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Synthesis and Characterization of Schiffbases Andcr (Ii), Fe (Ii) and Cd(Ii) Complexes Derived From Ethelene Diammine With 1-Phenyl-1, 3-Butanedion and 4-Aminoantipyrine

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Israa Jirjees
College of Science,Unvirsty of Thi-qar
Email: israajirjees95@gmail.com

Abstract

Schiff base ligand **[**(4Z,11aE,15E) -2,3,59,10 - pentamethyl -1,7,11-triphenyl-2,6,10,11,13,14-hexahydro -1H - dipyrazol [4,3-b:3',4'-h][1,4,7,10] tetraazacyclotridecine**]** was synthesized by reacting 1-Phenyl,1,3-butanedion and 4-aminoantipyrin with Ethylenediamine.Its complexes with Cr (II),Fe (II) and Cd (II) reaction of the metal salt with the ligand characterization ligands and its complexes were characterized by elements analyses , FT-IR , Mass techniques and ^{1}H-NMR

Keywords: Schiff Base, Synthesis, ethylene diamine, 1-Phenyl,1,3-butanedion ,Transition Metal complex.

تحضيروتشخيص قواعد شف ومعقداتها الكروم (II) والحديد(II) والكادميوم (II) المشتقة من ١- فنيل-١، ٣- بيوتان دايون واثلين ثنائي امين مع ٤- امينوانتبايرين

الملخص

تم تحضير قاعدة شف جديدة من تكثيف ١- فنيل-١، ٣ - بيوتان دايون و اثلين ثنائي امين مع ٤- امينو انتبايرين باستعمال كحول الايثانول كمذيب وحامض الخليك الثلجي كعامل مساعد . وشخصت القاعدة المحضرة باستخدام تقنية التحليل الدقيق للعناصروطيف الاشعة تحت الحمراءوطيف الرنين النووي المغناطيسي للبروتون وقد تبين من النتائج ان قاعدة شف المحضرة رباعية السن. كذلك تم مفاعلة القاعدة الناتجة مع بعض ايونات العناصر الانتقالية ثنائية التكافؤهي ايون الكروم **(II)** وايون الحديد**(II)** وايون الكادميوم **(II)** ومن نتائج التشخيص تبين ان الشكل الهندسي للمعقدات المحضرة هوهيئة ثمانية السطوح .

Introduction

Schiff bases are chemical compounds usually formed by the condensation of an aldehyde or ketone with primary amine [1] (Fig. 1) and generally take place under acid, base catalysis or with heat [2] [3]. It contains the dual carbon-nitrogen bond (HC=N) called a azomethine group. Schiff base ligands are essential in the field of coordination chemistry[4][5], especially in the development of complexes of Schiff bases because these compounds are potentially capable of forming stable complexes with metal ions [6][7] initially developed by Hugo Schiff in 1864 [8] [9]. It has a wide range of applications in many analytical[10], clinical, biologic[11] and applied fields because of its physical and chemical properties. Schiff bases are very important tools of the inorganic chemists as these are widely used to design molecular ferromagnetism [12] Schiff bases play an important role in inorganic chemistry as they can easily form stable complexes with most transition metal ions. [13] The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve for biologically important. Schiff base metal complexes were investigated for and are of special interest because of the variety of ways in which they are bonded to metal ions. Schiff bases are very good chelating ligands and transition metals could form highly efficient Schiff base complexes [14][15]. Atoms like N, O and S present at the active site of bimolecular play a key role in the coordination of transition metals [16] [17]. The present work was devoted to elucidating the structures of new series of Cr(||), Fe(||) and Cd(||)complexes with 1-Phenyl,1,3-butandion, 4-aminoantipyrin and Ethylenediamine.

