Preparation and Characterization of Some Chelate Complexe with New bi-dentate (N,O)bis-Schiff base Ligand

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الخلاصة

حضر في هذا البحث معقدات كلابية لكل من الكروم(III) و المنغنيز(II) والكوبلت(II) و النيكل(II) والنحاس(II)مع ليكاند جديد ثنائي المخلب قاعدة الشف[2-(-((4-(- 1-(2-فنيل هايدرازونو) اثيل) فنيل) ايمينو) مثيل) فينول (M-Sal).شخص الليكاند الجديد اعتمادا على نتائج اطياف الاشعة فوق البنفسجية ـ المرئية والاشعة تحت الحمراء وطيف الرنين النووي المغناطيسي للبروتون وطيف الكتلة. بينت نتائج الامتصاص الذري اللهبي ان نسبة (الفلز:ليكاند), كانت (1:1)لمعقدات الكروم(III) والنحاس(II) بينما كانت النسبة (2:1) لمعقداتالمنغنيز(II) والكوبلت(II) و النيكل(II). وقد تم اقتراح الاشكال الفراغية للمعقدات المحضرة على وفق معطيات نتائج اطياف الاشعة فوق البنفسجية ـ المرئية والاشعة تحت الحمراء والحساسية المغناطيسية و التوصيل المولاري والامتصاص الذري اللهبي حيث امتلك معقدي النحاس والنيكل الثنائيين بنية المربع المستوي فيما كانت باقي المعقدات ثمانية السطوح.

Abstract

In this research newchelation complexes were prepared for Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) ions with new bis schiff base ligand [2-(-((4-(-1-(2-phenylhydrazono)ethyl)phenyl)imino)methyl)phenol](M-Sal). The new ligand chracterized depends on (Uv-Vis, IR) spectroscopies, ^{1}H-NMR andMass spectra. The results of flame atomic absorption indicate that (Metal:Ligand) portions were (1:1) for Cr(III), Ni(II) and Cu(II) complexes and were (1:2) for Mn(II) and Co(II) complexes. The geometries of prepared complexes suggested according to the results of Uv-Vis and IR spectroscopies, magnetic susceptibility, molar conductance and flame atomic absorptionwhich were squar plannar for Ni(II)and Cu(II) complexes while the rest complexes have the octahedral geometry.

Introduction

Among different types of coordination ligands, Schiff bases ligands which containing hetero atoms (N and O) as donor atoms are of considerable interest due to their potential application in catalysis, medicine and material science[1-5].Schiff bases derived from Salicylaldehyde or its derivatives and their complexes are extensively studied due to synthetic flexibility ,selectivity and sensitivity towards a variety of metal ions. The azomethine (C=N) linkage is essential for biological activity, several azomethines were reported to possess remarkable antibacterial[6], antifungal[7], anticancer[8], antitumor[9], anti-inflammatory[10], anti-tuberculosis[11] and antimalarial[12] activities.

Materials and methods

Apparatus and materials

All reagents and solvents were obtained from commercial sources and used as received. Melting points were recorded by a Stuart melting point (digital) SMP30 apparatus. FTIR spectra were recorded by a Shimadzu (FT-IR) model 4800s spectrophotometer in the range (4000-400) cm^{-1} by using KBr-disc. The Uv-Visible spectra of compounds were recorded by using a (U.V-Visible) spectrophotometer type Cary 100con. in the range (800–200) nm. ^1H-NMR spectra of precursor and ligand were recorded in DMSO-d_6 by using a Bruker DMX-500 spectrophotometer (300 MHz).

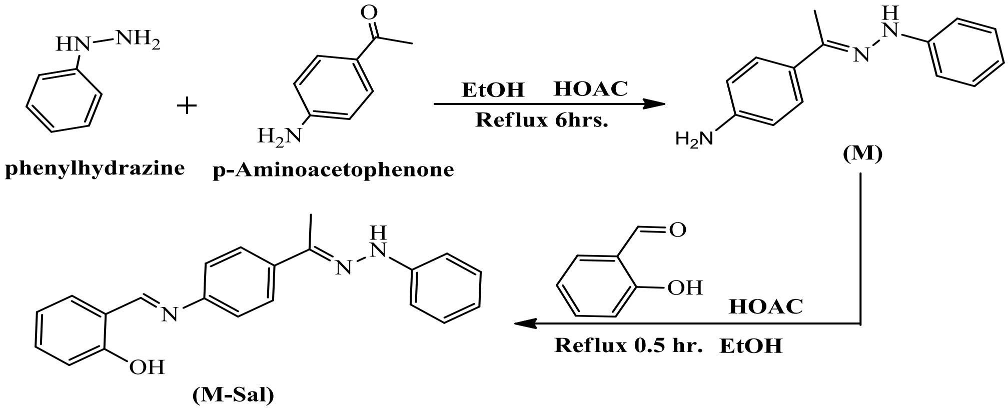
Magnetic susceptibility of prepared complexes was determined at (R.T) °C by Auto Magnetic Susceptibility Balance (Sherwood Scientific). The metal percentages were determined by using a Phoenix-986 AA spectrophotometer. Conductivity measurements were recorded at (R.T) °C for solutions of samples in DMSO solvent using an Inolab Multi 740, WTW 82362 Weilhiem-Germany.

