Ministry of Higher Education

and Scientific Research

Journal of Kufa for Chemical Sciences

A refereed

Research Journal Chemical Sciences

Vol.2 No.9 Year 2022

ISSN 2077-2351

Synthesis, Identification and Spectral Studies of Some New Schiff base ligand Complexes Contained 3,4-Diaminobenzophenone and pyridoxal hydrochloride Compounds

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Abstract

Anew Schiff base ligand. (HMPHM) 3-((4-chlorobenzylidene)amino)-4-((€-(3-hydroxy-5-(hydroxyl methyl)-2-Methyl)puridin-4-yl)methylene)amino)phenyl)(phenyl)methanon has been Prepared from reacting(3-amino-4-(((3-hydroxy-5-(hydroxylmethyl)-2-methylpyridin-4-yl)methylene)amino)phenyl)(phenyl)methanone with *P*-Chloro benzaldehyde Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Au(III) ions were used to create a new series of chelate complexes. The structures of the new Schiff base ligand and their transition metal complexes were characterized by using Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H-NMR) technique, ultraviolet visible spectroscopy (UV-Vis), mass analysis, molar conductance, and magnetic susceptibility. $[(M)(L)_2]$ where M = Co(II), Ni(II), Cu(II), Zn(II), and Cd(II), and [(M)(L)Cl]Cl where M = Au (III). The coordination sites of the Schiff base ligand were revealed by FTIR to be through oxygen of the hydroxyl group, and the nitrogen of azomethine groups. Based on data obtained, the octahedral geometry was suggested for all ligand complexes exception of the Au(III) complex, which had a square planar geometry.

Keywords: *3,4-diamino benzophenone; Schiff base ligand ; Transition metal complexes.*

Introduction

The organic compounds containing the azomethine group (-CH=N-) were named as an effective group in their composition with Schiff bases and that is through the condensation of aldehydes or ketones (alpha or aromatic) with primary amines (aliphatic or aromatic), in different solvents and in the presence of a catalyst through which the water molecules resulting from the reaction are with drawn(1,2). Because of their vast range of biological applications, ease of preparation, chelating characteristics, and stability, Schiff bases are the most important and studied class. Schiff bases ligands have also played a key role in the creation of inorganic biochemistry and pharmacological activities such as antibacterial, antioxidant, anticancer, antifungal(3-7) .Many studies have been carried out to study the uses in various fields such as antimicrobial and molecular docking studies as well as thermodynamics studies of complexes formation with metal ions. Schiff bases ligand of 3,4-diamino benzophenone and their complexes have a variety of biological, analytical, and pharmacological applications(8-10) .In this paper, we report Synthesis, Identification and Spectral Studies of Some New Schiff base ligand Complexes Contained 3,4-Diaminobenzophenone and pyridoxal hydrochloride Compounds.

Experimental

Materials and Methods

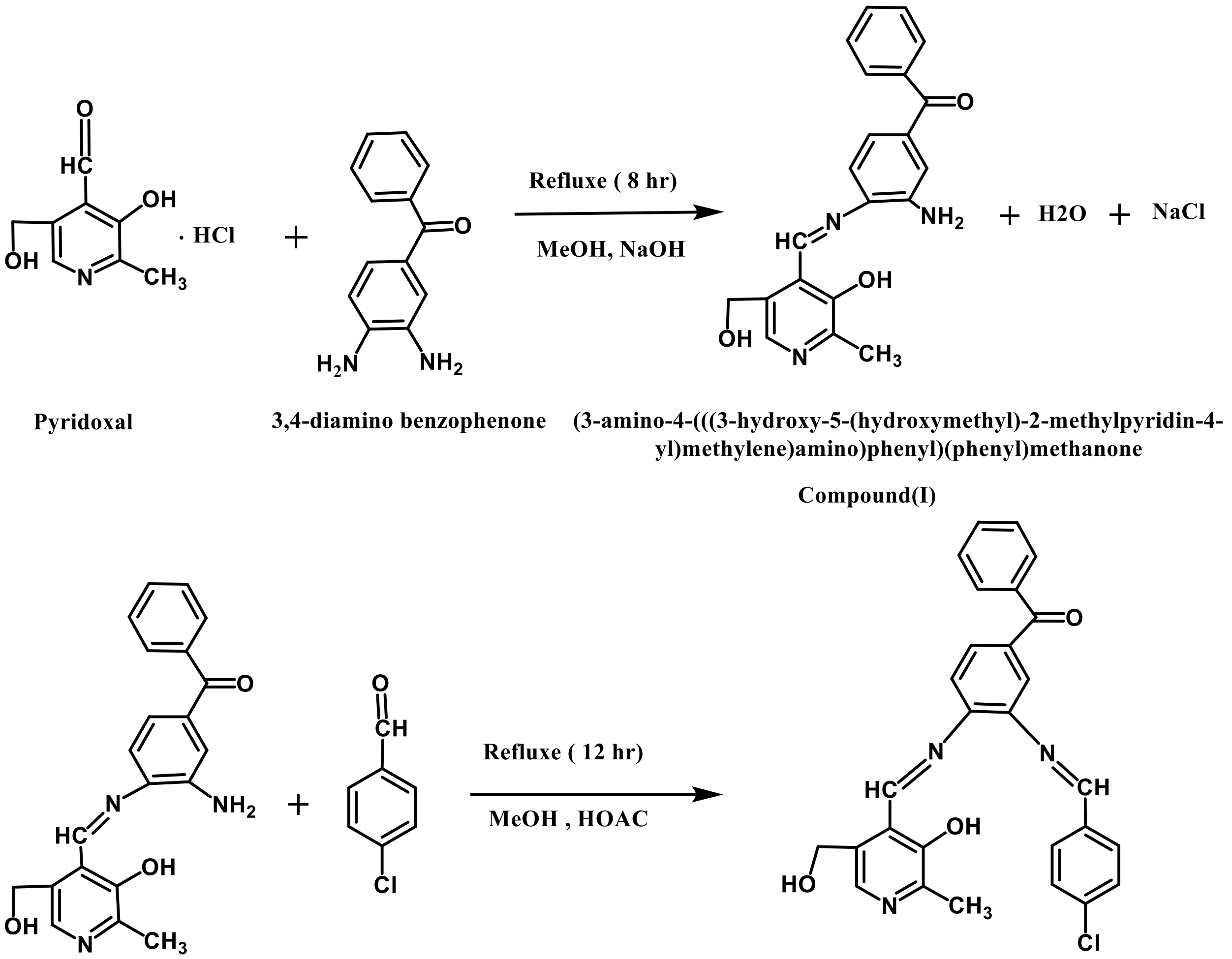
The electrothermal melting point model 9300 was used to measure the melting point of the ligand and its complexes. Elemental analyses were carried out by means of micro analytical unit of 1180 (C.H.N)elemental analyzer. Electronic spectra were recorded on Shimadzu spectrophotometer double beam model 1700 Uv-Vis spectrophotometer-FTIR spectra were recorded in KBr disc on FTIR Shimadzu spectrophotometer model 8400 at wave number(4000-400)cm-1. 1H-NMR -spectra in (ppm) unit were operating in DMSO-d^6 as solvent using (Bruker-Ultra Shield 3000 MHz Switzerland). Magnetic susceptibility were carried out on a balance magnetic(MSB-MKI)using faraday method. The diamagnetic corrections were made by Pascal's constants.