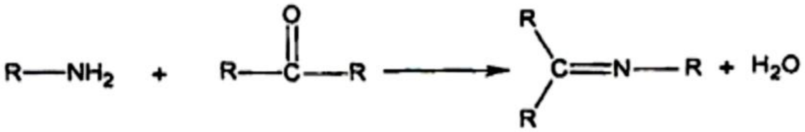


Fig.1 General synthesis of Schiffbas

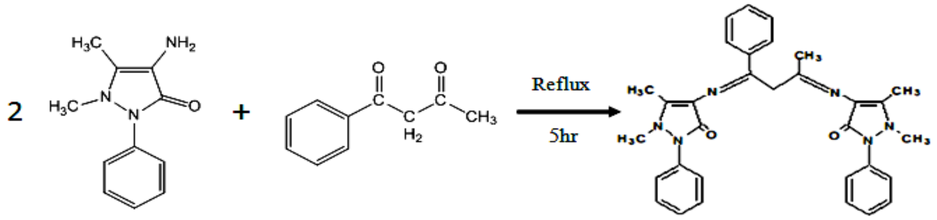
Materials and Methods

All chemicals were obtained from commercial sources and were used without further purification. the chemicals materials are 4-aminoantipyrin, 1-Phenyl,1,3-butanedion, Ethylenediamine , Acetic acid glacial ,$CrCl_2.6H_2O$, $FeCl_2.6H_2O$, $Cd(NO_3)_2.4H_2O$, Ethanol absolute, from (BDH) and G.C.C. The FTIR spectra of the ligand and its complexes were recorded using IR affinity (Spectrometer Shimadzu as KBr disc. Proton nuclear magnetic resonance (^{1}H-NMR; 500MHz) spectra were obtained at room temperature with Bruker DRX System using TMS as an internal standard in dimethylsulfoxide (DMSO-d6). The elemental analyses of carbon, hydrogen and nitrogen contents were performed using a Perkin Elmer Thermofinigan flash(CHN2400). The molar conductivities of freshly prepared 10^{-3}M dimethylsulfoxide solutions were measured for the dissolved complexes using Inolabcond720.The Mass spectral of the compounds were recorded by Work mass selective Detector 5973.

Synthesis of Schiff base (M)

The first step: An ethanolic solution (15ml) of (0.406g, 0.002mol) (4-aminoantipyrine) was added to an ethanolic solution (10ml) of 1-Phenyl ,1 , 3 - butanedion (0.162g , 0.001mol) and few drops of glacial acetic acid were added to reaction mixture with continuous stirring and refluxing at (60C) for (5hr), It was filtered and re-crystallized from Ethanol.

The second step: was added Ethylenediamine (1ml, 0.001 mol) to (0.532g, 0.005 mol) to the ethanolic solution (30ml) the result at the first step . Then few drops of glacial acetic acid were added to the mixture. The mixture was refluxed for (10 hr). The green solid (M) product was separated. It was filtered and re-crystallized from ethanol Fig.2. Yield:54%



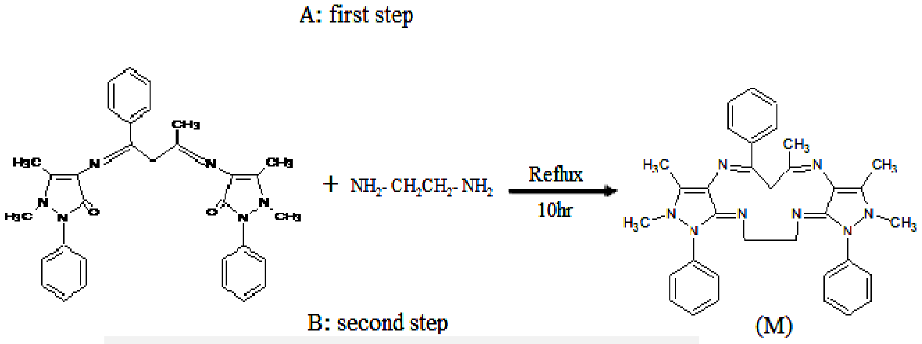


Fig.2 Synthesis of Schiff base (M)

Synthesis of complexes (M)

Chromium complex synthesis

The Schiff base (M) (0.278g, 0.0005 mol) dissolved in hot ethanol (10ml) was added to a hot ethanolic solution (10ml) of the $CrCl_2.6H_2O$ (0.115 g, 0.0005 mol) and refluxed for 5 hr. The solid product separated was filtered and washed with hot ethanol. Yield:66%; m.p141- 140°C .

