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Synthesis and Spectral Identification of New Azo-Schiff base Ligand Derivative from Aminobenzylamine and its Novel Metal Complexes with Cu(II), Zn(II) and Cd(II)

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ABSTRACT

The research included the preparation of the New Azo Schiff Ligand derived from 4,5-diphenyl imidazole. The ligand was prepared from the amine reactor with the coupling component in order to prepare the azo amino benzayl amine. After that the last compound and vinilline which obtained the ligand mentioned some metallic complexes were prepared for the ions of Cu(II), Zn(II) and Cd(II). The New azo- Schiff ligand complexes after purification were identification by using the available spectral and analytical methods such as Mass spectrum for the New ligand and (ultraviolet- visible, FTIR) spectroscopy, CHN analytics', Atomic absorption, and conductivity measurement. According to these techniques the New Azo – Schiff ligand was pidentate and the proposed geometrical shape was octahedral for the three complexes.

KEYWORDS

Azo – Schiff ligand, 4,5-diphenyl Imidazole, Metal Complexes.

Introduction

Schiff base derivatives attract significant interest and occupy an important role in the development of coordination chemistry. Moreover, Schiff base complexes containing transition metals have been studied in several research areas such as structural chemistry(1). Azo compounds with two phenyl rings separated by an azo bond are very important in fundamental research area and applications(2). In addition, azo-Schiff base derivatives are known to be important in several classes of medicinal and pharmaceutical fields. Furthermore, some of them show biological activities such as antibacterial, antifungal, anticancer and herbicidal activities(3-12). However, the light induced interconversion allows systems incorporating azo group to be used as reversible control over a variety of chemical, electronic and mechanical applications(2). Azo compounds metal complexes have also been attracting much attention because of their applications in dyes, pigment, functional materials and optical computing(4). As part of our research in the study of coordinating capabilities of Azo-schiff base derivatives and their coordination compounds(5), we report herein the synthesis and spectroscopic studies as well as the thermal investigation of a novel Azo-schiff base derivative Ligand .Schiff bases are capable of coordinating with metal ions via the imine nitrogen and other groups linked to the Schiff base(6). Schiff bases are called privileged ligands since they can be prepared simply by condensation between aldehydes and primary amines(7). Most of the Schiff bases have Nitrogen or Oxygen donor atoms, but sometimes sulfur or selenium can replace Oxygen atom(8). Schiff bases may serve as monodentate, bidentate, tridentate or tetradentate ligands depending upon the number of donor atoms present in the molecule. They can make chelates (typically five or six-membered) on reaction with metal ion(9). Some of the Schiff bases in combinations with metal ions are used as insecticides, fungicides, and herbicides(10).

Experimental

In this Work, the analytical and spectral measurements of the prepared ligand and the derived complexes of some selected metallic ions were used. The ultraviolet spectra of ligand and its chelating complexes were recorded using a device (Shimadzu 1700) within range (200-800 nm) dissolve in ethanol using quartz cell. The melting points of ligand and its solid canine complexes were measured using the device (Stuart melting points SMP 10). The molecular conductivity measurements were recorded for the complexes at 25 ± 2 C̊ for solution (1×10^{-3}) of the sample in ethanol using a device (Digital conductivity meter Alpha -800).The infrared spectra of the azo compound and its metallic complexes are recorded in their solid state within the rang (400-4000cm^{-1}) in the solid potassium bromide with the apparatus completion (Shimadzu FTIR 8400 spectrophotometer). The mass spectrometer was also recorded

