Synthesis and Spectral Analysis of Mn (II), Cu (II) ,Ni (II) and Cd (II) Complexes with Mixed Ligands containing 1,10-phenanthroline and Schiff base derived of 4-aminoantipyrine

*Waleed Ali Mahmoud** *Israa Hmood Ibraheem**

Received 9, October, 2013
Accepted 3, November, 2013

Abstract:

The complexes of Schiff base of 4-aminoantipyrine and 1,10-phenanthroline with metal ions Mn (II), Cu (II), Ni (II) and Cd (II) were prepared in ethanolic solution, these complexes were characterized by Infrared , electronic spectra, molar conductance, Atomic Absorption ,microanalysis elemental and magnetic moment measurements. From these studies the tetrahedral geometry structure for the prepared complexes were suggested.The prepared ligand of 4-aminoantipyrine was characterized by using Gc-mass spectrometer .

Key words: 1,10-phenanthroline, Schiff base, metal complexes, 4-aminoantipyrine.

Introduction:

Schiff base named after Hugo Schiff base described the condensation between an aldehyed and an amine, Schiff base ligands are able to coordination metals through imine nitrogen and another group usually linked to aldehyde [1,2]. Schiff bases and their metal complexes are growing importance in coordination chemistry, attributed to react observations in antibacterial, antifungal and oxygen carrier properties. The investigations of structure and bonding of Schiff complexes help understand the complexes. Schiff base of 4-aminoantipyrine and its complexes have a variety of application in biological ,clinical, analytical and pharmacological areas[3]. Earlier work reported that some drugs showed increased activity when administered as metal complexes rather than organic compound[4]. Metal complexes of 4-aminoantipyrine and biological behavior involving the amino group of 4-aminoantipyrine has been studied exhaustively ,when compared to the work carried out on the chemistry of transition metal complexes and biological behavior involving the amino group of 4-aminoantipyrine[3].Various metal complexes with bidentate Schiff base containing nitrogen and oxygen donor atoms play important role biological system and represent interesting models for metalloenzymes,Which efficiently catalyze the reduction of dinitrogen and dioxygen[5].The aims of this work involve synthesis metal complexes from mixed ligands and spectral analysis by different technique.

Materials and Methods:

All chemicals were obtained from commercial sources and were used without further purifications(4-aminoantipyrinSalicyadehyde,Acetic acid glacial,$MnCl_2.4H_2O$, $CuCl_2.2H_2O$, $Cd(NO_3)_2.4H_2O$,$Ni(NO_3)_2.6H_2O$, Ethanol absolute, dimethyl sulphoxide