Synthesis of the Precursor 4-(1-(2-phenylhydrazono)ethyl)aniline (M)

In (100mL) round bottom flask, (1.352g, 10mmol) of *p*-Aminoacetophenone dissolved in (15 ml) of absolute ethanol, then acidified with few drops of glacial acetic acid. (1.08 g, 10mmol) of phenylhydrazine dissolved in (15 mL) of absolute ethanol, then added gradually to previous solution. The final reaction mixture refluxed for 6 hrs. then left to the next day and poured in the ice. The off white precipitate was formed, filtered off, washed with distilled water, dried at room temperature, and finally recrystallized from hot absolute ethanol. The purity of precursor was detected by (TLC) using (Chloroform/ Ethanol) as eluent, in ratio (8: 2). **Scheme 1** represents the preparation reaction of precursor (M) and ligand (M-Sal).

Synthesis of the ligand [2-(-((4-(-1-(2-phenylhydrazono)ethyl)phenyl)imino) methyl) phenol] (M-Sal)

(2.25 g, 10mmol) of the precursor (M) dissolved in (20 mL) of absolute ethanol, added gradually acidified solution of (1.22 g, 10mmol) of salicylaldehyde which dissolved in (10ml) from same solvent. The final reaction mixture refluxed for 0.5 hr., the formed bright yellow precipitate filtered off, wished with distilled water and absolute ethanol. The prepared ligand was soluble in Methanol, Ethanol, DMSO, DMF, Benzene and Chloroform.



Scheme 1: Preparation reaction of the (M) and (M-Sal)

Synthesis of Chelation Complexes

All chelation complexes were prepared by the same method, where (5 mL) hot ethanol solution of (0.1mmol) metal chloride salts were added slowly to a stirred (25mL) hot ethanol solution of (M-Sal) (0.329 g, 1mmol). Color change has been noticed after mixing both solutions. The resulting solutions then heated under reflux. Although some complexes need a period of time to precipitate, the others precipitated either immediately or after reducing the volume of reaction mixture by slow evaporation at room temperature. All obtained chelation complexes were filtered off, dried, washed with distilled water and finally recrystallized from hot absolute ethanol.

Results and Discussion

Table 1 represents some physical properties and metal percentage of precursor (M), ligand (M-Sal) and its metal complexes.

Table 1: Some physical properties, yield percentage and metal percentage of precursor (M, ligand (M-Sal) and its metal complexes.

Compound symbol	Empirical formula	M.wt g.mol^{-1}	Color	Yield%	m.p°C	M% Calculated (found)
M	$C_{14}H_{15}N_3$	225	Off white	68	90-92	-----
M-Sal	$C_{21}H_{19}N_3O$	329	Yellow	92	144-146	-----
Cr-complex	$C_{21}H_{26}Cl_2CrN_3O_5$	459.5	Light brown	65	210-212*	11.29 (11.12)
Mn-complex	$C_{42}H_{40}MnN_6O_4$	747.74	Greenish yellow	58	258-260*	7.34 (6.98)
Co-complex	$C_{42}H_{40}CoN_6O_4$	751.71	Dark brown	67	184-186*	7.83 (8.15)
Ni-complex	$C_{42}H_{36}N_6NiO_2$	715.47	Dark green	70	280-282*	8.2 (9.30)
Cu-complex	$C_{21}H_{22}ClCuN_3O_3$	463.42	Dark brown	72	206-208*	13.70 (14.28)

***= decompose**

^{1}H-NMR-Spectrua of precursor (M) and ligand (M-Sal)

^{1}H-NMR spectral data of the precursor (M) and ligand (M-Sal) is as shown in the **Table 2**. ^{1}H-NMR spectrum of the precursor (M), **Figure 1**, showed a signal at (δ=8.91 ppm, 1H) assigned to (-NH)[13], while the singlet signal appeared at (δ=5.24 ppm, 2H) referred to (NH_2)[13] group. The signal appeared at (δ=2.16 ppm, 3H) was attributed to methyl protons[14]. The protons of aromatic rings appeared at (δ=7.51-6.55 ppm, 9H)[15].

^{1}H-NMR spectrum of the ligand (M-Sal), **Figure 2**, showed a signal at (δ=9.34 ppm, 1H) assigned to (-OH) group [16]. While the singlet signal appeared at (δ=9.00 ppm, 1H) referred to (NH)[17] group. The signals of azomethine group [18] and aromatic rings appeared at (δ=7.89-6.77 ppm, 14H)[15].The singlet signal at (δ=2.35 ppm, 3H) was assigned to methyl group protons[17].