Synthesis of the new Schiff base ligand (HMPHM)

Synthesis of 3-((4-chlorobenzylidene)amino)-4-((€-(3-hydroxy-5-(hydroxyl methyl)-2Methyl)puridin-4-yl)methylene)amino)phenyl)(phenyl)methanon

The Schiff base ligand was prepared by condensation : The first step, (250 ml) to which (2.03g, 0.01mol) was added From pyridoxal hydrochloride (PL.HCl) dissolved in (25 ml) of absolute methanol to (2.12g, 0.01mol) of 3,4-Diaminobenzophenone in (25 ml) of absolute methanol after adding (3drops) of (5%) sodium hydroxide (medium basic), the mixture was reflexed for (8hr) with continuous stirring, following its reaction using thin later chromatograph, after that it was cooled and evaporated from the methanol solvent, and a yellow precipitate was obtained with a water molecule, filtered, then dried and recrystallized from absolute ethanol, its melting point was measured and it was (252) ^{0}C.

As for the second step, it included the preparation of a Schiff base ligand, where (3.47g,0.01mol) was reacted from resulting solution prepared in the first step and dissolved in (30 ml) of absolute methanol with a solution of (1.40g,0.01mol) *p*-chlorobenzaldehyde dissolved in (25 ml) of absolute methanol The mixture was was reflexed for (12hr) with continuous stirring and addition of (2-3) drops of glacial acetic acid, after that it was noticed that the color of the solution changed to a dark orange color, leaving the reaction mixture to settle to complete The precipitation process and obtaining more product, after that the precipitate was filtered, dried and recrystallized using hot absolute ethanol, the melting point was measured and it was (235C^0). **Scheme 1**. shows the course of chemical reactions of Schiff base ligand.



Pyridoxal

3,4-diamino benzophenone

(3-amino-4-(((3-hydroxy-5-(hydroxymethyl)-2-methylpyridin-4-yl)methylene)amino)phenyl)(phenyl)methanone

Compound(I)

P-Chloro benzaldehyde

(3-((4-chlorobenzylidene)amino)-4-(((*E*)-(3-hydroxy-5-(hydroxymethyl)-2-methylpyridin-4-yl)methylene)amino)phenyl)(phenyl)methanone

Compound (II)

Scheme 1 : Synthesis of the New Schiff base ligand

Synthesis of metal complexes:

The metal complexes were prepared in the solid state of Schiff base ligand (HMPHM) with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions in a molar ratio (1:2) and with the Au(III) ion molar ratio (1:1) by dissolving the weights of each of the metal salts in (30 ml) of absolute ethanol (1 mmol) to a solution of ligand (0.483 g, 0.002 mmol) dissolved in (30 ml) of the same solvent, then the mixture was escalated for an hour after Adding (0.5ml) of an alcoholic ammonium hydroxide solution, after which the appearance of complexes was observed, Leave the solution The precipitate was dried with recrystallization of the solid product from hot absolute ethanol, the pure solid precipitate was collected and the melting point of the prepared metal complexes was measured (>310 ^{0}C), except Zn(II) complex was (235-239) ^{0}C.

Results and Discussion:

All our complexes are Freely soluble in DMF, DMSO, Methanol and Ethanol. Also They are stable in air. The metal complexes were characterized by elemental analysis, molar conductivities, magnetic susceptibility, IR, UV-Vis, Mass and ^{1}H,MNR spectra. The analytical data of the complexes are in agreement with the experimental data. The value reveal that the metal to ligand ratio is(1:2), except the Au(III) complex (I:I) .The magnetic susceptibility of the chelate complexes at room temperature were consistent with octahedral geometry, except the Au(III) complex suggest a square planar geometry around the central metal ion. Most of chelate complexes prepared in this work showed conductivity values of the complexes. This proves that complexes have nonelectrolytic nature, except Au(III) complex has electrolytic nature

Micro analysis:

The elemental analysis data of 1:2 [M:L] ratio complexes showed that the theoretical values are in a good agreement with the found data ,as listed in table(1).The purity of Schiff base ligand were tested by TLC technique and C.H.N analysis.