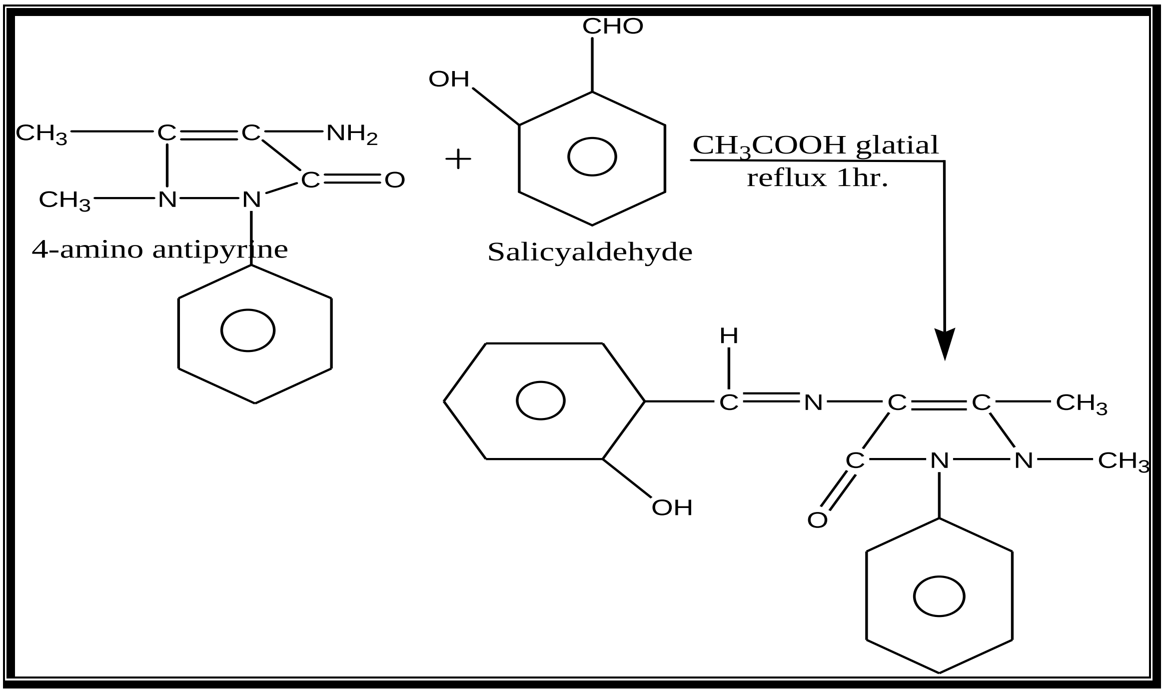
---

*Chemistry Department, College of Science for Women, Baghdad University

from BDH. Potassium hydroxide and 1,10-phenanthroline from Fluka.UV-Visible Spectra were recorded in dimetheylsulphoxide(DMSO) using Shimadzu Uv-160 Spectrophotometer. The FTIR spectra of the ligand and its complexes were recorded using IR Prestig-2 Spectrophotometer as KBr disc. The molar conductance of the complexes were measured in DMSO as a solvent at room temperature using Conductometer WTW, the metals analysis were measured using flame atomic absorption 680A Spectrophotometer, the element microanalysis were recorded [microanalysis (C.H.N)], EA-101.mth,the magnetic susceptibility measurements of the complexes in the solid state were determined using magnetic susceptibility blance Johnosnmatthey, the prepared ligand was recorded by using (GCHS-QP 2010Ultra Shimadzu).The melting apparatus of Gallenkamp M.F.B-60 was used to measure melting point of all prepared ligand and its complexes.

Synthesis of ligand(2-hydroxybenzaldine)4-aminoantipyrine(L)

4-Aminoantipyrine (0.2 gm,0.98 mmole) was dissolved in absolute ethanol (15 ml). Salicyaldehyed (0.12 gm,0.98 mmole) was added to the solution of 4-aminoantipyrine and then added three drops of glacial acetic acid.The mixture was heated under reflux at temperature 70 °C for one hour. During this period the yellow solid was formed.The yellow solid was then collected by filtration , and then recrystallized from absolute ethanol.