Table 2: ^{1}H-NMR spectrum data of (M) and (M-Sal) in DMSO-d$_6$

Comp.	*Assignment*	*Chemical shifts δ (ppm)*
(M)	(NH), (Aromatic Protons) (NH$_2$),(CH$_3$)	(8.91, S, 1H), (7.51-6.55 , 9H) (5.24, 2H), (2.16, 3H)
(M-Sal)	(OH), (NH) (-CH=N- + Aromatic) Protons (CH$_3$)	(9.34 , 1H), (9.00, 1H) (7.89-6.77, 14H) (2.35, 3H)

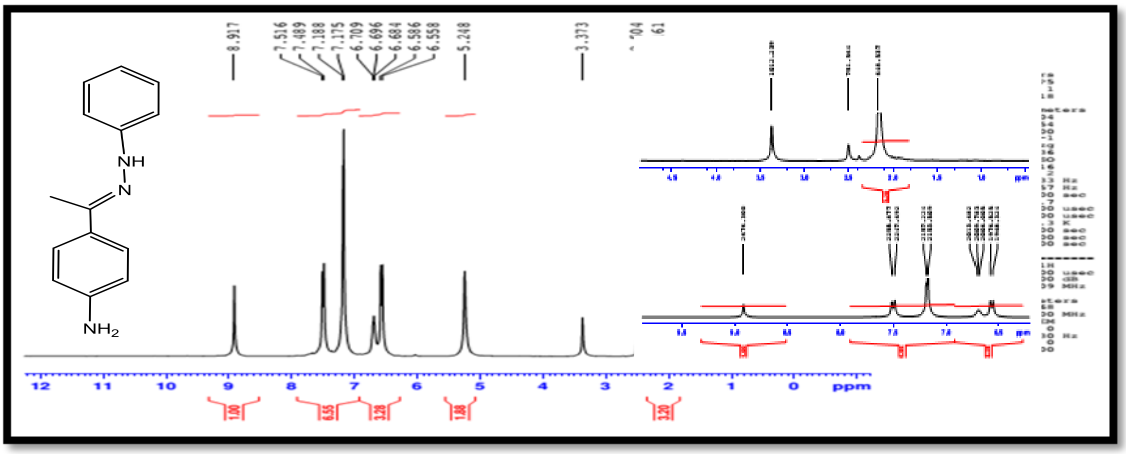


Figure 1: ^{1}H-NMR Spectrum of Precursor (M)

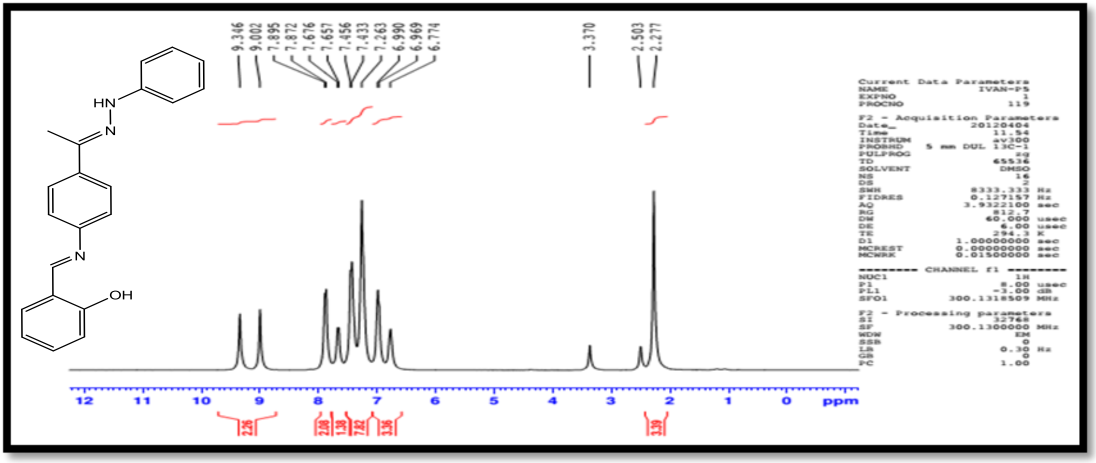


Figure: (2): ^{1}H-NMR Spectrum of Ligand (M-Sal)

Mass Spectrum of Ligand (M-Sal)

The mass spectrum of ligand, **Figure 3**, showed the mother ion peak at (*m/z*=329), as a base peak, which is corresponds to (M$^+$). The other fragments and their relative abundances and fragmentation pathways are shown in **Scheme 2**.

