

**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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Abstract

Schiff base ligand [(4Z,11aE,15E) -2,3,5,9,10 - 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 ¹H-NMR

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

تحضير وتشخيص قواعد شف ومعقداتها الكروم (II) والحديد (II) والكاديوم (II) المشتقة من 1- فنيل-3,1- بيوتان دايون واثلين ثنائي امين مع 4-امينوانتبايرين

المخلص

تم تحضير قاعدة شف جديدة من تكثيف 1- فنيل-3,1- بيوتان دايون و اثلين ثنائي امين مع 4-امينو انتبايرين باستعمال كحول الايثانول كمذيب وحامض الخليك الثلجي كعامل مساعد . وشخصت القاعدة المحضرة باستخدام تقنية التحليل الدقيق للعناصر وطيف الاشعة تحت الحمراء وطيف 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 التكافؤ هي ايون الكروم (II) وايون الحديد (II) وايون الكاديوم (II) ومن نتائج التشخيص تبين ان الشكل الهندسي للمعقدات المحضرة هو هيئة 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(II), Fe(II) and Cd(II) complexes with 1-Phenyl,1,3-butandion, 4-aminoantipyrin and Ethylenediamine.

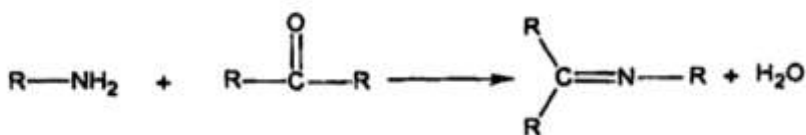


Fig.1 General synthesis of Schiffbas

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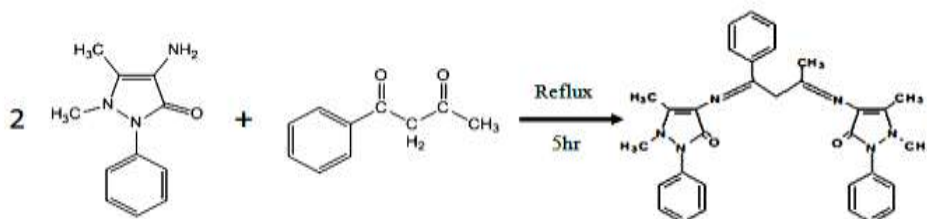
Materials and Methods

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 ,CrCl₂.6H₂O , FeCl₂.6H₂O, Cd(NO₃)₂.4H₂O, 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 (¹H-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 10⁻³M dimethylsulfoxide solutions were measured for the dissolved complexes using Inolabcond720. The Mass spectral of the compounds were recorded by Work mass selective Detector 5973.

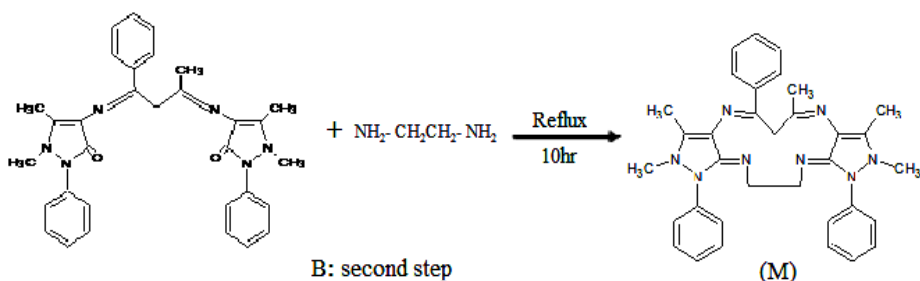
Synthesis of Schiff base (M)

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%



A: first step



B: second step

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 $\text{CrCl}_2 \cdot 6\text{H}_2\text{O}$ (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 ($\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (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 $1616\text{-}1602\text{-}1535\text{ cm}^{-1}$ for (M) which are shifted to higher frequencies in the spectra of all the complexes like Chromium complex in the range $(1636\text{-}1545)$, $(\text{M-N at } 486)\text{ cm}^{-1}$ and Iron complex in the range $(1648\text{-}$