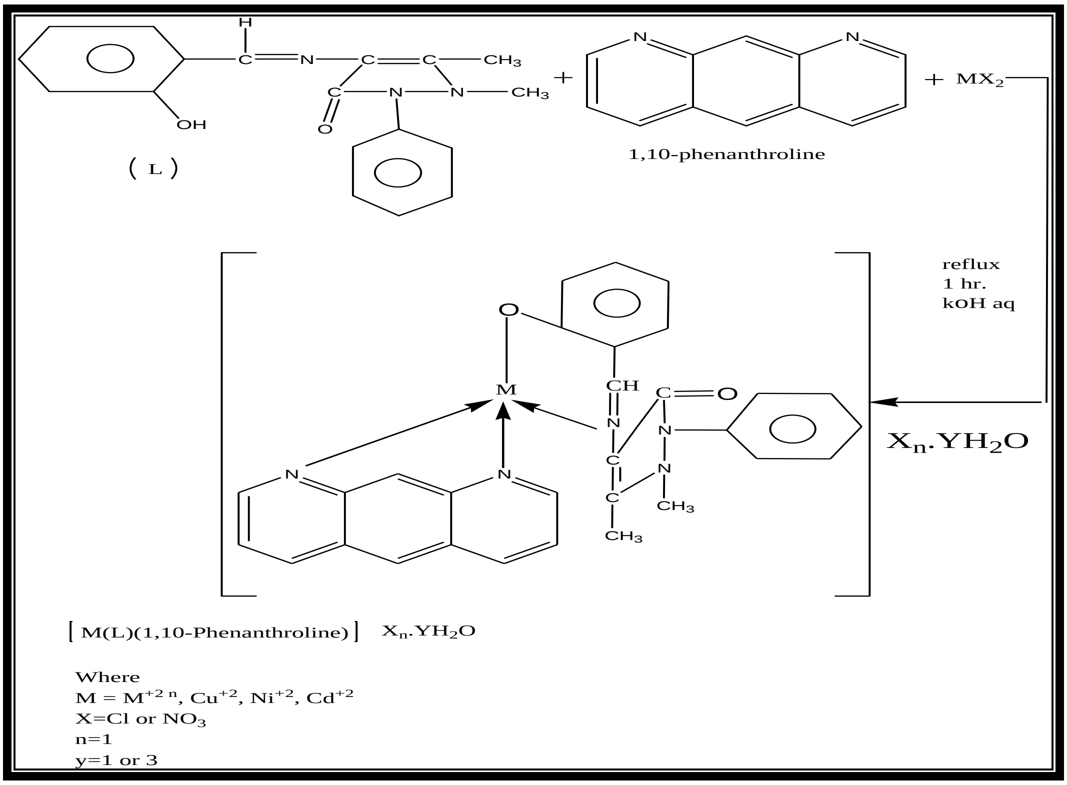


Scheme 1: Synthesis rout of (2-hydroxybenzaldine)4-aminoantipyrine

Synthesis of Metal Complexes

Ligand (L) (0.3 gm,0.97 mmole) was dissolved in absolute ethanol (10 ml). 1,10-phenanthroline (0.19gm,0.95mmole) was dissolved in (10 ml) absolute ethanol added to the solution of (L) and then metal salts[(0.19gm,0.95mmole of $MnCl_2.4H_2O$) (0.17gm,0.99mmole of $Cu.Cl_2.2H_2O$), (0,30gm,0.97mmole of $Cd(NO_3)_2.H_2O$) and (0.29gm,0.99 mmole of $Ni(NO_3)_2.6H_2O$)]

respectively was dissolved in (5 ml) absolute ethanol added to the mixed ligands solution,aqueous solution (0.01 M) of potassium hydroxide three drops was added to the mixture,and then heated under reflux at temperature 70^0C for one hour. During this period, the color solid was formed.The colour solid was then collected by filtration, and then recrystallized from absolute ethanol.



Scheme 2:Synthesis rout of metal complexes from the prepared ligand (L) and 1,10-phenanthroline

Results and Discussion:

The ligand (L) was synthesis by the condensation reaction of 4-aminoantipyrine with salicyaldehyde in 1:1 mole ratio using ethanol as a solvent and the complexes were prepared from the reaction of the ligand (L), ligand(1,10-phenanthroline) and metal salts (MX) in 1:2 mole ratio at reflux in ethanol as a solvent, potassium hydroxide was used a base and pure complexes were formed, these complexes characterized by different techniques. The magnetic moment has been determined in the solid state by faraday's method. The magnetic properties of these complexes should provide a testing ground for the oxidation state of the complexes , therefore provides a way of counting the number of unpaired electron.This should help in predicting to bonding model and electronic structure. The conductivity measurement for a complex is used to determine the conduntance to the compound (electrolyt or nonelectrolyte).

Table 1:The physical properties of ligand (L) and its metal complexes,molar conductivity, magnetic susceptibility measurements for metal complexes

Compound	**M.wt**	**Color**	**Yield%**	**m.p(^{0}C)**	***μeff (B.M)***	**Molar Conductivity (Ω^{-1}.cm^2.mol^1)**
L	307	Yellow	87	240	-	-
[Mn(L) (1,10-phenantholine)] Cl.3H_2O	648.66	PallYellow	64	180 d.	4.88	35
[Cu(L) (1,10-phenanthroline)] Cl.3H_2O	658.27	Green	57	192 d.	1.86	38
[Ni(L) (1,10-phenathroline)] NO_3.3H_2O	678.92	Light green	75	140 d.	3.11	32
[Cd(L)(1,10-phenanthroline)] NO_3.H_2O	696.64	Yellow	78	145 d.	0.00	36