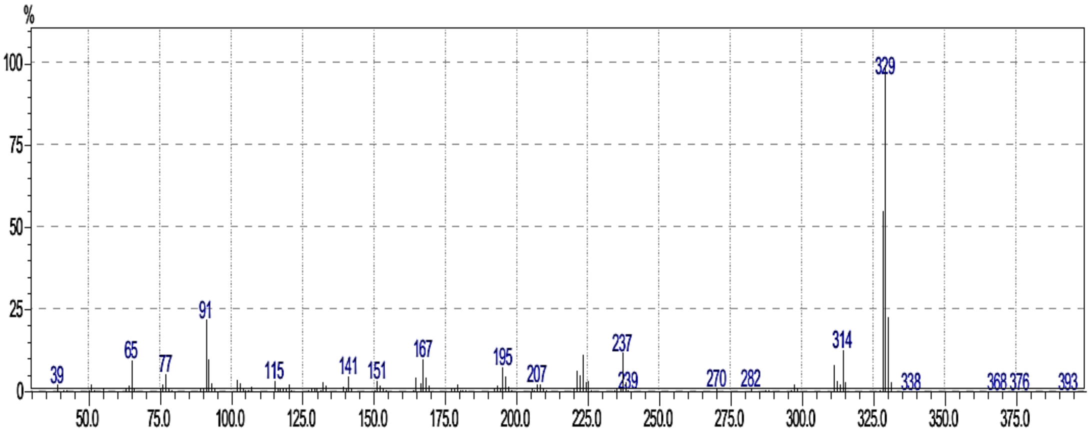
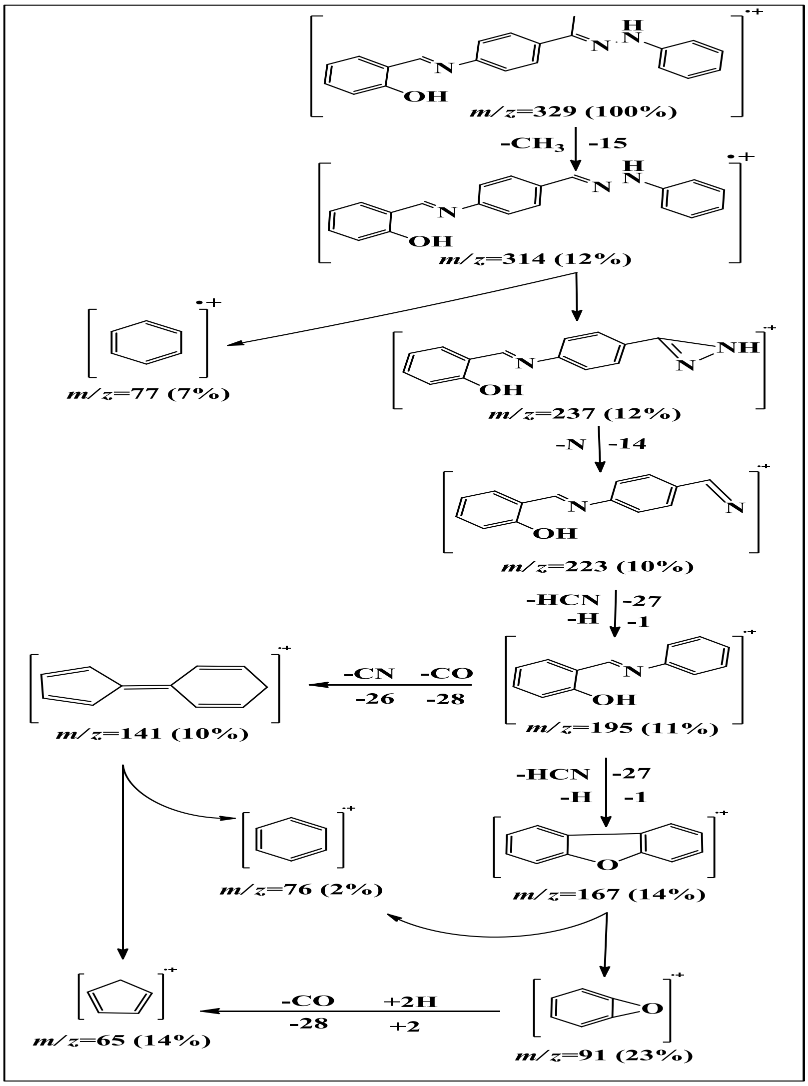


Figure 3: Mass Spectrum of Ligand (M-Sal)

FTIR-Spectrum of precursor (M), ligand (M-Sal) and Complexes

In FTIR spectrum of precursor (M), **Figure 4**, the stretching frequency of carbonyl group of p-Aminoacetophenone was disappeared, with appearance of new band at 1622 cm^{-1} related to azomethine group.

The υ(O-H) vibration of phenolic hydroxyl group which appeared at (3441 cm^{-1}) in free ligand spectrum, **Figure 5**, disappeared[19] in FTIR spectra of its complexes which is indicated clearly the participation of this group in coordination with metal ions. The υ(C=N) vibration of complexes, shifted to lower[19] or higher frequencies compared with free ligand spectrum. The υ(C–N) and υ(C–O) vibrations suffered from significant changes as a result of coordination. The υ(M–O) and υ(M–N) vibrations were observed at (548-540) cm^{-1} and (465-448) cm^{-1}, respectively[6, 19]. The important characteristic bands related to the ligand (M-Sal) and its complexes and their assignments are listed in **Table 3**.