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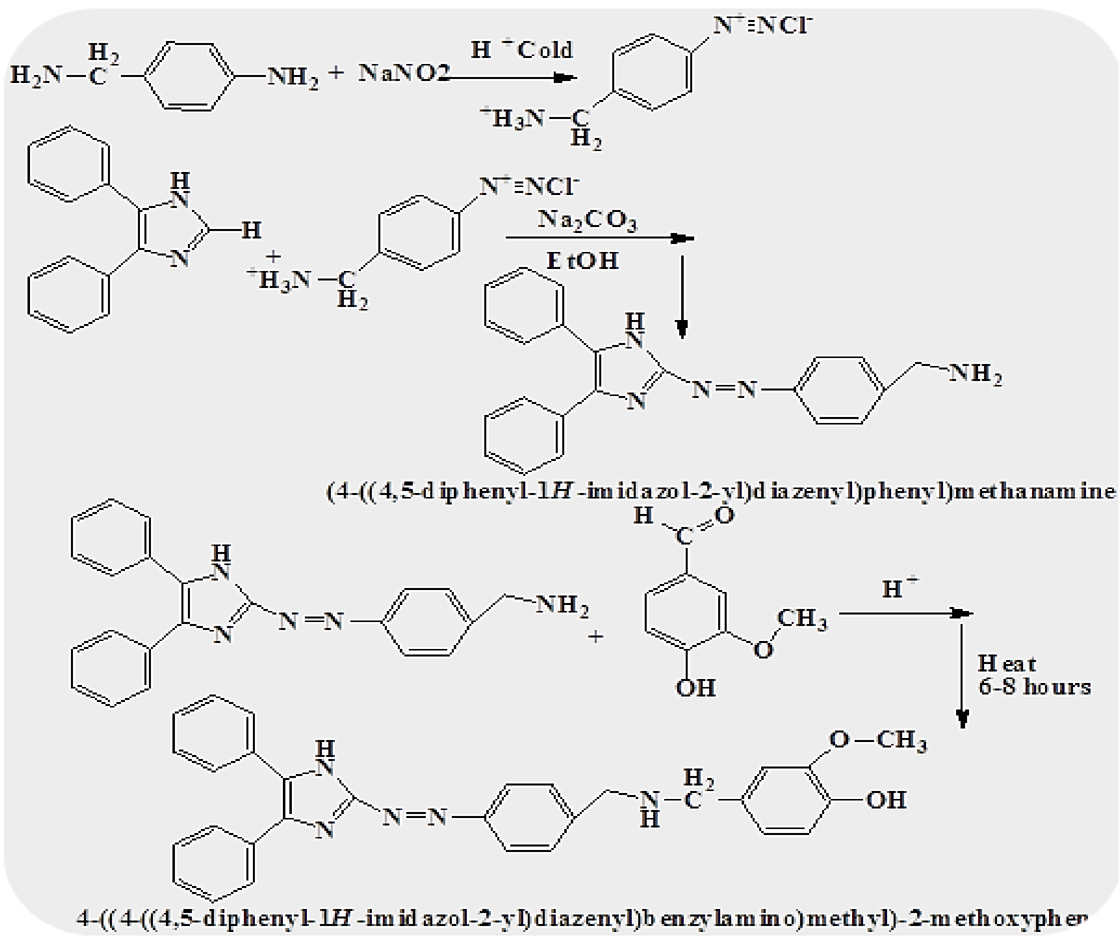
by advice (MSD Direct Probe). Measurements of magnetic sensitivity of solid complexes and at laboratory temperature were performed using a device (Balance Magnetic Susceptibility Model-M.S.B Auto).

Synthesis of the New Azo Schiff base Ligand

The new azo-schiff base ligand is prepared by coupling reaction of diazonium salt with appropriate amount of (amidazole derivative) as coupling component in alkaline solution. Adiazonium solution is prepared by dissolving (5.3ml) of ortho aminobenzylamine in (100ml) distilled water with (8ml) of concentrated HCl acid with continuous shaking . To this mixture a solution of (3gm) of sodium nitrate in 25ml of distilled water was added drop wise to the Diazonium solution with shaking and stirring to complete the aromatic amine Azotization process. at(0-5)ºC ,and left to stand(30min) .This diazonium solution was added drop wise to (8.8gm) of the amidazole derivative dissolved in(30ml)of ethanol and(50ml) of(2N)sodium hydroxide at(0-5)ºC. A drop by a drop was observed to change the color to orange-Red, indicating that the process of coupling between the two solutions and the formation of the azo compound (the azo dye) was then neutralized by adding drops of dilute HCl to the acidic function PH ~ 7.5. After that, The mixture was allowed to stand overnight and then the solution was filtered off, washed with distilled water, and recrystallized twice from hot ethanol and then dried in oven at 40ºC for 1 hours.

(3.53 gm) from pure azo dye dissolved in absolute alcohol (50ml) and then mixed with (1.22gm) (vinilline) dissolved in absolute alcohol .Three drops from glacial acetic acid ware added and the mixture was refluxed with stirring for 6 hrs. Azo-Schiff base ligand was isolated after the volume of the mixture was reduced to half by evaporation and precipitated product was recrystallized with hot absolute ethanol alcohol collected by filtered off and dried over anhydrous CaCl2 and its melting point was recorded at (118-110C^0) while the product percentage reached 80%. scheme1.