Iron complex synthesis

The Schiff base (M) (0.278g, 0.0005 mol) dissolved in hot ethanol (10ml) was added to a hot ethanolic solution (10ml) of the ($FeCl_2.6H_2O$ 0.082g, 0.0005mol) and refluxed for 6 hr. The solid product separated was filtered and washed with hot ethanol. Yield:72%; m.p: 136-137

Cadmium complex synthesis

The Schiff base (M) (0.278g, 0.0005 mol) dissolved in hot ethanol (10ml) was added to a hot ethanolic solution (10ml) of the$Cd(NO_3)_2.4H_2O$ (0.154g, 0.005 mol) and refluxed for 5 hr. The solid product separated was filtered and washed with hot ethanol. Yield:64%; m.p154- 153°C .

Results and Discussion

FT- IR spectra

The spectrum of the ligands (M) shows three different bands –C=N in the region 1616-1602-1535 cm^{-1} for (M) which are shifted to higher frequencies in the spectra of all the complexes like Chromium complex in the range (1636-1545),(M–N at 486) cm^{-1} and Iron complex in the range (1648-

1577), (M–N at 432) cm^{-1} and Cadmium complex in the range (1639-1549), (M–N at 454) cm^{-1} Also indicating the involvement of –C=N nitrogen in coordination to the metal ion in the range(486-432) [18][19]. Accordingly, the ligand acts as a tetra dentate chelating agent, bonded to the metal ion via the four nitrogen C=N atoms of the Schiff base. These bands were absent in the spectra of free ligands, thus confirming participation of the (M-N)[20][21] in the coordination. The figures3,4,5

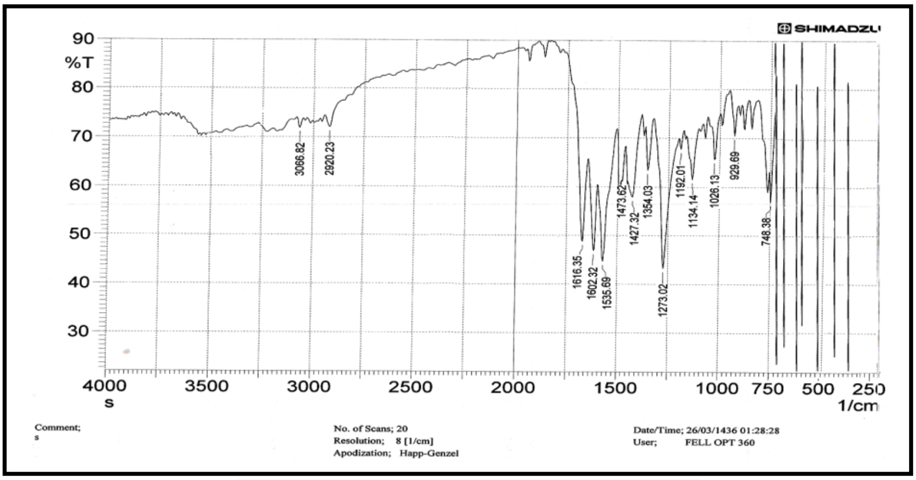


Fig.3 FT- IR of ligand (M)