Table.1: Physical properties and elemental analysis of Schiff base ligand and their metal complexes

Compounds	*M.Wt g/mole*	*Colour*	*M.p. ℃*	*Yield %*	*Found (Calc.)%*			
					%C	*%H*	*%N*	*%M*
HL= $C_{28}H_{22}N_3O_3Cl$	483.5	dark orange	>310^{0}C Dec	88	(69.4) 69.5	(4.55) 4.73	(8.68) 8.45	----
[Co(HL)$_2$].H_2O	1041.9	Dark green	>310^{0}C Dec.	76	(32.81) 31.65	(4.03) 4.75	(8.06) 7.45	(5.65) 5.84
[Ni (HL)$_2$].H_2O	1041.6	Light green	>310^{0}C Dec.	80	(32.88) 32.67	(4.03) 4.63	(8.06) 8.76	(5.62) 5.46
[Cu (HL)$_2$].H_2O	1046.5	Green	>310^{0}C	85	(32.10) 33.87	(4.01) 4.28	(8.02) 8.53	(6.06) 6.03
[Zn (HL)$_2$]	1030.4	Green	(235-239)^{0}C	83	(32.62) 32.98	(4.07) 4.86	(8.15) 7.93	(6.30) 6.34
[Cd(HL)$_2$]	1077.4	Light green	>310^{0}C Dec.	77	(31.59) 32.65	(3.89) 4.65	(7.79) 7.94	(10.39) 10.56
[Au(HL)Cl]Cl.H_2O	767.5	Green	>310^{0}C Dec.	80	(43.77) 42.76	(2.86) 4.98	(5.47) 5.87	(25.53) 25.78

Infrared spectra studies of the ligand and its complexes

FTIR spectra the new Schiff base ligand and their metal complexes are shown in table (2). In The infrared spectrum of the ligand exhibit broad band at (3425) cm^{-1} were assigned to υ(OH) group in the free Schiff base ligand confirmed that hydroxyl group was presented in Schiff base ligand, which is absent in all metal complexes, revealed that it was coordinated to metal ions via deprotonation of phenolic υ(OH)(11-13) the Band at (1708) cm^{-1} due to carbonyl υ (C=O) of benzophenone group, this band unchanged in the spectra of complexes (14)The bands at (1653, 1566) cm-1 that were assigned to υ(CH=N) in the free Schiff base ligand, the azomethine peak in ligand is shifted, which indicated the coordination through υ (-C=N-) group(15,16).

The appearance of new absorption bands at (511-574) cm-1 and (430-495) cm-1 refer to υ(M-N), υ(M-O) sequence in some complexes, confirmed that Oxygen and Nitrogen atoms of the ligand banded with the metal ions(17). The spectra data of the new Schiff base ligand and the Cu(II) complex were shown in (Figure 1 and 2)

Table. 2: Characteristic FTIR absorption bands of the Schiff base ligand and its complexes

Compounds Formula	*υ (H2O) OH*	*υ(OH) methanolic*	*υ(C=N) Schiff*	*υ(M-N)*	*υ(M-O)*
HL= $C_{28}H_{22}N_3O_3Cl$	3425	3695	1653,1566	-----	-----
$[Co(HL)_2].H_2O$	3402	3770	1637,1614	549	495
$[Ni\ (HL)_2].H_2O$	3414	3741	16271541	501	553
$[Cu\ (HL)_2].H_2O$	3412	3774	1647,1612	511	457
$[Zn\ (HL)_2]$	-----	3739	1676,1585	513	443
$[Cd(HL)_2]$	-----	3772	1651,1604	574	530
$[Au(HL)Cl]Cl.H_2O$	3442	3741	1676,1598	513	430