Scheme 1. Preparation of new (azo-Schiff base) ligand

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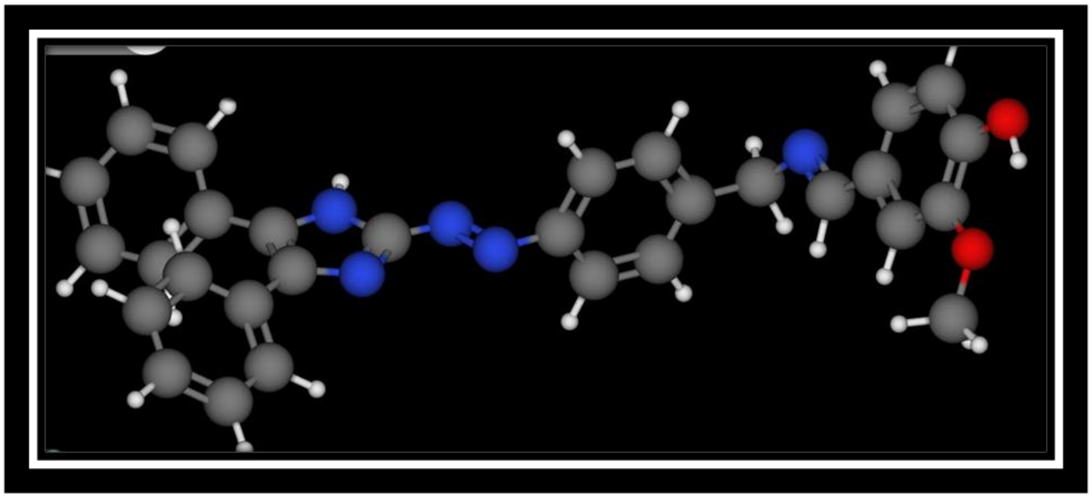

Fig. 1. Structure of new Azo-Schiff base ligand

Preparation of Metal Complexes

The metal complexes were prepared by mixing of 30ml ethanol solution of each of ($CuCl_2$,$2H_2O$, $ZnCl_2$ and $CdCl_2.2H_2O$) with 30ml ethanol solution of (0.441g) of new (azo-Schiff base) ligand in (1:2) (metal: ligand) ratio. the resulting mixture was refluxed for 1h.The products of complexes were isolated after reduced of volume by evaporation .They were filtered off ,washed with ethanol and dried under vacuum. Melting points were recorded and measurement results were listed in table (1).

Table 1. Shows the physical properties of the new Azo Schiff base ligand and its complexes

No.	Compound	Colour	M.p.°C	Yield %	Rf(1:4)
1	**L_2= $C_{29}H_{23}N_5O_2$**	Red	118-110	82	0.80
2	**$[Cu(L_2)_2]Cl_2$**	Per pile	115-117	74	0.61
3	**$[Zn(L_2)_2]Cl_2$**	Red	123-125	73	0.52
4	**$[Cd(L_2)_2]Cl_2$**	Red	128-130	81	0.68

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 Table (2), 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 was (1:2) (M:L) and were presented in table.2. The magnetic susceptibility of the chelate complex of Cu(II) at room temperature was consistent with octahedral geometry, So as the Zn(II) and cd(II) complexes suggest a an octahedral geometry around the central metal ions. All of chelate complexes prepared in this work showed lower conductivity values. This proves that complexes have non-electrolytic nature.

Table 2. Shows the element Analysis the new azo Schiff base ligand and its complexes.

No	Formula	M.Wt	Found (Calc.)%			
			C%	H%	N%	M%
1	**L_2= $C_{29}H_{23}N_5O_2$**	473.5	(73.49) 73.54	4. 85 4.95	14.78 14.80	-----
2	**$[Cu(L_2)_2].Cl_2$**	1081	64.38 64.50	4.25 4.38	12. 95 13.01	5.82 5.94
3	**$[Zn(L_2)_2].Cl_2$**	1083.3	64.24 64.36	4.24 4.38	12.00 12.11	6.03 6.12

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4	**$[Cd(L_2)_2].Cl_2$**	1129.5	(61.62) 61.79	4.07 4.14	(12.39) 12.43	(9.95) 9.99

Mass Spectrum

The mass spectra of the new azo Schiff base ligand was recorded at room temperature .The obtained peaks confirm the proposed formulae for the compound .The mass spectrum of Ligand show the molecular ion peak at m/z 457.53 compound ($C_{28}H_{21}N_5O$)confirm the proposed formulae for compound.