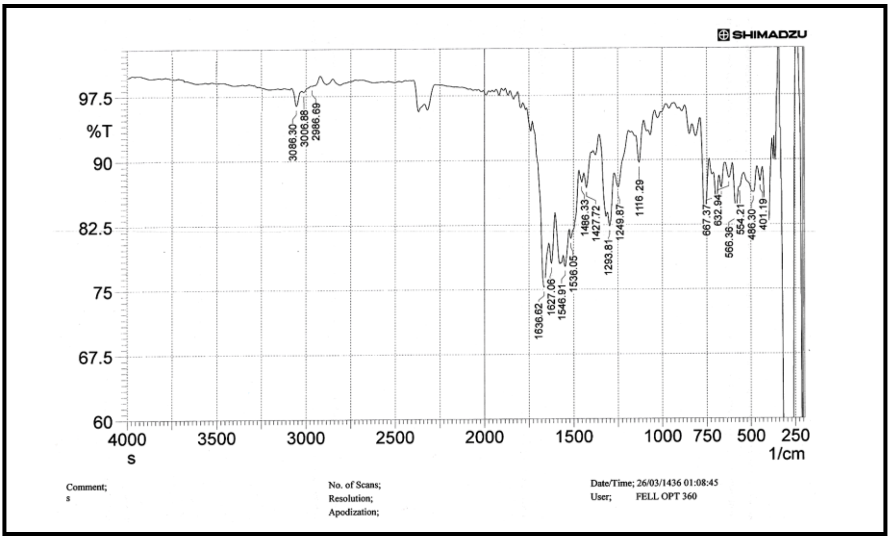


Fig.4 FT- IR of $[Cr(M)Cl_2]$ complex

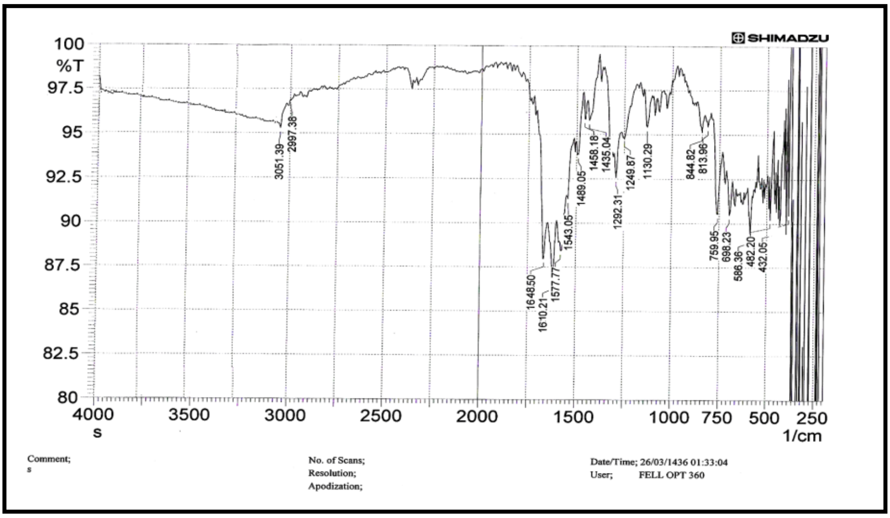


Fig.5 FT- IR of[Fe(M)Cl_2]complex

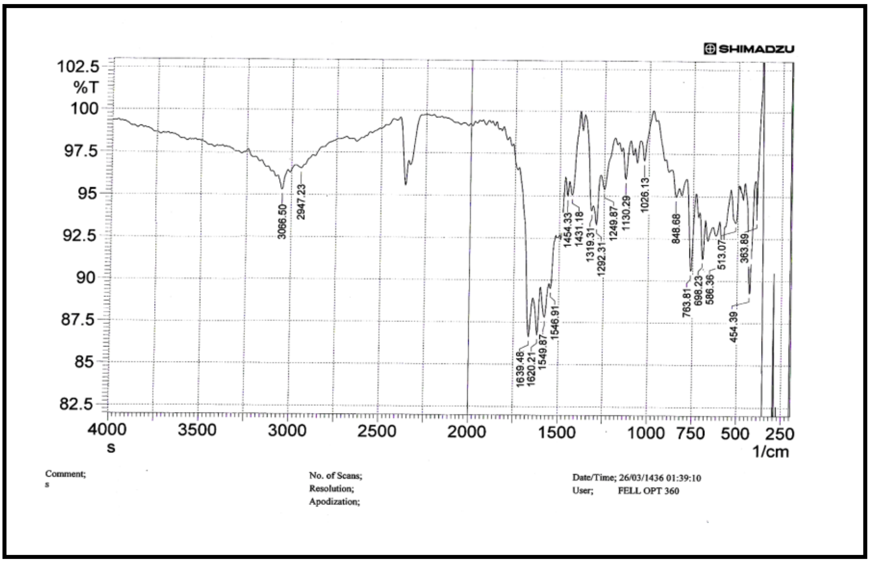


Fig.6 FT- IR of [Cd (M)(NO_3) $_2$] complex

^{1}*H NMR*

The ^{1}H NMR spectrum of Schiff bases ligand (M) in $CDCl_3$ gives the following signals: (CH_3)at 1.85ppm (CH_3-C=) at 1.915 ppm,(CH_2) at 3.122

ppm ,(CH_3-N) at 3.442 ppm The peak at 3.744 ppm to the (CH_2 - CH_2) and phenyl a

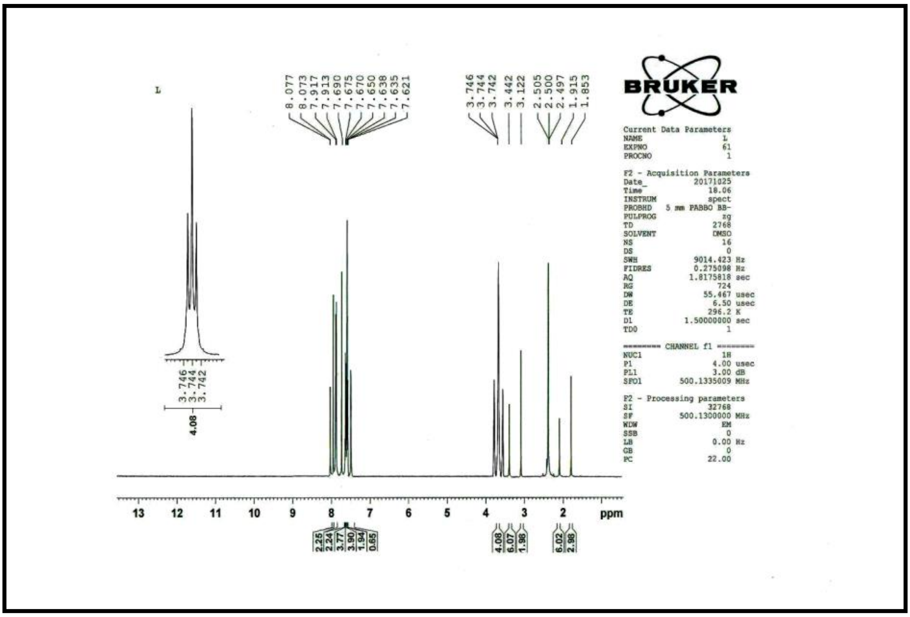


Fig.7 ^{1}H NMR spectrum of ligand(M)

Mass spectra

The mass spectra of Schiff bases ligand and their complex molecular ion peak for the ligand is observed at 556 m/z ratio which is