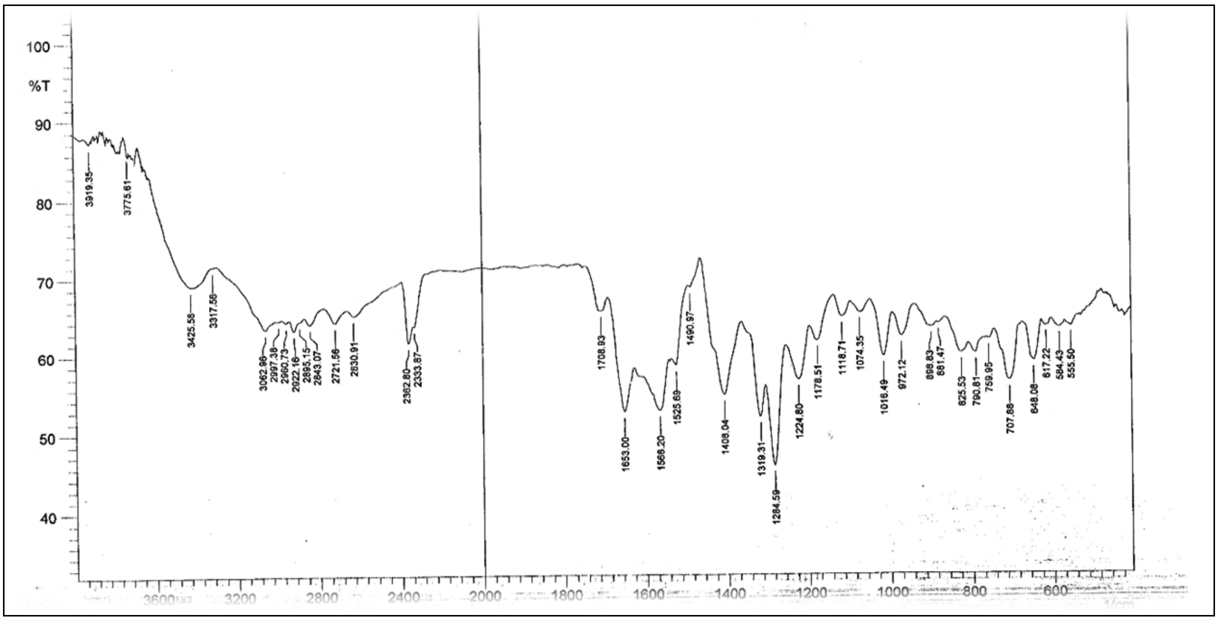


Fig. 1 FTIR spectrum of Schiff base ligand

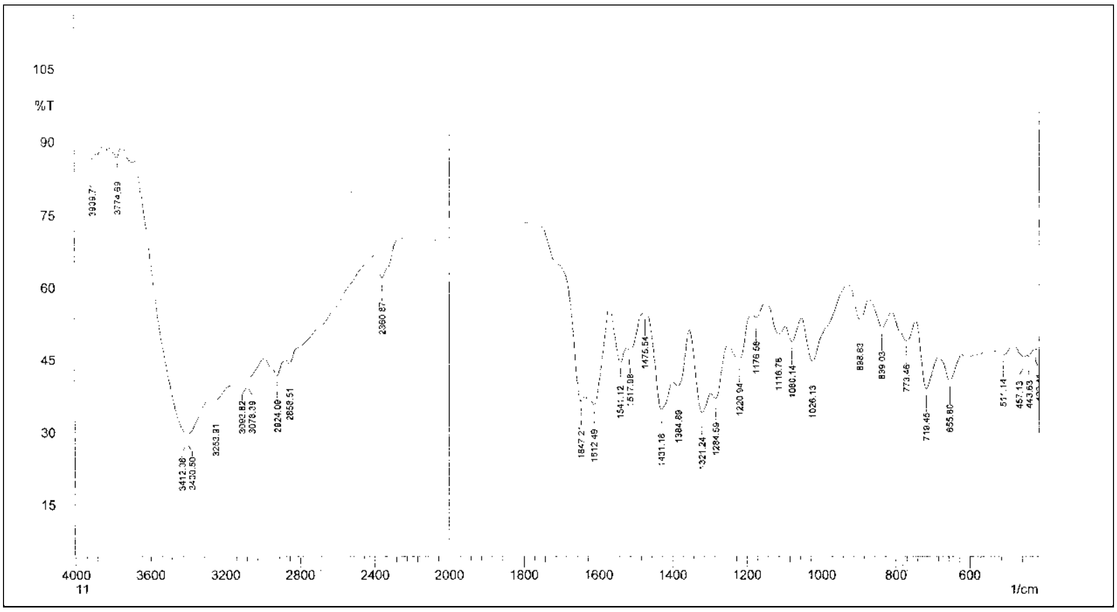


Fig. 2 FTIR spectrum of Cu (II) complex.

Electronic spectra and magnetic susceptibility measurements

Ultraviolet – visible spectra is one of on important methods used in the field of coordination chemistry, it is studied and compared metal complexes spectra with free ligand spectra .

The electronic absorption spectra of the new Schiff base ligand and its complexes were recorded in freshly ethanol solution (10^{-3}) at room temperature. The absorption region band assignment and the proposed geometry of the complexes Co(II), Ni(II), Cu(II), Zn(II),Cd(II) are octahedral except Au(III) complexes, which had square planar geometry. Their relevant data shown in **Table. 3** .

The new Schiff base ligand shows two charge transfer (CT) absorption bands in the region Uv-Visible at (254)nm (39370)cm^{-1}, and (312)nm (23051) cm^{-1}which were allotted to (π -π*) and (n-π*) transition within molecule(18). In the metal complexes, These absorption bands undergo of red-shifted indicating that the Schiff base ligand are coordinated to the metal ions (19).

The band observed at 312 nm in the spectrum of the free ligand (HL) was red-shifted to 402-597 nm in the complexes due to ligand to metal charge transfer (LMCT) transition (20), suggesting an octahedral geometry around metal(II) in the complexes (21), except the Au(III) complexes, which had square planar geometry. The UV-Vis spectra of the new Schiff base ligand and Cu(II) complex are shown in **(Figure 3).**

Magnetic measurements

The magnetic moment value The Co(II) complex has 3.3 BM, which was in agreement with the reported value for octahedral Co(II) complexes (22). The present Ni(II) complex showed a magnetic moment value of 2.4 within the range of 2.9-3.3 BM(23), suggesting an octahedral environment. The Cu(II) complex showed a magnetic moment value of 1.78 BM, higher than the spin-only value 1.73 BM as expected for one unpaired electron, which was monomeric and consistent with a distorted octahedral geometry (24). The Zn(II), Cd(II), Au(III) were diamagnetic and according to the empirical formulae of complexes(25). An octahedral geometry was proposed , except the Au(III) complex suggested a square planar geometry around the central metal ion (26). Based on the above results, we could deduce the probable structures of the complexes as shown in Fig. 6.