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 figures 3,4,5

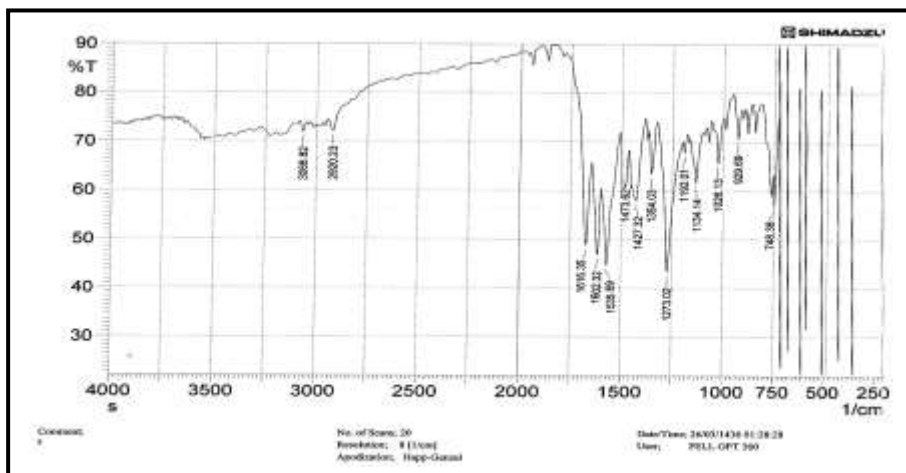


Fig.3 FT- IR of ligand (M)