also supported by the “Nitrogen Rule”, since the compound possesses the even number of nitrogen atoms. The molecular ion peak for the Chromium complex ,Iron complex and Cadmium complex was observed at 714,717and 792 m/z which confirms the stoichiometry of metal chalets as $MLCl_2$ or $ML(NO_3)_2$ type. . It is also supported by the mass spectra of other complexes. Micro analytical data are also in close agreement with the values calculated from molecular formula assigned to these complexes, which is further supported by the mass studies of representative complexes. Fig.8,9, 10,11.

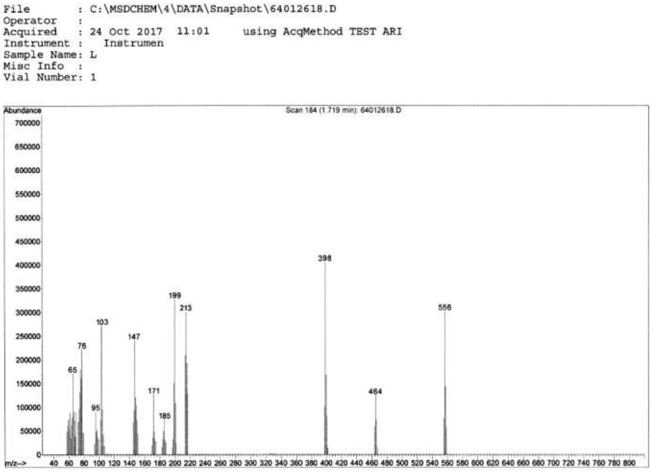


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Fig.8 Mass spectrum of ligand (M)