Where d.= decomposition

Table 2:Microanalysis of Schiff base ligand(L) and its metal complexes

Compound	Elemental microanalysis (calc.) found %			Metal percentage (calc.) found %
	C	H	N	
L	(70.34) 70.65	(5.54) 5.13	(13.68) 12.92	-
[Mn(L) (1,10-phenanthroline)] Cl.3H_2O	(55.49) 55.20	(4.93) 4.11	(10.79) 9.83	(8.52) 8.46
[Cu (L) (1,10-phenanthroline)] Cl.3H_2O	(54.63) 54.32	(4.86) 4.55	(10.63) 9.88	(9.42) 9.65
[Ni (L) (1,10-phenanthroline)] NO_3.3H_2O	(53.02) 53.78	(4.71) 4.52	(12.37) 11.52	(7.88) 8.64
[Cd (L) (1,10-phenanthroline)] NO3. H_2O	(51.67) 52.66	(4.01) 4.02	(12.5) 12.47	(16.98) 16.13

GC-Mass Spectrometer for the prepared ligand (L)

The molecular ion peak for the prepared ligand (2-hydroxybenzaldine) 4-aminoantipyrine is observed at m/z = 307 (M) (relative abundance is 100%) for $C_{18}H_{17}N_3O_2$ which excellent agreement with theoretical values[6],these results showed in figure(1).

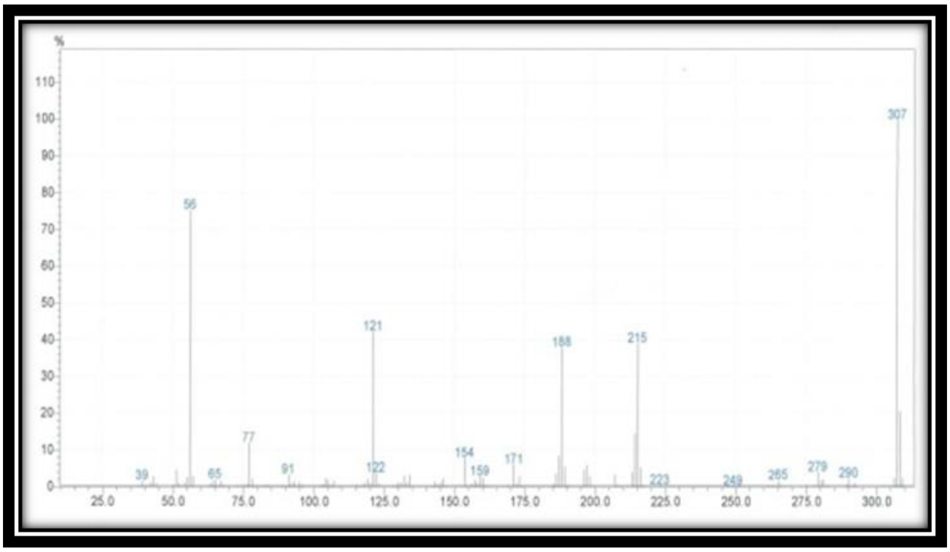


Fig. (1): Gc-Mass spectrum of ligand (L)

The Infrared Spectral Studies

The stretching vibration band at (3420 cm^{-1}) was attributed to ν (OH) group of phenolic, the disappearance vibration (OH) of this band in the spectra off all complexes indicated the deprotonation of the phenolic oxygen with the central metal atom [7],the band at (1654 cm^{-1}) was attributed to carbonyl group present in the free

Schiff base ligand.This band shifted to lower frequency (1651,1624,1639 and 1635) cm^{-1} in IR spactra for manganese,copper,nickel and cadmium complexes respectively,which indicated the complexes formation[8]. The band at (1593 cm^{-1}) which is attributed to ν(C=N) azomethine of Schiff base ligand and shifted to lower frequency can be attributed to the coordination of the central metal atom with the nitrogen atom of azomethine group[9],the band at (1616) cm^{-1} in the spectrum of 1,10-phenanthroline was shifted to lower frequency in the IR spectra of all complexes and appeared at rang (1581-1604) cm^{-1}, these shifting indicate the coordination between two nitrogen atoms at 1,10-phenanthroline and metal [10].