Scheme 2: Proposed fragmentation pathways of (M-Sal)

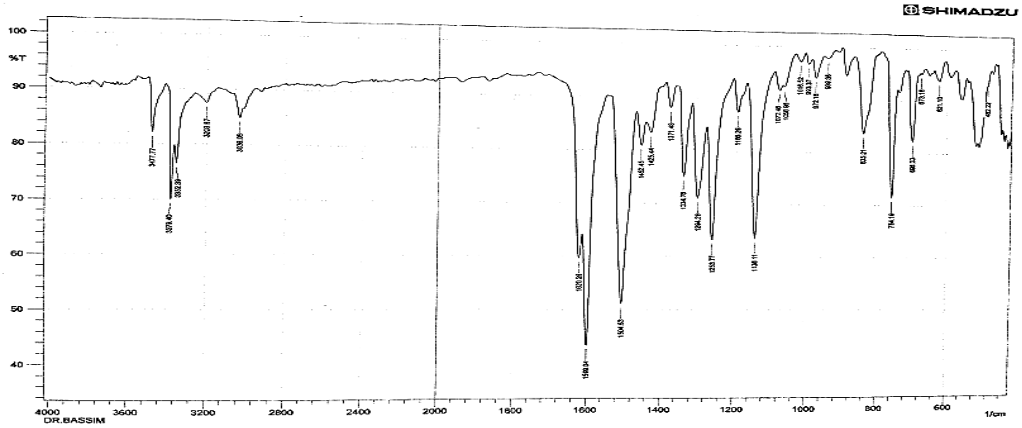


Figure 4: FTIR Spectrum of precursor (M) Ligand

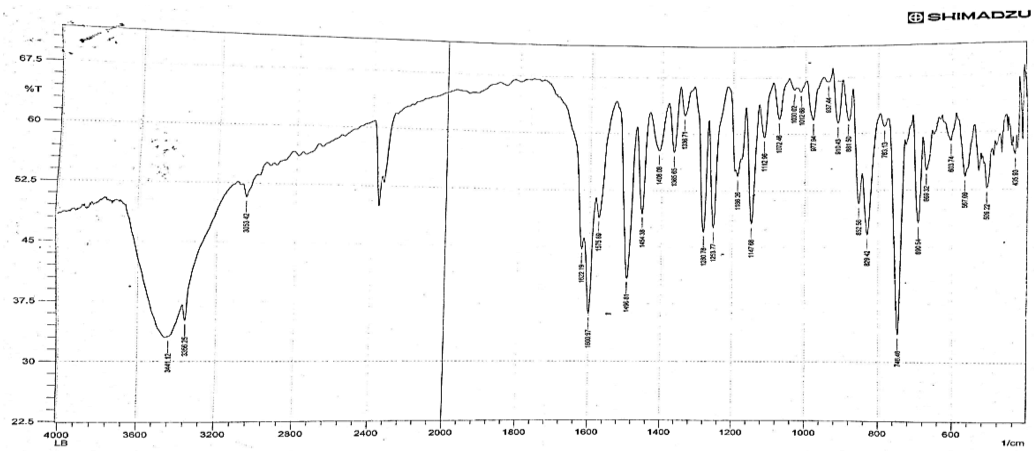


Figure 5: FTIR Spectrum of M-Sal Ligand

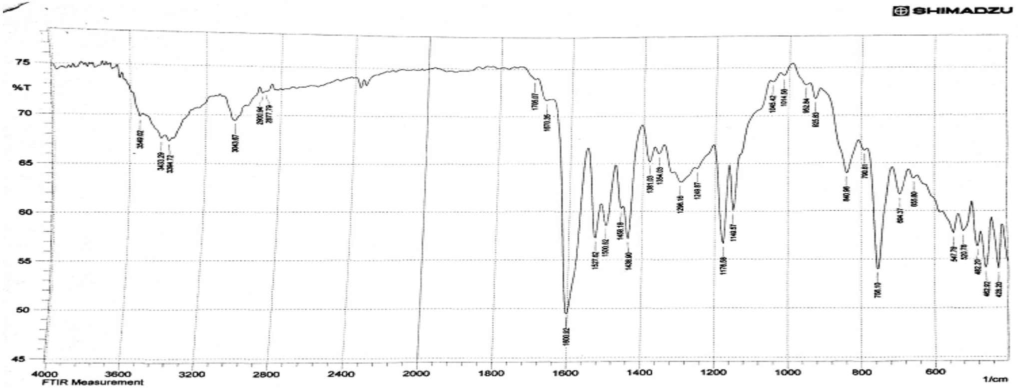


Figure 6: FTIR Spectrum of Co(II) Complex

Table 3: IR Spectral Data (cm-1) for ligand (M-Sal) and its Complexes

Comp.	*(M-Sal)*	*Complexes*				
		Cr(III)	**Mn(II)**	**Co(II)**	**Ni(II)**	**Cu(II)**
υ(O-H)	3441(br)	---	---	---	---	---
υ(N-H)	3356(sh)	---		---	---	3394(w)
Coord.(H_2O)	---		---			
υ(C–H) Arom.	3053(w)	(3062-3016)(w)	3059(w)	3043(w)	3055(w)	3047(w)
υ(C–H) Aliph.	2999(w)	(2978,2927)(w)	(2978) (2927)(w)	2900,2875(w)	---	2978(w)
υ(C=N)	1622(m)	1600(s)	1597(s)	1600(s)	1612(s)	1593(s)
υ(C=C) Benzen	1600(s), 1575(m) 1496(m)	1531(m) 1496(m)	1539(w) 1516(w) 1489(w)	1527(m) 1500(m) 1458(m)	1600(s) 1539(m) 1496(m)	1531(m) 1500(w) 1462(w)
υ(C-O)	1280(m)	1276(m)	1273(m)	1296(w)	1296(w)	1269(w)
υ(C-N)	1253(m)	1253(w)	1230(w)	1249(w)	1249(w)	1230(w)
υ(M-O)	---	569(w)	524(w)	543(w)	551(w)	547(w)
υ(M-N)		486(w)	482(w)	459(w)	459(w)	462(w)

s = strong w = weak m = medium sho=shoulder

Electronic Spectra and Magnetic Properties

The spectral data and the magnetic moments of prepared complexes are listed in **Table 4**.The electronic spectra of ligand and its metal complexes were recorded in absolute ethanol solutions in the range from (200-800) nm. The UV-Vis spectrum of light yellow solution of prepared ligand, reveals thee peaks at (247nm, 40458cm^{-1}),(290nm, 34482cm^{-1}) and (384 nm, 26041cm^{-1}), the first two absorption peaks may be assigned to $\pi\rightarrow\pi^*$ transitions of benzene rings and -CH=N- groups, the third high intensity absorption peak may be assigned to intra-ligand charge transfer transitions (ILCT)[20].

the UV-Vis spectrum of Cr(III) complex, exhibits new bands[21], in visible region, at (560nm, 17857cm^{-1}) and (495nm, 20202cm^{-1}),which assigned to first and second spin allowed transitions; ($^4A_2g_{(F)}\rightarrow{}^4T_2g_{(F)}$) ($\upsilon_1$)(10 Dq)[22], and ($^4A_2g_{(F)}\rightarrow{}^4T_1g_{(F)}$) ($\upsilon_2$)[23],respectively. The spectrum also exhibits other two bands at (221 nm, 45248 cm^{-1}) and (330 nm, 30303cm^{-1}), respectively, were assigned to ligand field spectra. The obtained magnetic moment value was (3.70BM), which confirm an octahedral geometry around Cr(III) ion[22, 23].