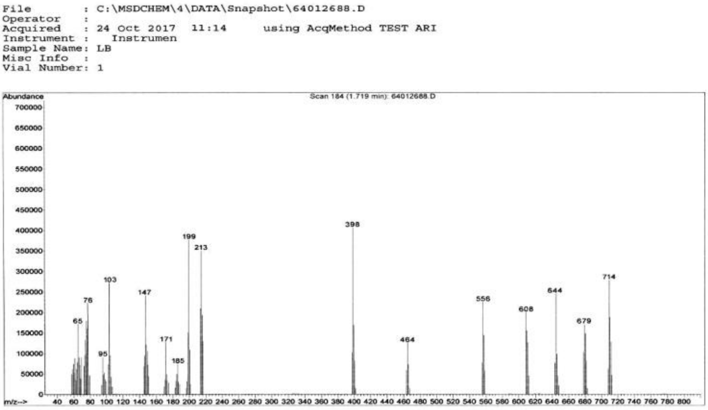

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Fig.9 Mass spectrum of [Cr(M)Cl_2]complex

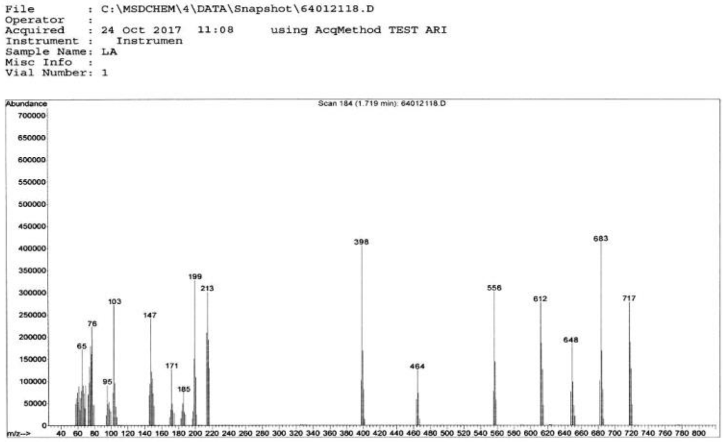

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Fig.10 Mass spectrum of [Fe(M)Cl$_2$]complex

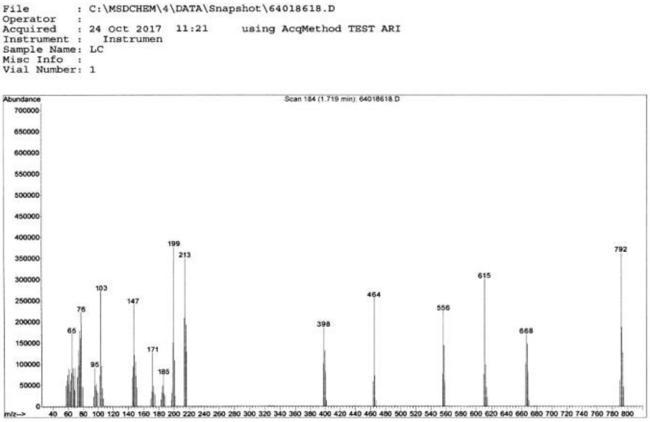

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Fig.11 Mass spectrum of[Cd (M) (NO$_3$) $_2$]complex

Elemental Analysis

The results of the precise analysis of the elements of the ligand record are shown in (Table1), which shows the correspondence between the practical and calculated percentages of the compound.

table 1: analysis of the elements of the ligand (M)