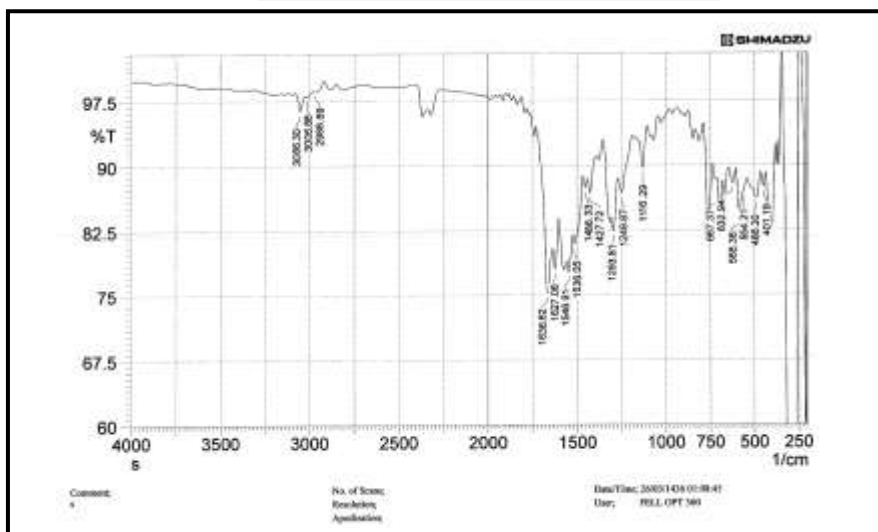


Fig.4 FT- IR of [Cr(M)Cl₂] complex

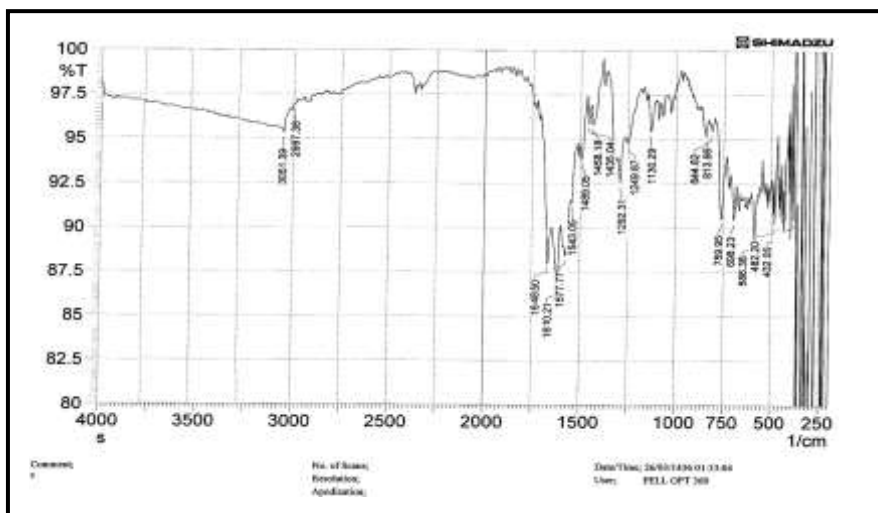


Fig.5 FT- IR of $[Fe(M)Cl_2]$ complex

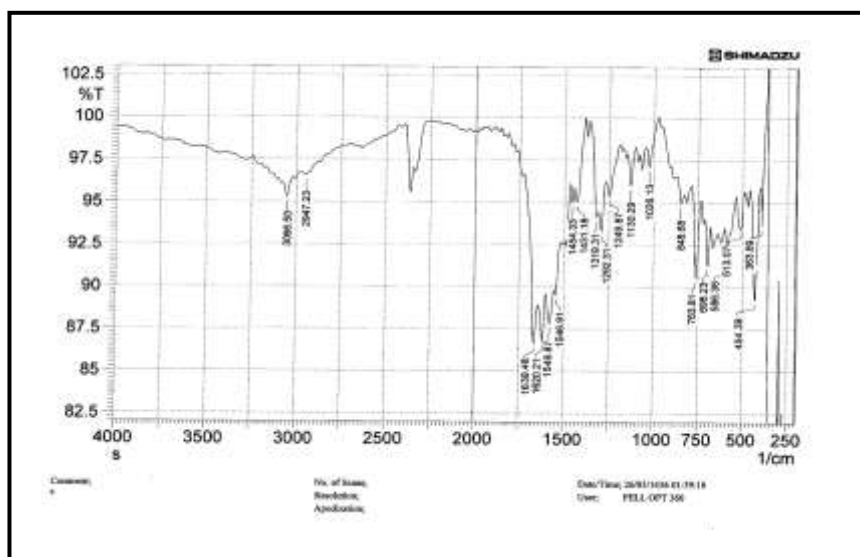
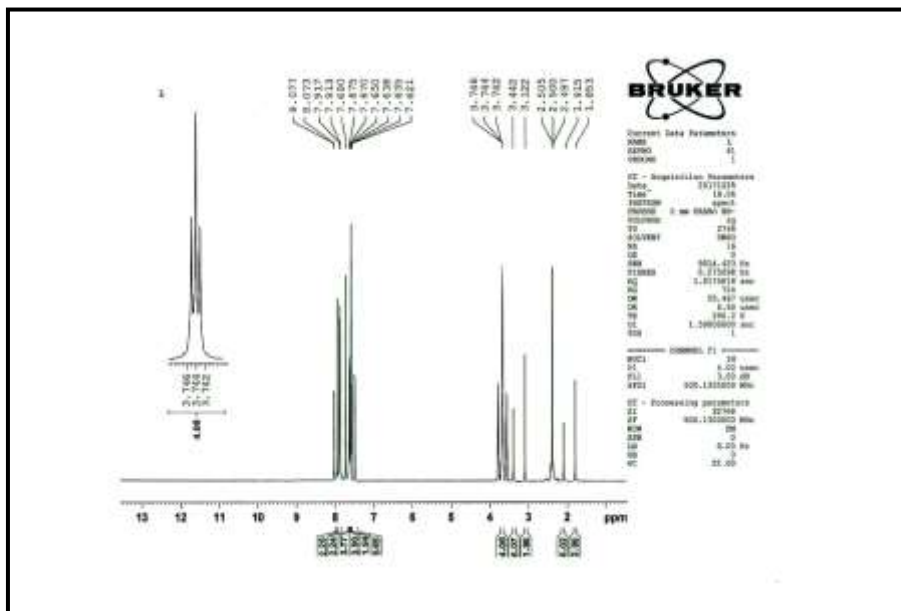