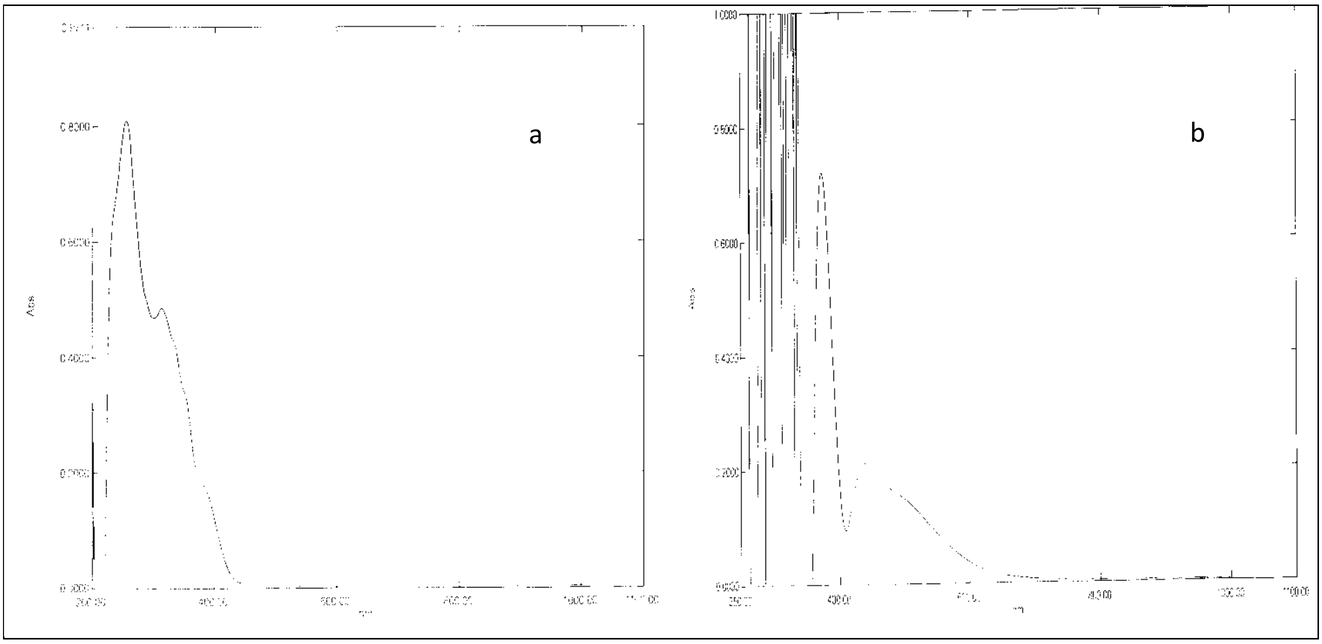


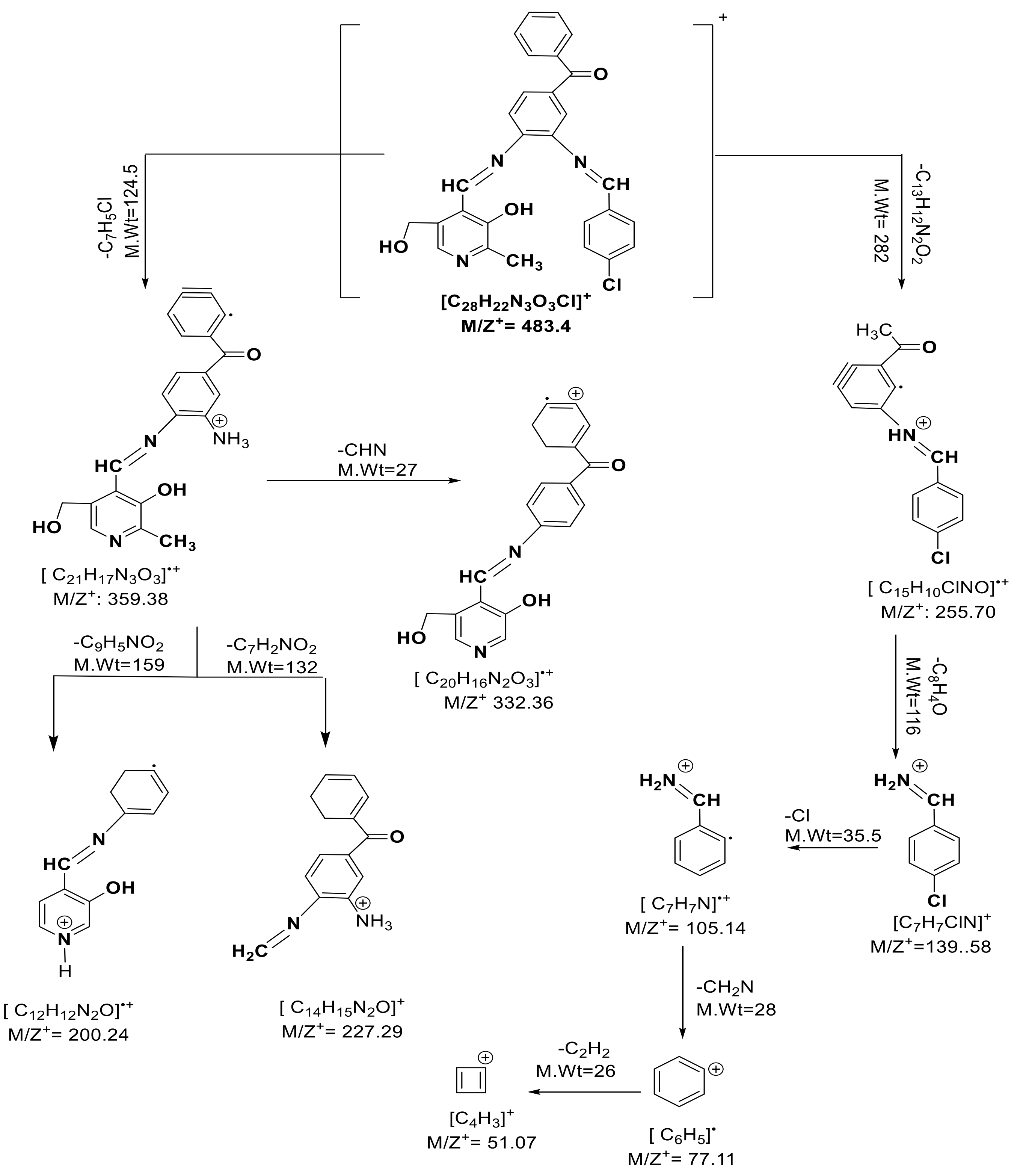
Fig. 3 Electronic spectrum of (a) Schiff base ligand and (b) Zn(II) complex.

Table(3):- Electronic spectra (nm, cm^{-1}) magnetic moments, geometry, hybridization and conductivity.

Compounds	λ_{max} (nm)	Absorption bands(cm^{-1})	Transitions	μ_{eff} (B.M)	Geometry	Hybridization	Conductivity S.mol^{-1}. cm^2
HL= $C_{28}H_{22}N_3O_3Cl$	254 312	39370 35051	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	----	----	----	----
$[Co(HL)_2].H_2O$	547	18281	MLCT	3.3	Octahedral	Sp^{3}d^2	12
$[Ni (HL)_2].H_2O$	402	24875	MLCT	2.4	Octahedral	Sp^{3}d^2	15
$[Cu (HL)_2].H_2O$	597	16750	MLCT	1.78	Octahedral	Sp^{3}d^2	19
$[Zn (HL)_2]$	444	22522	MLCT	Dia	Octahedral	Sp^{3}d^2	13
$[Cd(HL)_2]$	439	22779	MLCT	Dia	Octahedral	Sp^{3}d^2	15
$[Au(HL)Cl]Cl.H_2O$	434	23041	MLCT	Dia[	square planar	dsp^2	33

Mass spectra

Mass spectra of new Schiff base ligand is shown in **Figuer1,**and the suggested mass spectral fragmentations of the ligand and its chelate complex is shown in **schemes** 2. The mass spectrum ligand displays abase peak at M/Z$^+$=483 is attributed to the original molecular weight. which are in good agreement with their formula as expressed from micro analytical data .



Scheme 2. Suggested fragmentation pathways of the new Schiff base ligand and structural assignments of fragments.