The spectra appeared new bands at rang (447-609) cm^{-1} and (401-417) cm^{-1}which were assignable to stretching vibration of (M—Nitrogen) and (M—Oxygen) respectively [11]. The bands at (3412, 3375,3429 and 3411) cm^{-1} can be assigned to the stretching vibration of (OH) of water molecules for manganses, copper,nickel, and cadmium complexes respectively.The result led to assugestion of presence of water molecules in all complexes [12].The figures 2,3,4 and 5 show the FTIR for the prepared ligand, 1,10-phenanthroline, copper and nickel complexes respectively.

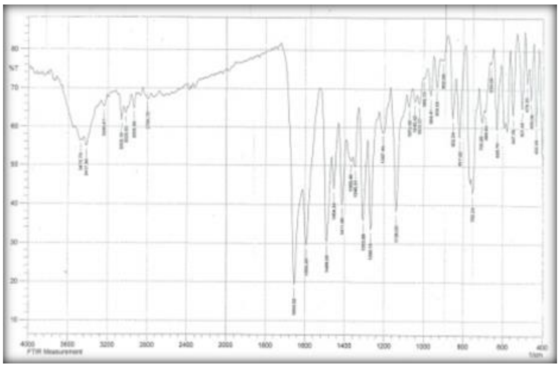


Fig.(2):FT-IR of prepared ligand(L)

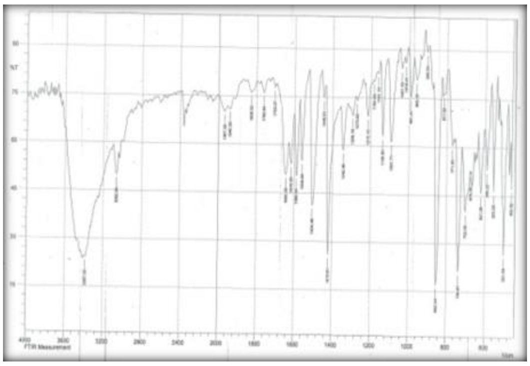


Fig. (3):FT-IR of 1,10-phenanthroline

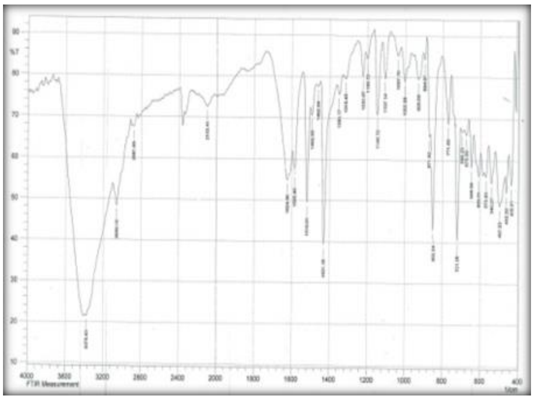


Fig.(4):FT-IR of Cu complex

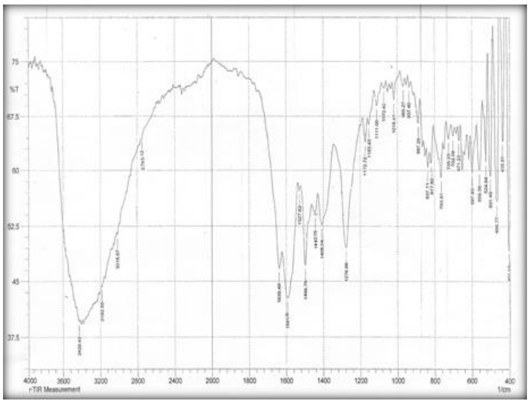


Fig.(5):FT-IR of Ni complex

Table 3: The Infrared data of mixed ligands and its metal complexes

compound	ν (OH) water	ν (OH)pheolic	ν (C=O)	ν (C=N)	ν (M-N)	ν (M-O)
L	-	3240	1654	1593	-	-
1,10-phenanthroline	-	-	-	1616	-	-
[Mn(L)(1,10-phenanthroline]Cl.3H_2O	3412	-	1651	1512	447	416
[Cu(L)(1,10-phenanthroline)]Cl. 3H_2O	3375	-	1624	1519	609	417
[Ni(L)(1,10-phenanthroline)]NO_3.3H_2O	4329	-	1639	1527	524	401
[Cd(L)(1,10-phenanthroline)]NO_3.H_2O	3411	-	1635	1522	609	413

