transitions respectively[17]. The Cr(III) complex spectrum exhibits absorptions at 38833 cm^{-1} attributed to n→π* transition, and show a band at 18433 cm^{-1}, which is due to $^4A_{2g}\rightarrow{}^4T_{1g}$ transition, an octahedral structure is suggested for Cr(III) complex[18,19]. The electronic absorption spectrum of Mn(II) complex exhibit an absorption band at 38314 cm^{-1} which are due to n→π* transition, and show two bands at 24630 cm^{-1} and 21367 cm^{-1}, attributed to $^6A_1g\rightarrow{}^4T_1g(P)$ and $^6A_1g\rightarrow{}^4T_1g(P)$ transitions, which indicates the presence of Mn(II) complex in octahedral structure[20]. The electronic absorption spectrum of Ni(II) complex exhibits two absorptions bands at 47393 cm^{-1} and 38167 cm^{-1}, attributed to π→π* and n→π* charge transfer and two bands at 22988 cm^{-1} and 16129 cm^{-1} which are due to $^3A_2g(F)\rightarrow{}^3T_1g(P)$ and $^3A_2g(F)\rightarrow{}^3T_1g(F)$ transitions, respectively, which favours an octahedral geometry for the complexs[21]. Cu(II) complex spectrum exhibits two absorption bands at 38461 cm^{-1} which attributed to n→π* and 19607 cm^{-1} assigned to $^2Eg\rightarrow{}^2T_2g$ transition suggesting an octahedral geometry[22,23].

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

Ligand/ Complexes	IR (cm^{-1})					UV - Vis
	υNH₂	υC=N	υC=S	υM-N	υM-N	λ_{max} (cm^{-1})
L $C_5H_9N_3OS$	3278	1616	1081	-	-	38833,47058
$[CrL(H_2O)_2Cl_2]Cl.H_2O$	3295	1618	1091	552	552	38986,18433
$[MnL(H_2O)_2Cl]Cl$	3291	1613	1092	566	566	21367,38314 24630
$[NiL(H_2O)_2Cl]Cl.2H_2O$	3299	1613	1086	594	594	22988,38167,47393 16129
$[CuL(H_2O)Cl_2]2H_2O$	3178	1628	1116	605		38461,19607