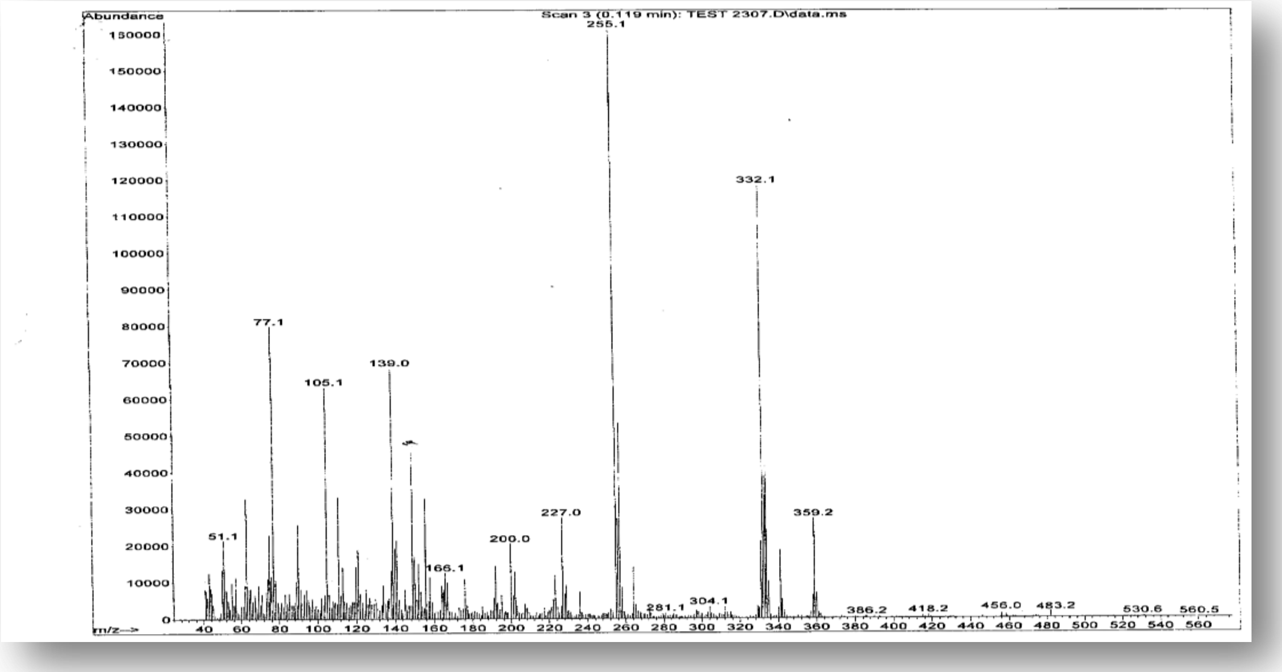


Fig. 3: the mass spectrum of the new Schiff base ligand

^{1}HNMR spectra

The data of ^{1}H-NMR spectra of Schiff base ligand and Zn(II) complex are show in **Figure 4,5** was measured in d^{6}-DMSO solvent with TMS as an internal reference. The ^{1}HNMR spectrum of the ligand shows the following signals : phenyl multiples at (7.4-8.0)ppm, CH-methane at (8.9) ppm**,** CH_2-pyridin ring at (4.7)ppm, CH_3-pyridin ring at (3.5)ppm**(27)**. Methanolic-OH at (5.3)ppm, Phenolic-OH at (10.0)ppm**(28)**. This signal disappear in spectra of Zn(II) complex indicates to absence(OH) proton and contribute the oxygen atom in complexity. There is no appreciable change in all other signals in complex.