The Electronic Spectral Studies

The electronic spectra of free Schiff base derived from 4-aminoantipyrine show one strong peak at 450 nm (28589 cm^{-1}) which was assigned to ($\pi\rightarrow\pi^*$) electronic transition.The electronic spectrum of 1,10-phenanthroline shows one strong peak at 318 nm (31446 cm^{-1}) can be assigned to ($n\rightarrow\pi^*$) electronic transition of aromatic rings and unconjugated chromophore[13].The electronic spectrum of manganese complex showed four peaks, the first strong peak at 345 nm (28589 cm^{-1}) was attributed to charge transfer transition, other three peaks 755nm (13245 cm^{-1}),842 nm (11876 cm^{-1}) and 976 nm (10245 cm^{-1}) were found to be caused by(d─d) electronic transition which was assigned to ${}^6A_1\rightarrow{}^4E_1$, ${}^6A_1\rightarrow{}^4T_2(G^4)$, and ${}^6A_1\rightarrow{}^4T_1(G^4)$ respectively, suggestion tetrahedral geometry around manganese ion [14].

Electronic spectrum of copper complex , showed peak at 304 nm (32894 cm^{-1}) attributed to charge transfer transition (C.T), the peak at 737 nm (13568 cm^{-1}) attributed to ${}^2T\rightarrow{}^2E$ electronic transition,these transition were indicated the complex is tetrahedral.The electronic spectrum of nickel complex appeared at 301 nm (33222 cm^{-1}) attributed to ${}^3T_1\rightarrow{}^3T_1(P)$ which was overlaped with the peak charge transfer transition (C.T), the other peak at 360 nm (27777 cm^{-1}) can be assigned to ${}^3T_1\rightarrow{}^3A_2$ electronic transition, suggestion tetrahedral geometry around the nickel ionThe electronic spectrum of cadmium complex, showed two peaks at 314 nm (3184 cm^{-1}) and 345 nm (28985 cm^{-1}) were assigned to charge transfer, suggestion tetrahedral geometry around cadmium ion[15].The figure 6,7,8 and 9 show the electronic spectrum for the prepared ligand,1,10-phenanthroline, manganese and cadmium complexes respectively.

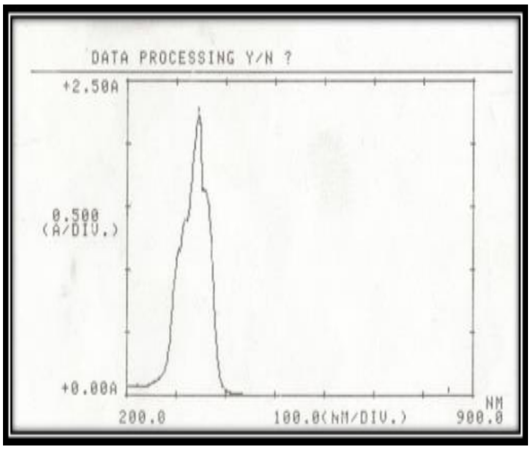


Fig.(6):Electronic sprctrum of prepared ligand(L)