Element	**C**	**H**	**N**
Theoretical Percent	73.56	6.82	20.03
Experimental Percent	73.48	6.67	20.02

Molar conductance

The analytical data for the ligand (M) and complexes together with some physical properties are summarized in (Table2). The molar conductance values are in the range of 12 - 30 ohm^{-1} cm^{-2}mol^{-1} indicating the non electrolytic nature of the complexes[22]. The analytical data of the complexes correspond well with the general formula MXA_2, where X = Cr (II), Fe (II) and Cd (II) ; M $C_{34}H_{36}N_8$; A =Cl ,NO_3. The Molar Electrical Conductivity of the complexes at room temperature are consistent with octahedral geometry around the central metal ion.

Table2:Molar conductance data of the (M) and its complexes

Compound	**Molecular formula**	**Color**	**Molar Conductance Λ m (mho cm^2 /mol^{-1})**
M	$C_{34}H_{36}N_8$	Green	----
[Cr (M)Cl_2]	[Cr($C_{34}H_{36}N_8$) Cl_2]	Brown	12
[Fe(M)Cl_2]	[Fe ($C_{34}H_{36}N_8$) Cl_2]	Dark brown	30
[Cd (M)(NO_3) $_2$]	[Cd ($C_{34}H_{36}N_8$) NO_3) $_2$]	Dark yellow	22

Conclusion

The ligand (M) was successfully synthesized. The ligand was treated to different transition metal salt to afford the corresponding complexes such as Cr(||),Fe(||),Cd(||)The ligands and their complexes are characterized using Element analysis and molecular conductivity, as well as the use of infrared spectra, NMR spectra and mass spectrometry.These analytical and spectral data suggests It was concluded that the ligand(M) acts as a tetra dentate chelating agent, and obtains consistency through nitrogen atoms for C=N groups with atoms of transient elements. Octahedral geometry was proposed for the prepared complexes.

References

1- H Schiff Mitteilungen aus dem university atslaboratorium in Pisa: Eineneue reihe organischer basen. Justus Liebigs Ann Chem. (1864), 131: 118.

2- Abbas, S.A., Munir, M., Fatima, A., Naheed, S. and Inlays, Z. Synthesis, Characteriza- tion and Biotical Studies of Some Transition

Metal Complexes Containing Tetra Dentate and Neutral Bi Dentate Schiff Base. Electronic-Journal of Life Science. (2010), 1: 37- 40.

3- El-Mossalamy, E.H., Al-Thabati, S.A., Al- Nowalser, F.M. and Al-Sulami, Q.A. Solvent Effects on the Electronic Absorption Spectra and Dissociation Constants of Some Sulfa Drugs. Sciences University of Ankara Series. (2005), 51:21-30.

4- A. M. Hamil, K. M. Khalifa, A. Al-Houni, and M. M. El-Ajaily. Synthesis, spectroscopic investigation and ant activity of Schiff base complexes of cobalt (II) and copper (II) ions. Rasayan Journal of Chemistry. (2009), 2:261-266.

5- A. P. Mishra and N. Sharma. Synthesis, characterization, X-ray and thermal studies of some Schiff base metal complexes. Journal of the Indian Council of Chemists. (2009),26:125–129.

6- Losada, J., Del Peso I. and Beyer L. Electro chemical and Spectro electro chemical Properties of Copper(II) Schiff-Base Complexes. Inorganic Chemical Acta . (2001), 321: 107-115.

7-Santos, M.L.P., Bagatin, I.A., Pereira, E.M. and Ferreira, A.M.D.C.: Redox Behavior and Reactivity of Di-Schiff Base-Copper(II) Complexes toward Reduced Oxygen Species. Journal of the Chemical Society, Dalton Transactions, (2001) , Issue 6:838-844.

8- Khouba, Z., Benabdallah, T. and Maschke, U. photometric Study of Liquid Crystals Containing Pentadentate Schiff Base Type Systems. Physics (2009), Procedia. 2:1305-1311.