Fig.6 FT- IR of $[Cd (M)(NO_3)_2]$ complex

1H NMR

The 1H 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 ,($\text{CH}_3\text{-N}$) at 3.442 ppm The peak at 3.744 ppm to the ($\text{CH}_2 - \text{CH}_2$) and phenyl a



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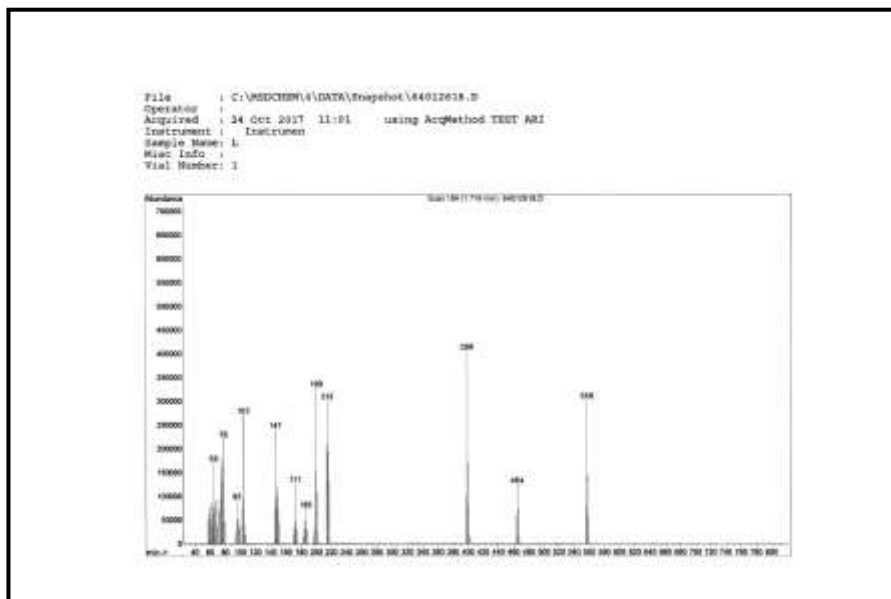
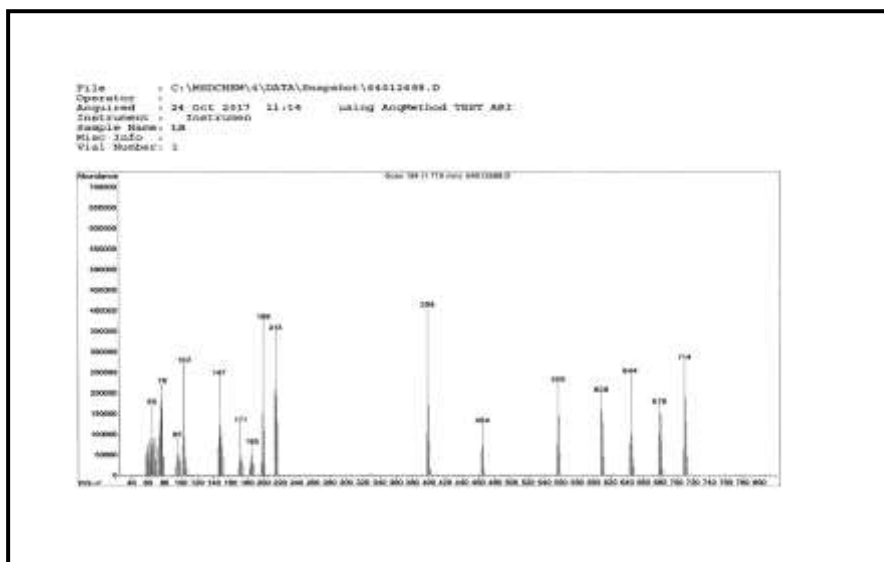