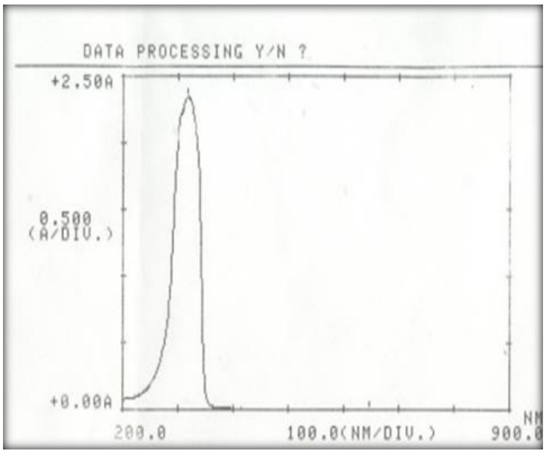


Fig. (7):Electronic spectrum of 1,10-phenanthroline

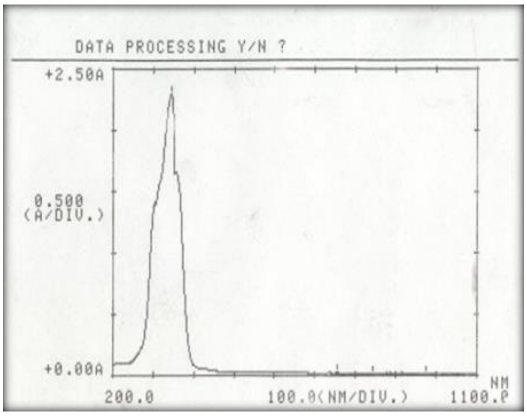


Fig.(8):Electronic spectrum of Mn complex

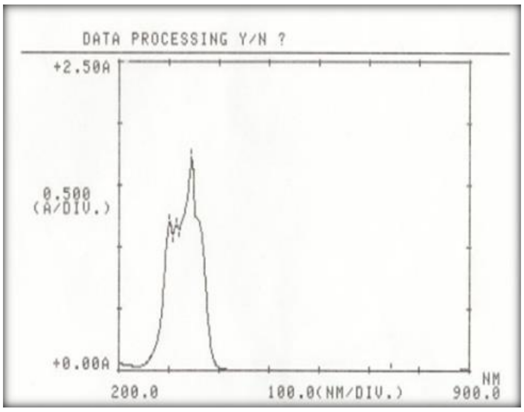


Fig.(9):Electronic spectrum of Cd complex

Table 4: Electronic spectrum data of free Schiff base ligand ,1,10- henanthroline and its metal complexes

Compound	λmax (nm)	Wave Number(cm^{-1})	ABS.	Σ max ($mol^{-1}.\ell.cm^{-1}$)	Assignment	Suggested Structure
1,10-phenanthroline (L)	345 318	28589 31446	2.2333 2.340	2233 2340	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-
[Mn(L)(1,10-phenanthroline)]Cl.3H_2O	345 755 842 976	2898 13245 11876 10245	2.297 0.022 0.018 0.020	2297 22 18 20	Charge transfer $^6A_1 \rightarrow {}^4E, {}^4A_1$ $^6A_1 \rightarrow {}^4T_2(G^4)$ $^6A_1 \rightarrow {}^4T_1(G^4)$	Tetrahedral
[Cu (L)(1,10-phenanthroline)]Cl.3H_2O	304 737	32894 13568	1.854 0.044	1854 44	Charge transfer $^2T \rightarrow {}^2E$	Tetrahedral
[Ni (L)(1,10-phenanthroline)] NO_3.3H_2O	301 360	33222 27777	1.478 1.689	1478 1689	$^3T_1 \rightarrow {}^3T_1$ (p) $^3T_1 \rightarrow {}^3A_2$	Tetrahedral
[Cd (L)(1,10-phenanthroline)] NO_3. H_2O	314 345	31847 28985	1.172 1.734	1172 1734	Charge transfer Charge transfer	Tetrahedral

Conclusion:

The prepared ligand is bidentate, the molecular structures for all the prepared metal complexes from mixed ligands [(2-hydroxybenzaldine)4-aminoantipyrine and 1,10-phenanthroline] are tetrahedral and these metal complexes have electrolyte nature,the magnetic moment measurements for the prepared metal complexes are paramagnetic except the cadmium complex is diamagnetic.

References:

[1] Seitz M., Kaiser A., Stempfhuber S., Zabel m., Reiser O., 2004. Helical, nonracemic inorganic hybrid polymers of cadmium halides with pentadentatebis (oxazoline) ligands, J.Am.Chem. Soc.126(37):11426.

[2] Shibuya Y., Nabari K., Kondo M., Yasue S.,Maeda K., Uchida F.,Kawaguchi H.,2008.The copper (II) complex with two didentate Schiff base ligands,the unigue rearrangement that proceeds under alcohol vaper in the solid state to contract noninclusion structure .Chem. Lett. 37(1):78.

[3] Raman N.,Thalamuthu S., Dhaveedhuraja J.,Neelakandan M.N.,Sharmilla Banerjee. 2008. DNA cleavage and antimicrobial actimicrobial activity studies on transition metal (II) complexes of 4-aminoantipyrine derivative. J. Chilian Chem .Soc., 53N.