The spectrum of Mn(II) complex, exhibits two peaks only, at (321nm, 31152cm^{-1}) and (233nm, 42918cm^{-1}), respectively. These bands could be assigned to ligand field transitions. Further (d-d) bands at visible region didn't observe[24]. The low value of effective magnetic moment, (2.5 B.M), confirm the presence of octahedral low spin[25] Mn(II) with one unpaired electron and orbital contribution.

The strong absorption peaks observed in spectrum of Co(II) complex at (221 nm, 45248 cm^{-1}) and (264nm, 37878cm^{-1}), respectively assigned to ligand field transitions. The spectrum also reveals new low intensity absorption peak at (425nm, 23529cm^{-1}), assigned to the (MLCT) transition[26] and to a higher energy, third spin allowed ($^4T_1g(F)\rightarrow{}^4A_2g(F)$) ($\upsilon_3$) transition[27]. The calculated value of effective magnetic moment was seen at (5.4 B.M) with in the expected range of (4.7-5.2) B.M for octahedral geometry.

The absorption peak which observed in ligand spectrum at (384nm, 26041cm^{-1}), blue shifted to (354 nm, 28248 cm^{-1}) in spectrum of Ni(II) complex. This hypsochromic[28] shift assigned to participation of azomethine group nitrogen atom of Schiff base in coordination with Ni(II). The spectrum also showed other peaks at (219nm, 45662cm^{-1}), (236nm, 42372cm^{-1}) and (287nm, 34843cm^{-1}) assigned to ligand field. The ($d\rightarrow d$) transitions bands didn’t observe[29] even at high concentrations, because it obscured by (MLCT) band[30]. The calculated values of magnetic moment were (0.00 B.M). This confirms the diamagnetic character of complex. So we can suggest a square planar geometry around the Ni(II) ion.

The spectrum of Cu(II) complex displayed new peak at (393 nm, 25445 cm^{-1}) assigned to (MLCT) transitions[31]. The spectrum also reveals other two absorption peaks at (220nm, 45454cm^{-1}) and (290nm, 34482 cm^{-1}) assigned to ligand field. The expected (d→d) transition have been not observed[32], because it may be hidden or obscured with those high intensity and strong bands related to ligand field. The value of magnetic moment was (1.77B.M), which confirm square planar geometry around Cu(III) ion.