9- Jafar Attar Gharamaleki1, Fahimeh Akbari1, Akram Karbalaei1, Kamran B. Ghiassi, Marilyn MOlmstead. Synthesis, Characterization and Crystal Structure of a New Schiff Base Ligand from a Bis(Thiazoline) Template and Hydrolytic Cleavage of the Imine Bond Induced by aCo(II) Cation Open Journal of Inorganic Chemistry. (2016), 6: 76-88

10-Z. Cimerman, C. Miljanic, N. Galie, Croatica Chemica Acta. Schiff Bases Derived from Aminopyridines as Spectro fluorimetric Analytical Reagents . (2000), 73: 1- 81.

11- Kadhiravansivasamy K, Sivajiganesan S, Periyathambi T, Nandhakumar V, Chidambaram S and Manimekalai R. Synthesis and Characterization of Schiff Base CoII, NiII and CuII Complexes Derived from 2-Hydroxy-1-naphthaldehyde and 2-Picolylamine) . Mod Chem appl . (2017), 5:1 DOI : 10.4172 / 2329-6798.1000197.

12- C.Dominik K. Branko, crysteng-comm. Schiff base derived from 2-hydroxy-1-naphthaldehydeand liquid-assisted mechanic chemical synthesis of its isostructural Cu(II) and Co(II) complexes. CrystEng Comm Issue(2011), 13:4351.

13- Mostafa Y. Nassar, Ibrahim S. Ahmed, Hasssan A. Dessouki, Sobhia S. Ali. Synthesis and characterization of some Schiff base complexes derived from 2, 5- dihydroxy acetophenone with transition metal ions and their biological activity Journal of Basic and Environmental Sciences. (2018) ,5: 60-71.

14- Clarke B, et al. Transition-metal Schiff-base complexes as ligands in tin chemistry. Part 7. Reactions of organotin (IV) Lewis acids with [M (L)] 2 [M-Ni], Cu and Zn; H2LN, N-bis (3-methoxysalicylidene) benzene-1, 3-diamine and its -1, 4-diamine analog. J Organomet Chem. (1998), 559: 55-64.

15 - Angela Patti, Sonia Pedotti , Francesco Paolo Ballistreri and Giuseppe Trusso Sfrazzetto. Synthesis and Characterization of Some Chiral Metal-Salen Complexes Bearing aFerro- cenophane Substituent Molecules. . (2009), 14: 4312-4325.

16- Cozzi PG .Metal–Salen Schiff base complexes in catalysis practical aspects. Chem Soc.(2004), Rev.33: 410-421.

17- Antony A, Fasna F, Ajil PA and Varkey JT. Amino Acid based Schiff Bases and its Zn (II) Complexes Research and Reviews: Journal of Chemistry. (2016), p-ISSN:2322-00.

18- H. Keypour, M. Shayesteh, M. Razaeivala, F. Chalabein, Y. Elerman. Synthesis, spectral characterization, structural investigation and antimicrobial studies of mononuclear Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) complexes of a new potentially hexadentate N_2O_4 Schiff base ligand derived from salicylaldehyde, Journal of Molecular Structure. (2013) ,1032:62-68.

19- M. S Nair, R. S. Joseyphus.Synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes of tridentate Schiff base derived from vanillin and DL-α-aminobutyric acid, Spectro chimica Acta. (2008), 70: 749-753.

20- Amina Mumtaz, Tariq Mahmud, Elsegood MR and Weaver GW. Synthesis and Characterization of New Schiff Base Transition Metal Complexes Derived from Drug Together with Biological Potential Study Nuclear Medicine & Radiation. (2016), DOI: 10.4172/2155-9619.1000310.

21- N. Raman, JDRaja, A. Sakthivel, J. Synthesis, spectral characterization of Schiff base transition metal complexes: DNA cleavage and antimicrobial activity studies. Journal of Chemical Sciences**.** (2007)**,** 119: 303–310.

22- Badma Priya D, Santha Lakshmi S. Synthesis, Spectral and Antimicro bialInvestiga- tion of some Ternary Schiff Base Transition Metal Complexes .International Journal of ChemTech Research CODEN(USA). (2014), 6: 87-94.