Figs. (3-7): Electronic spectra of the Schiff base and its complexes

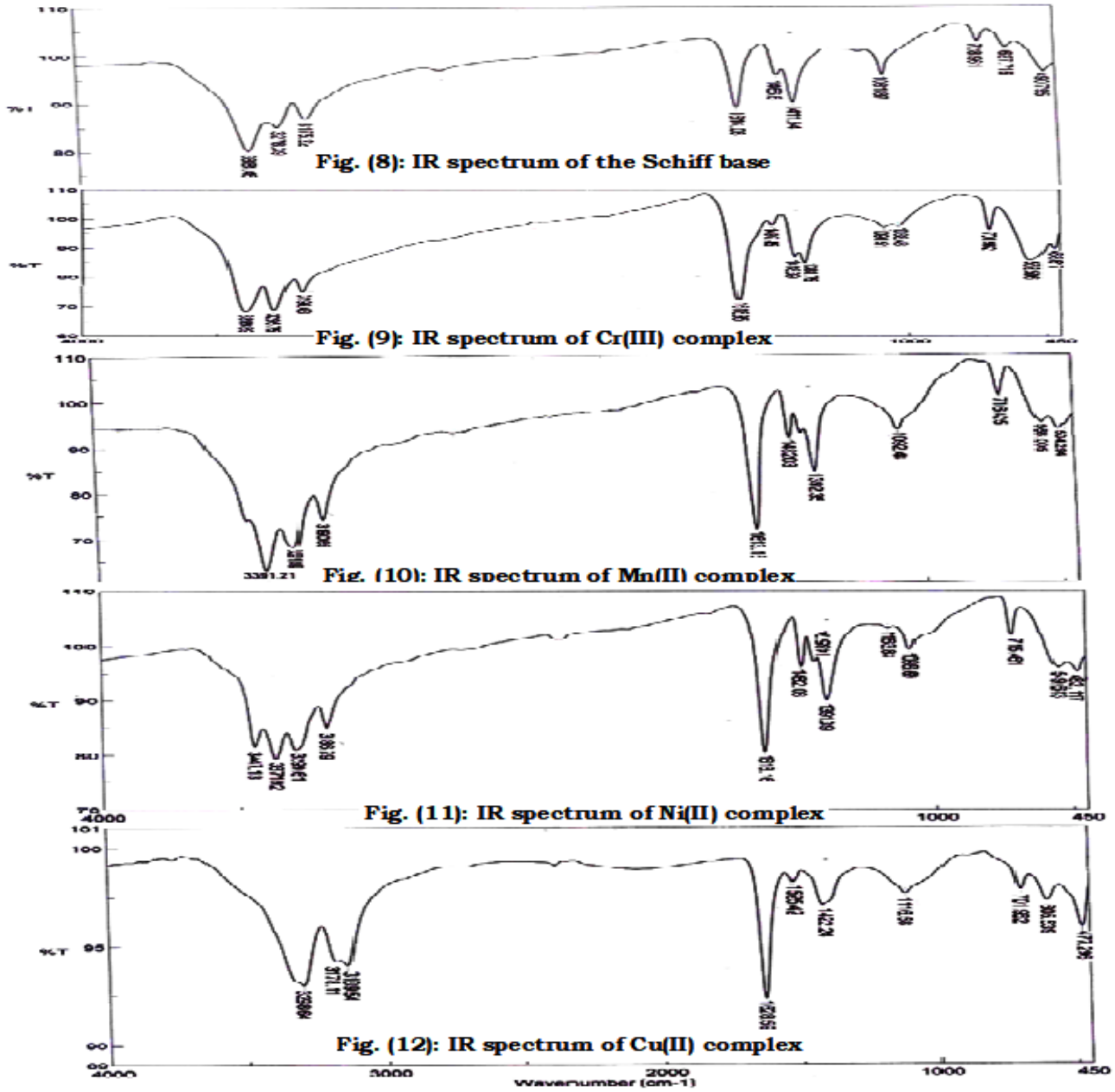
Magnetic susceptibility measurements:

The Cr(III) magnetic moment complex value is 3.84 BM suggests an octahedral geometry[24]. Mn(II) complex is 5.65 BM which suggests the high spin six-coordinated octahedral arrangement of the ligand around the metal ion[25]. The Ni(II) complex has a value of 2.73 BM indicating a spin-free octahedral configuration[21]. Cu(II) complex magnetic moment is 1.79 BM which suggests a distorted octahedral geometry around the metal ion[26].

IR spectra:

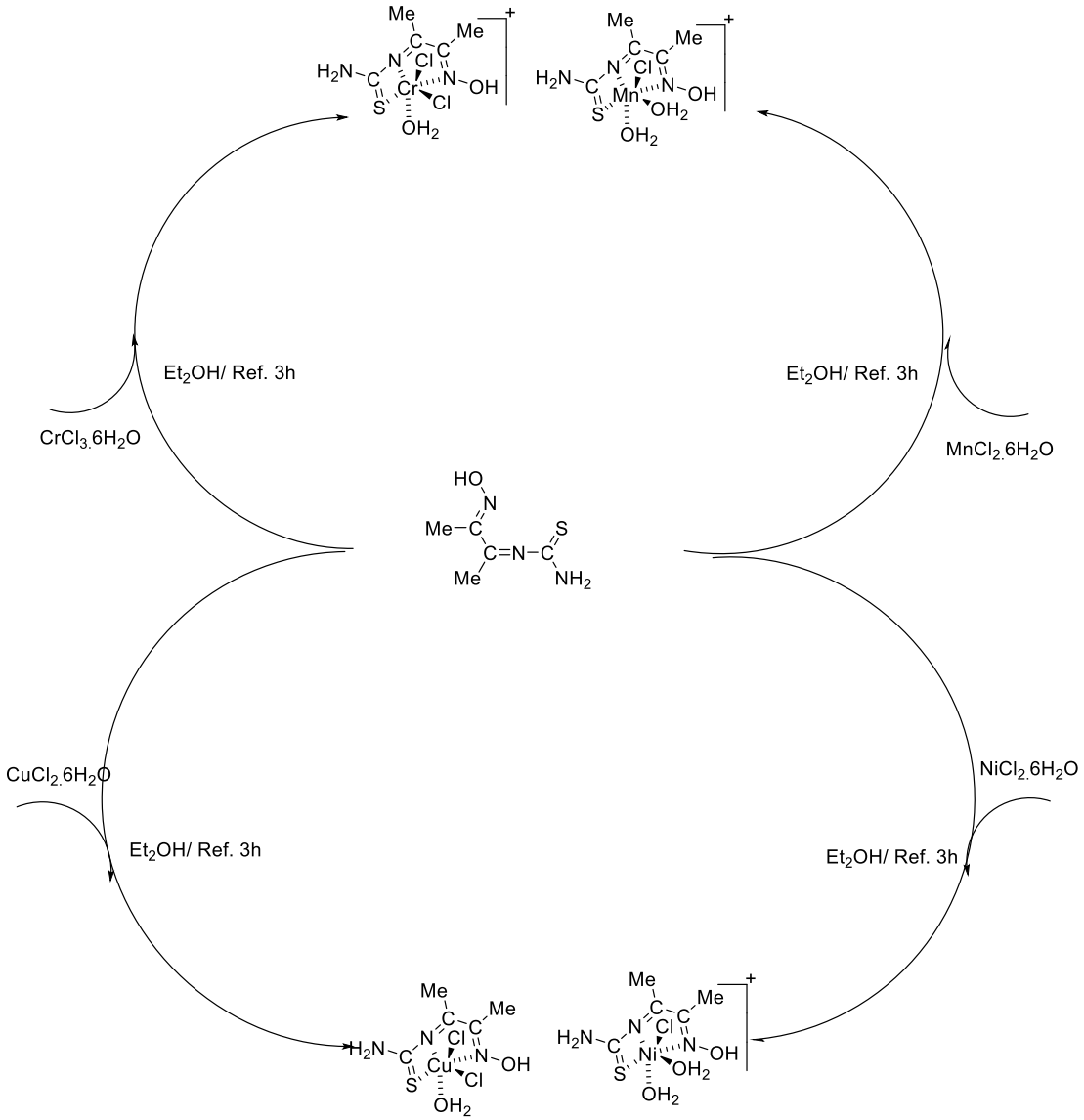
The infrared spectral data of the ligand and its complexes are presented in table 2 and figs. 8-12, IR spectrum of the Schiff base show bands at 3384 cm^{-1} assignable to OH group, and at 1081 cm^{-1} attributed to C=S, the band at 1616 cm^{-1} attributed to C=N of azomethine group[27,28]. Verification of the structures of the metal complexes can be achieved by comparing the IR spectrum of the Schiff base ligand with the IR spectrum of synthesized 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[30]. The IR spectra of the complexes display broad bands in the range of 3399 – 3298 cm^{-1} which is attributed to stretching vibration νOH of coordinated water molecules bandings with complexes formation[31,32]. The band assigned to the azomethine group in the free Schiff base ligand was observed at νC=N 1616 cm^{-1} and shifted to lower or higher wave numbers ranging from 1613-1628 cm^{-1} in the spectra of all

complexes, this indicates the participation of the nitrogen atom of the azomethine group in coordination[33,34]. The band at 1081 cm^{-1} in the spectrum due to υ(C=S) stretching vibrations in the Schiff base, in the metal complexes this band is shifted to higher frequency which indicates the coordination through sulphur atom[35]. The band in the range of 3178-3299 cm^{-1} indicates that the NH_2 group is not participating in coordination with the metal ions[36]. New bands in the range of 504-605 cm^{-1} which could be attributed to νM-N modes which are in good agreement with those reported in literature[37,38].



Figs. (8-12): IR specta of the Schiff base and its complexes

Conclusion: The obtained Schiff base and its Cr(III), Ni(II), Mn(II) and Cu(III) complexes were synthesized and characterized by several physical techniques, molar conductivity, elemental analysis, infrared, proton nuclear magnetic resonance, electronic and mass spectroscopes. All the experimental data confirm the existence of an octahedral geometry for all complexes as shown in **scheme** 3



Scheme 3: Synthesis and structures of the complexes

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