Molar Conductance of Prepared Complexes

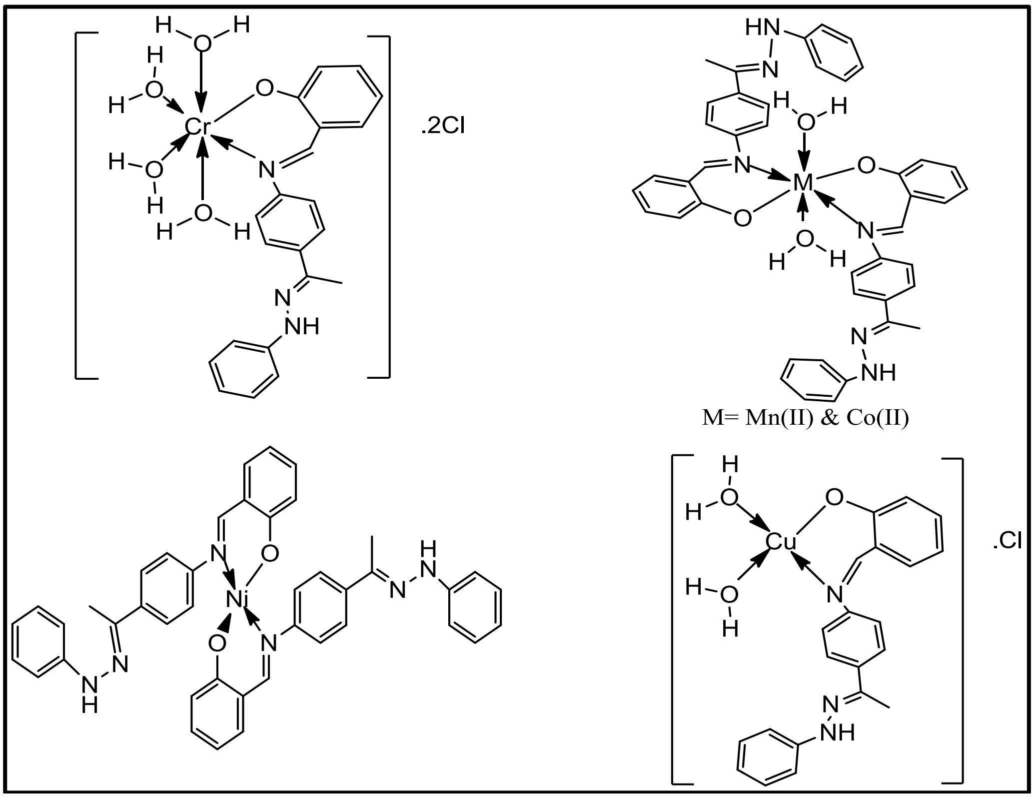
The values of molar conductance of Cr(III) and Cu(II) complexes in DMSO were (76.2 & 34.9 S.cm^2 .mole^{-1}), indicated the (1:2) and (1:1) ratios electrolyte nature[33]. The values of the other complexes Mn(II), Co(II) and Ni(II)in DMSO were within the range (14.8-19.2 S.cm^2 .mole^{-1}), indicated the non-electrolyte nature[33] of these complexes. According to all previously mentioned analyses we can proposed the following structures of prepared complexes.

Table 4: Electronic spectral data, Magnetic moments and geometry of Ligand and its complexes

Compound	*λ_{max} nm ($\bar{\upsilon}$ cm^{-1})*	*Assignment*	*μ_{eff} (B.M)*	*Molar conductance S.cm^2.mole^{-1}*	*Geometry*
Ligand	247(40458) 290(34482)	($\pi\rightarrow\pi^*$)	---	----	---
	384(26041)	(ILCT)			
Cr(III)	221(45248) 330(30303)	Ligand field	3.70	76.2	O.h
	560(17857) 495(20202)	$^4A_2g_{(F)}\rightarrow{}^4T_2g_{(F)}(\upsilon_1)$(10 Dq) $^4A_2g_{(F)}\rightarrow{}^4T_1g_{(F)})$ (υ_2)			
Mn(II)	233(42918) 321(31152)	Ligand field	2.5	14.8	O.h
Co	221 (45248)	Ligand field	5.4	16.7	O.h

Ni	264 (37878)		0.0	19.2	S.P
	425 (23529)	(MLCT) & $^4T_1g_{(F)}\rightarrow{}^4A_2g_{(F)}(\upsilon_3)$			
	219 (45662)	Ligand field			
	236 (42372)				
	287 (34843)				
	354 (28248)	(LMCT)			
Cu	220 (45454)	Ligand field	1.77	34.9	S.P
	290 (34482)				
	393 (25445)	(MLCT)			

Suggested Structures of Prepared Complexes



References

1) Gupta, K. C., Sutar, A.K., Lin, C.C. [2009]. ***Coord. Chem. Rev.*** 253, pp: 1926-1946.