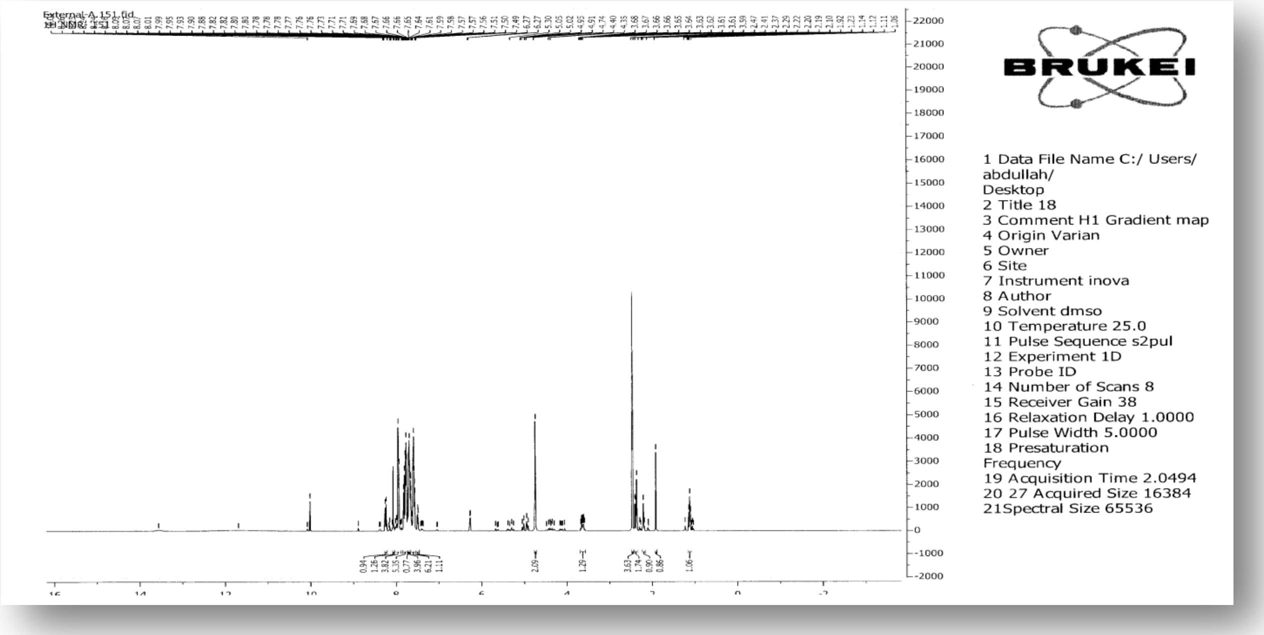


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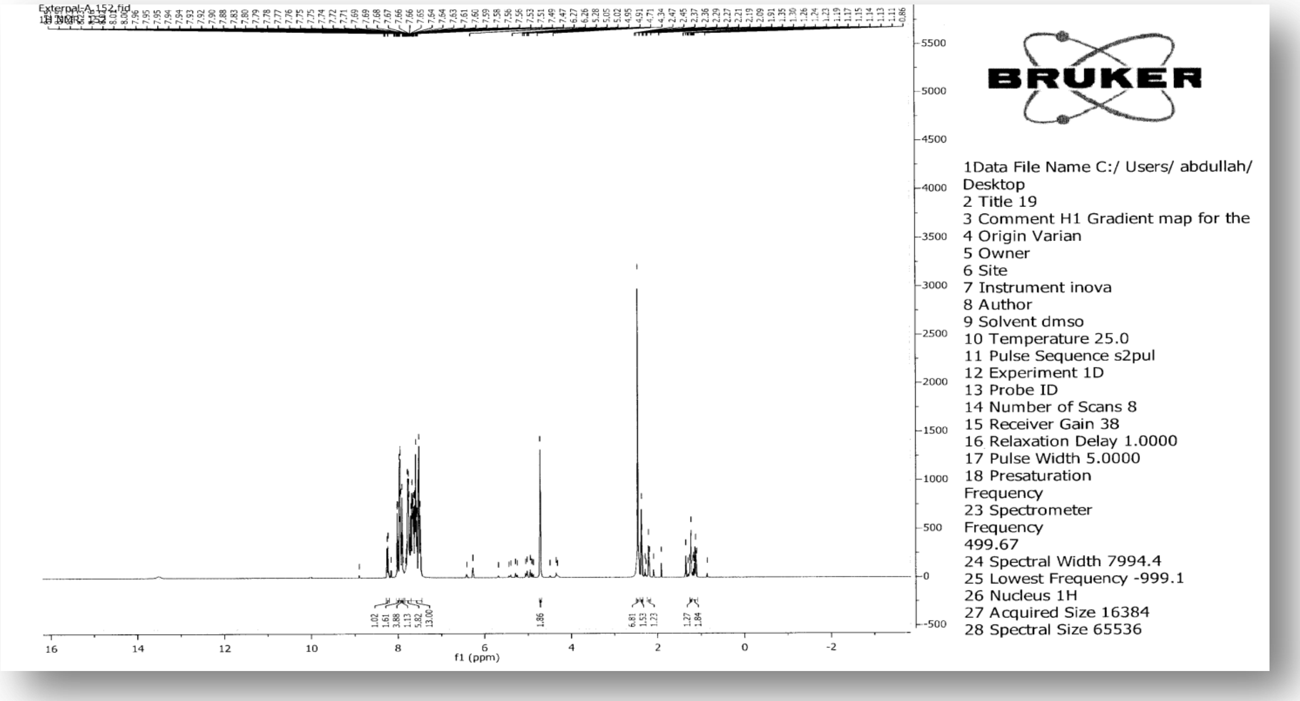
Fig.4: ^{1}H-NMR Spectrum of the new Schiff base



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24 Spectral Width 7994.4
25 Lowest Frequency -999.1
26 Nucleus 1H
27 Acquired Size 16384
28 Spectral Size 65536

Fig 5: ^{1}H-NMR Spectrum of Zn(II) complex.

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Molar conductivity measurements

The conductivity values (Λμ) of prepared complexes in DMSO solvent at a concentration of (10^{-3}M) in room temperature are listed in **Table (3).** The result explained molar conductance in the range between (11 – 19) S.cm^2.mol^{-1}, indicating that the compounds are non- electrolytes(29), except the molar conductance of Au(III) complexes are (33) S. $cm^2.mol^{-1}$ respectively suggesting that the electrolytic nature, indicate are present chloride ions outside the coordination sphere (30).

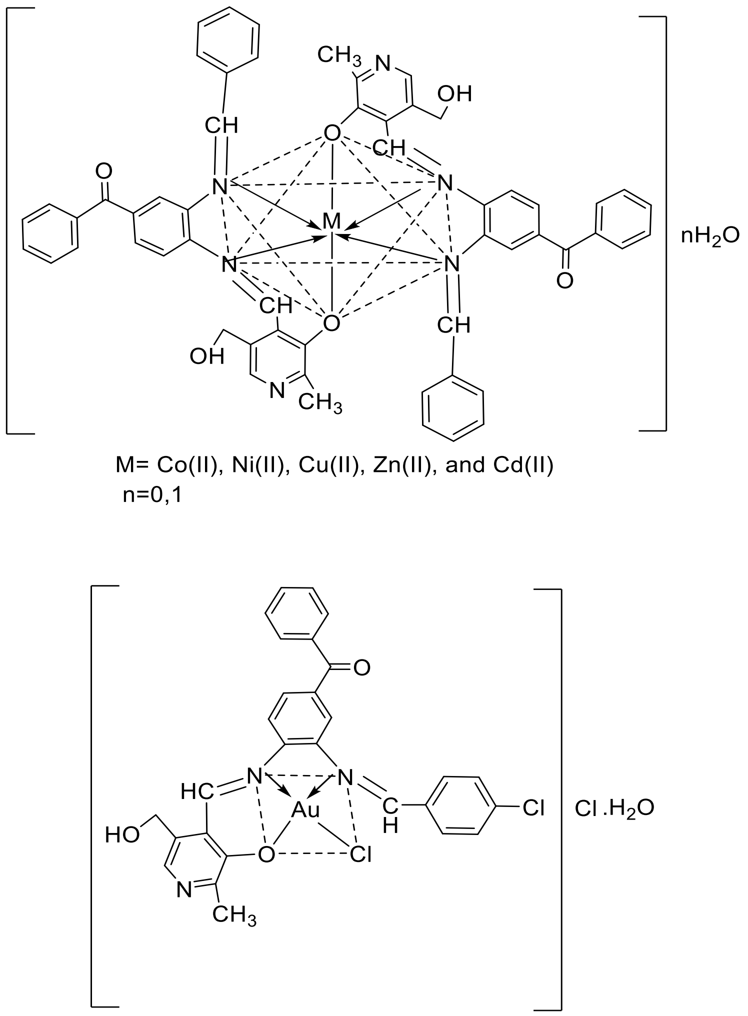
The suggested structures of the metal complexes

According to the analytical data and spectroscopic studies of the prepared metal complexes are show in **Fig. 2**. The new Schiff base ligand behaves as a tridentate chelating agent coordination through the nitrogen atoms of azomethine group, and oxygen atom of (-OH) phenolic group.