Fig.8 Mass spectrum of ligand (M)



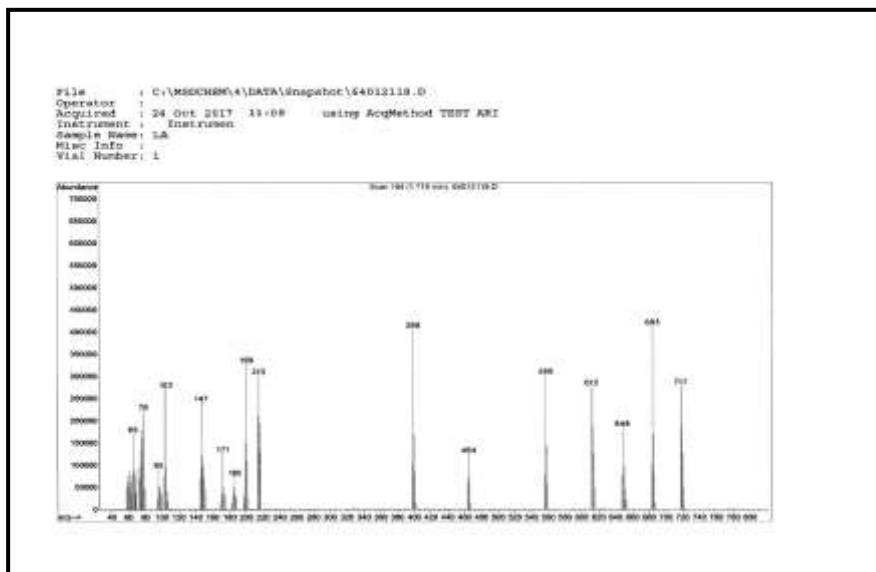


Fig.10 Mass spectrum of [Fe(M)Cl₂]complex

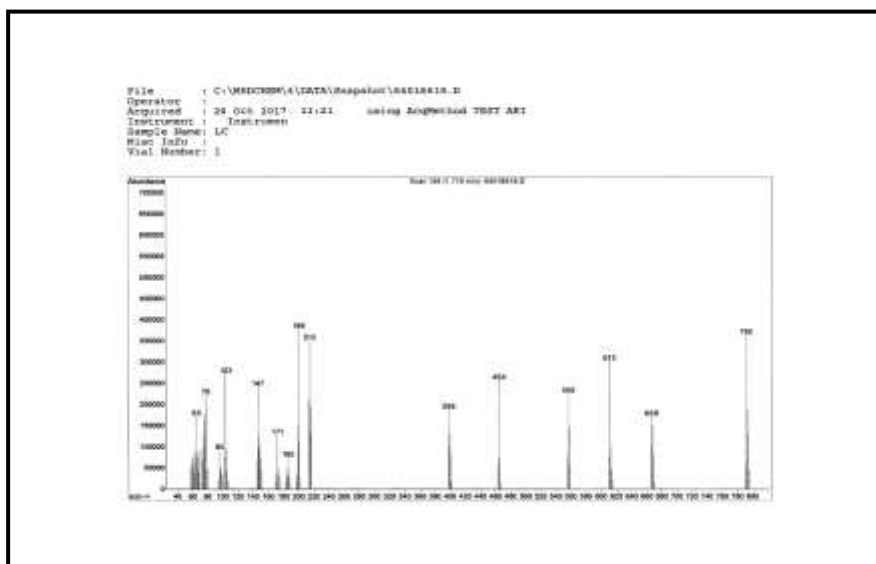


Fig.11 Mass spectrum of [Cd (M) (NO₃)₂]complex

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 cm²mol⁻¹ indicating the non electrolytic nature of the complexes^[22]. The analytical data of the complexes correspond well with the general formula MXA₂, where X = Cr (II), Fe (II) and Cd (II) ; M C₃₄H₃₆N₈ ; A =Cl ,NO₃. 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(II), Fe(II), Cd(II). 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.

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