2) Trakarnpruk, W. [2008]. ***Ind. Eng. Chem. Res.*** 47, pp: 964–968.

3) Donald, J., Darensbourg, Eric, B. Frantz. [2007]. ***Inorg. Chem***. 46, pp: 5967–5978.

4) Cozzi, P.G. [2004]. ***Chem. Soc. Rev.*** 33, pp: 410-421.

5) Gupta, K.C. [2008]. ***Coord. Chem. Rev.*** 252, pp: 1420-1450.

6) Nagajothi, A., Kiruthika, A., Chitra, S. and Parameswari, K**.** [2013]. ***Research J. of Chemical Sciences,*** 3(2), pp: 35-43.
7) Sharma, A. and Shah, M. K. [2013]. ***ChemSci Trans.,*** 2 (3)**,** pp: 871-876.
8) Abd El-All, A. S., Ragab, F. A. F. and El-Rashedy, A. A. [2013]. ***Global Journal of Pharmacology,*** 7 (2), pp: 143-152.
9) Al-Saif, F. A. [2013]. ***Int. J. Electrochem. Sci.***, 8, pp: 10424–10445.
10) Valli, G., Mahalakshmi, M. and Thirupathi, A.T. [2013]. ***International Journal of Advanced Research***, 1(5), pp: 609-613.
11) Manier, M. L., Reyzer, M. L. Goh, A. Dartois, V., Via, L. E. and Caprioli, R. M. [2011]. ***J. Am. Soc. Mass Spectrom.*** 22,pp:1409-1419.
12) Sopitthummakhun, K., Thongpanchang, C., Vilaivan, T. Yuthavong, Y. and Leartsakulpanich, U. [2012]. ***Malaria Journal***.
13) Moghimi, A., Khanmiri, R. H., Shaabani, A. and Hamadani, H. [2013]. ***J Iran Chem. Sos.***
14) Patil, S., Jadhav, S. and Deshmukh, M. B. [2012]. ***J. Chem. Sci.*** 124(5), pp: 1043–1048.
15) Shoaib, K., Rehmani, W., Mohammad, B. and Ali, S. [2012]. ***J. Proteomics Bioinform***.
16) Niazi, S., Javal, Paramesh, C. M. and Shavaraj, S. [2010]. ***Int. J. of Pharmacy Pharm. Sci.,*** 2(3), pp: 108-112.
17) Khan, M. A., Akhtar, S. and Shahid, K. [2014]. **Int. J. Pharm. Sci. Rev. Res.**, 28, pp: 147-151.
18) Mounika, K., Anupama, B., Pragathi, J. and Gyanakumari, C. [2010]. ***J. Sci. Res.,*** 2(3), pp: 513-524.
19) Mishra, A. P., Mishra, R. K. and Shrivastava, S. P. [2009]. ***J. Serb. Chem. Soc.***, 74 (5), pp: 523-535.
20) Turan, N., Körkoca, H., Adigüzel, R., Çolak, N. and Buldurun, K. [2015]. ***Molecules,*** *20*, pp: 9309-9325.
21) Akine, S. and Nabeshima, T. [2005]. ***Inorg. Chem.,*** 44, pp: 1205−1207.
22) Mishra, P. M. [2012]. ***Ultra Chemistry"***, 8 (3), pp: 401-408.
23) Kumar, R., Masih, I. and Fahmi, N. [2013]. ***Spectrochimica Acta Part A,*** 101, pp: 100–106.
24) Adediji, F., Adebayo, M. A. and Obaleye, J. A., [2011]. ***Asian Journal of Applied Science***, 4, pp: 4392-402.

25) Benmansour, S., Triki, S. and Gómez-García, C. J. [2016]. ***Magnetochemistry***, *2*, 1.

26) Pradeepa, S. M., Naik, H. S. B., Kumar, B. V. and Naik, T. R. R., [2013]. ***SpectrochemicaActa Part A,*** 101, pp: 132-139.

27) Kalita, M., Bhattacharjee, T. [2013]. ***Polyhedron***, 60, pp: 47–53.

28) Ghazizadeh, M., Sheikhshoaie, I. and Badiee, A. [2012]. ***Der ChemicaSinica***, 3 (1), pp: 29-37.

29) Kaya, M**.,** Yenikaya, C., Demir, I. and Kalfa, O. M. [2008]. ***Russian J. of General Chem.,*** 78(5), pp: 939–945.

30) Asadi, M., Khah, M. S. [2010]. ***J. Iran Chem. Soc.***, 7(4), 875-882.

31) Abdel-Kader, N. S. and Mohamed, R. R. [2013]. ***J Therm Anal Calorim***.

32) Sakthilatha, D. and Rajavel, R. [2013]. ***Journal of Chemical and Pharmaceutical Research***, 5(1), pp: 57-63.

33) Kettle, S.A. ***[1975]. "Coordination Compound"***, Thomas Nelson and Sons, London, p.3, 186, 212.