Conclusion

In this study has reported the synthesis and characterization of new Schiff base ligand containing two (-C=N-)groups and its Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Au(III) complexes were synthesized and characterized by various spectroscopic techniques. The result show octahedral geometry around of the complexes with mole ratio (1:2) metal: ligand while the complex of Au(III) show a square planar geometry around the complex with mole ratio (1:1) metal : ligand.

According to elemental analysis, Uv-Vis, FT-IR,spectroscopy, melting point, conductivity, data Atomic absorption, ^{1}HNMR spectra magnetic moment measurements, and mass spectrum studies . The following structures are suggested for the synthesized metal complexes as shown in Fig.2.



M= Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)
n=0,1

Fig.6. The proposed structural formula of the complexes.

Reference:

1- Shaimaa Adnan , Khalid J- Al-Adilee , Khamis A-Abedalrazaq **;** *Egypt. J. Chem.* Vol. 63 No. 12 pp. 4749 - 4756 (2020).

2- Gehad G. Mohamed, M. M. Omar,[a]and YasminM. Ahmed, Z. *Anorg.Allg.Chem*.,647, 2201–22. (2021)

3- Liana Ghasemi, Mahdi Behzad, Ali Khaleghian, Alireza Abbasi, Anita Abedi: *Appl Organomet Chem*.;36:e6639. (2022)

4- Ismail Warad , Oraib Ali , Anas Al Ali , Nidal Amin Jaradat , Fatima Hussein , Lubna Abdallah , Nabil Al-Zaqri , Ali Alsalme and Fahad A. Alharthi , *Molecules*, 25, 2253; doi:10.3390/molecules25092253. (2020)

5- H. Abd El-Wahaba , M. Abd El-Fattah b, H. M. Z. El-alfya , M.E. Owdaa , L. Linc , I. Hamdy, *Progress in Organic Coatings*, 142. 105577. ISSN 0300-9440, (2020)

6- Jailani, Abdul Khader; Gowthaman, N.S.K.; and Kesavan, Mookkandi Palsamy " *Karbala International Journal of Modern Science*: Vol. 6 : Iss. 2 , Article 15. (2020)

7- A. S. Shekhawat, N. P. Singh, N. S. Chundawat∗ , *J. Sci. Res*. 14 (1), 387-394 (2022).

8- Muna Abass Hadi, Ibtihal Kadhim Kareem, *Research Journal in Advanced Sciences*, Volume 1(1), (2020).

9- Mozaffar Asadii, Hajar Sephrpour, Khosro Mohammadi, *J. Serb. Chem*. Soc. 76 (1) 63–74 (2011).

10- B. S. Wankhede, and A. B. Patil, and Antimicrobial activity. *J. Phart, chem& Bio Scien*, 6: 2533, (2018).

11- S. H.Mahdi, and L. K. Abdul Karem, Oriental Journal of Chemistry, 34: 1565.(2018)

12- B. H. Al, Zaidi, A. H. Ismail, A. N, Naseaf, and W. Khamis,
, 30: 1157- 1164.(2018).

13- K. Mohammadi, M. Asadi, M. Setoodeh. Khah, and H. Sepehrpour,
. *Croat Chem Acta*, 89: 277-284.(2016)

14- Olfat. A. Nief , Hussein. N. Salman , Luma S. Ahamed; *Journal of Science*, 58, 4B, 1998-2011, (2017).

15- Xue-Jie. T , Di. W, Xiao-Ming. H, Feng-Cun. Y, Ya-Ling. Z, Dian-Xiang. X, & Jian -Ping. Ma; *Acta crystallographica SectionC*,76, part 1 Pages 44-63, (2020).

16- Suhad. K. A, Jassim. A. Al-Hilfi, Sawsan. K. Abbas, & Luma. M. Ahmed; *Indones. J. Chem*, 20(2), 404 – 412, (2020).

17- El-Ghamry. H. A, Gaber. M, & Farghaly. T. A; *Mini reviews in medicinal chemistry*, 19(13), 1068-1079, (2019).

18- Bergamo A, & Sava G. *Chemical Society Reviews*, 44, 8818 (2015).

19- Nisha. B, Nidhi. M,& Sonika. A; Journal of Chemical and Pharmaceutical Research, 6(9):194-200, (2014).

20- Ommenya. F. K, Nyawade. E. A, Andala. D. M, & Kinyua. J; *Hindawi Journal of Chemistry*, 8 pages, (2020).

21- Nasreen .R . Jber , Rana. S. Abood, & Yasmeen. A. Al-Dhaief; *Journal of Al-Nahrain University*, 14 (4), 50-56, (2011).

*22-*Oylumluaglu. G& Oner. J; *Materials Science and Engineering*, 254, 1-4, (2017).

23- Narendra K, and Parashuram M, *Bioinorganic Chemistry and Applications*, 1-13(2017).

24- Z.J. Mohamed, A.H. Al-Khafagy, *International Journal of Current Research*, 5(12): 3705-3710, (2013).

25- M.S. Mohamad,. *Acta Chimica Pharm Indica*, , 3(2): 140-148. (2013).

26-] Hammam. A. M, El-Gahami. M. A, Khafagi. Z. A, Al-Salimi. M. S, & Ibrahim. S. A; *J. Mater. Environ. Sci*., 6(6),1596-1605, (2015).

27- Al-Adilee. K. J, Al-shamis. H. A. H, & Dawood. M. N; *Research Journal of Pharmaceutical, Biological and Chemical Acience*. 7(4), 2882-2905, (2016).

28- Sarkar. D, Pramanik. A. K, & Mondal. T. K; Spectrochimica Acta Part A: *Molecular and Biomolecular Spectroscopy*, 153, 397-401, (2016).

29- Gokce. H, & Bahçeli. S; Spectrochimica Acta Part A: *Molecular and Biomolecular Spectroscopy*, 116, 242-250, (2013).

30- Bharati . A.B , Nath . P, Kumari . S, Singh . N . K , & Bharty . M.K ;*Inorganica chimica Acta* , 443 , 160-169, (2016).