[4] Dharmaraj N.,Viswanathamurthi P., Natarajan K., 2001. Ruthenium (II) complexes containing bidentate Schiff base and their antifungal activity.Transition Met. Chem., 26:105.

[5] Kasmov V.T.,Ozalp-Yaman S.,Tas E.,2005.Synthesis,spectroscopy and

electrochemical behaviors of nickel (II) complexes with tetradentate Schiff base derived from 3,5-Bu(2)(t)-salicyladehyde, Spectrochim. Acta A 62(1-3):716.

[6] Shdrick I.M.Paris,Unige A. Lasky, Staffen Tschirschwitz, 2010. Manganese (II) complexes of di-2-pyridinylmethylene-1,2-diimine di-Schiff base ligands:structure and reactivity,Inorg.Chim.Acta.363:(3390-3398).

[7] Ayari F., Srasra E.and Trabelsi M.A.,2007.Retention of Organic Molecules Quinalizarin by Bentonitic Clay Saturated with different cations, Desalination, 206:499.

[8] Suresh M.S. and V. Prakash,2010. preparation and characterization of Cr(II),Mn(II), Co(II),Ni(II), Cu(II), Zn(II)and Cd(II) chelates of Schiff base derived from Vanillin and 4-aminoantipyrine,Int.J.phy.Sci.,5:2203-2211.

[9] Shayma A.S., 2010. Sythesis, spectral and magnetic studies of Newly Mixed ligand complexes of 4-formylacetanilidethiosemicarbazone and 3,4-dihydroxy-cinnamic acid with some metal ions, Accepted in Journal of chemistry,(in press),7(5).

[10]Mohammed G.G., M.M. Omer and Hindy A.M.,2006.Metal complexes of Schiff base:Preparation ,characterization and biological activity.Turk.J.Chem.30:361-382.

[11]Cross A.D. and Alan J.,1969.An Introduction to practical Infrared Spectroscopy. Butter worths, London,3ed.

[12] Sonmez, M. and Sekerci M.,2002. Synthesis and characterization of Zn(II),Co(II),Ni(II) and Cu(II) Schiff bases complexes from 1-Amino-5-benzoyl-4-phenyl-1H–Pyrimidine -2-one with Salicyladehyd. Polish .J.Chem. 76(7):907-914.

[13]Huheey J.H, 1994. Inorganic Chemistry Principle of Structure and Reactivity. Harper and Row paper publishers, Harper Introduction Edition New York.

[14] Lutfullah,Ahmed U.,Mohammed M.R.,Mohammed M.K.and Yoon B.H., 2007.Synthesis and physic-Chemical and Spectroscopic Investigation of Sodium dihydrobis (1,2,3,-benzotriazoyl) borate ligand and its transition metal complexes ,Turk J.Chem.M31:179.

[15] Shayma A. Shaker, H.A. Mohammedana Abbas Ali Salih, 2010. Preparation, Physico-Chemical and Spectroscopic Investigation of Thiaacetazone and Quinalizarin Complexes with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pd(II).J. of Basic and Applied Sciences,4(10):5178-5183.

تحضير وتحليل طيفي لمعقدات المنغنيز، النحاس، النيكل و الكادميوم ثنائية التكافؤ مع ليكاندات مختلطه حاويه 1, 10 - فينا نثرولين وقواعد شيف المشتقه من 4-امينوانتي بايرين

وليد علي محمود   اسراء حمود ابراهيم**

*قسم الكيمياء، كلية العلوم للبنات – جامعة بغداد

الخلاصـه:

حضرت معقدات قاعدة شيف و1،10 – فينا نثرولين مع $Mn^{(II)}$ ، $Cu^{(II)}$ ، $Ni^{(II)}$ و $Cd^{(II)}$ في الايثانول ، شخصت هذه المعقدات بواسطة الاشعه تحت الحمراء ،طيف الاشعه فوق البنفسجيه – المرئيه ، التوصيليه المولاريه الكهربائيه والتحليل الدقيق للعناصر، تحليل محتوى الفلز وقياس الحساسيه المغناطيسيه بينت هذه الطرائق الشكل الهندسي المقترح للمعقدات هو رباعي السطوح ، كما تم تشخيص الليكاند بوساطه طيف الكتله اضافه الى الطرق الطيفيه المذكوره .