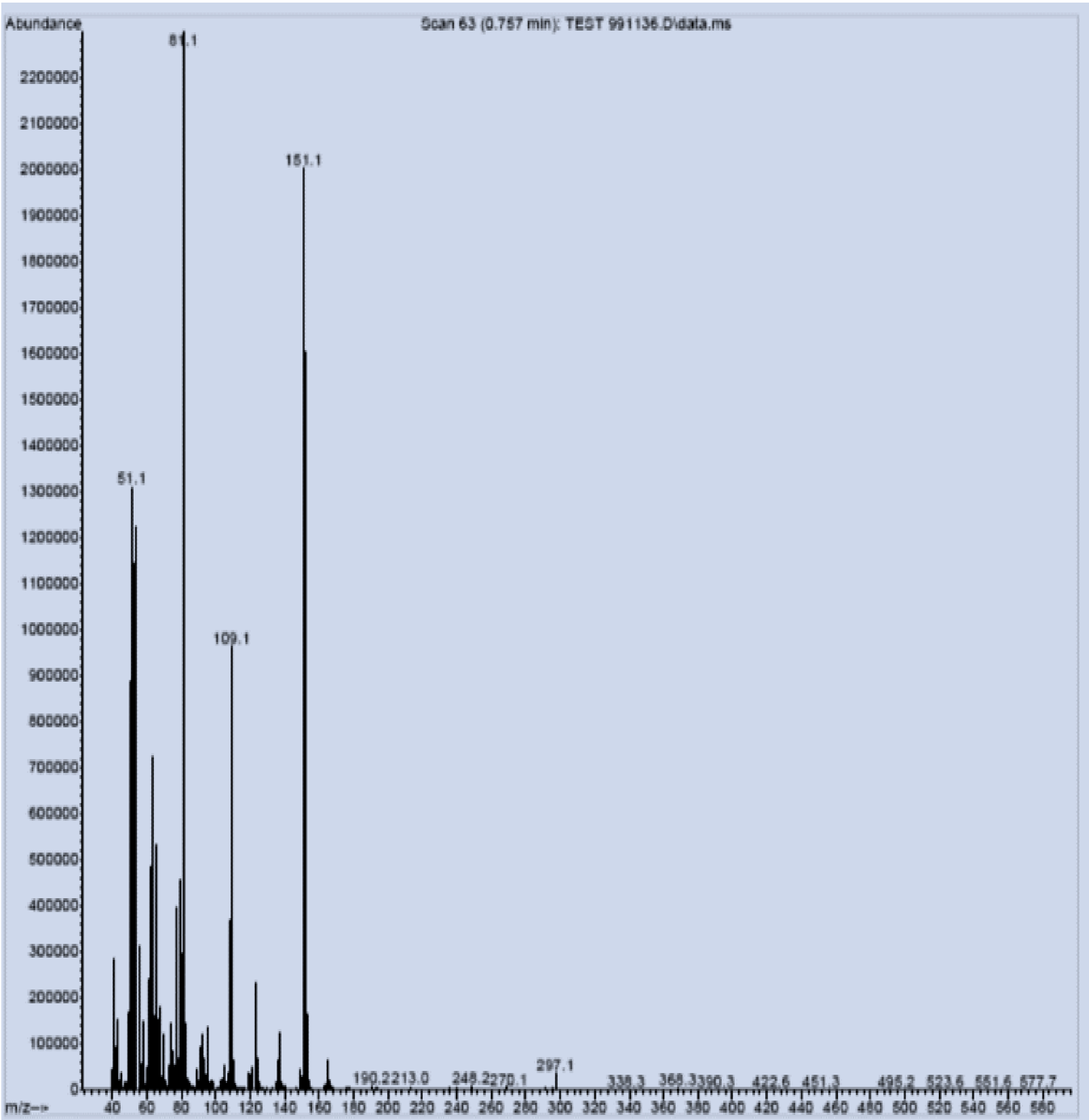
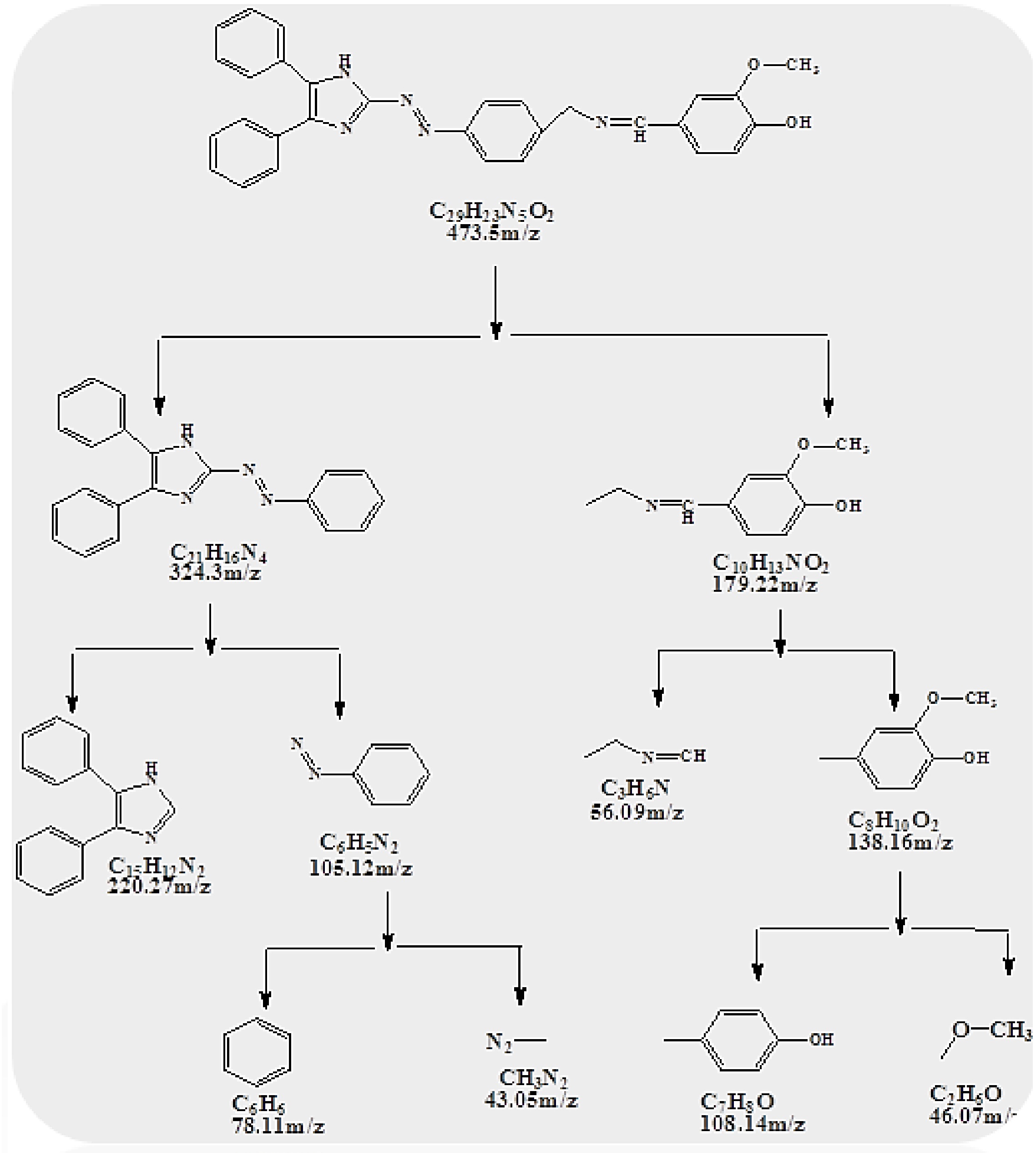


Fig. 2. Mass spectrum of the new azo Schiff base.



Scheme 2. Segment fractionation of the new azo Schiff base Ligand

[1]H-NMR Spectra

The spectrum of newly synthesized ligand gave a satisfactory data and the molecular structure was assigned on the basic of ^{1}H - NMR chemical shift by using DMSO as a solvent with tetra methyl saline as an internal reference. The 1H-NMR spectrum of the ligand showed clear signals involved singlet at δ (2.5) (ppm) belong to the protons of solvent (DMSO) and multiples signals at δ (7.3-7.9) ppm which were assigned to aromatic protons of phenyl ring of Imidazole and benzilidenimin. Multiple signals at δ (8.65) ppm which belong to (CH) benzylidenimin groups. Singlet at δ (4.8) ppm belong to the proton of methyl(CH_2). Singlet at δ (9.83) ppm belong to the proton of (–C-OH), Singlet at δ (13.4) ppm belong to the proton of –C-NH imidazole ring, as shown in Fig.(3).

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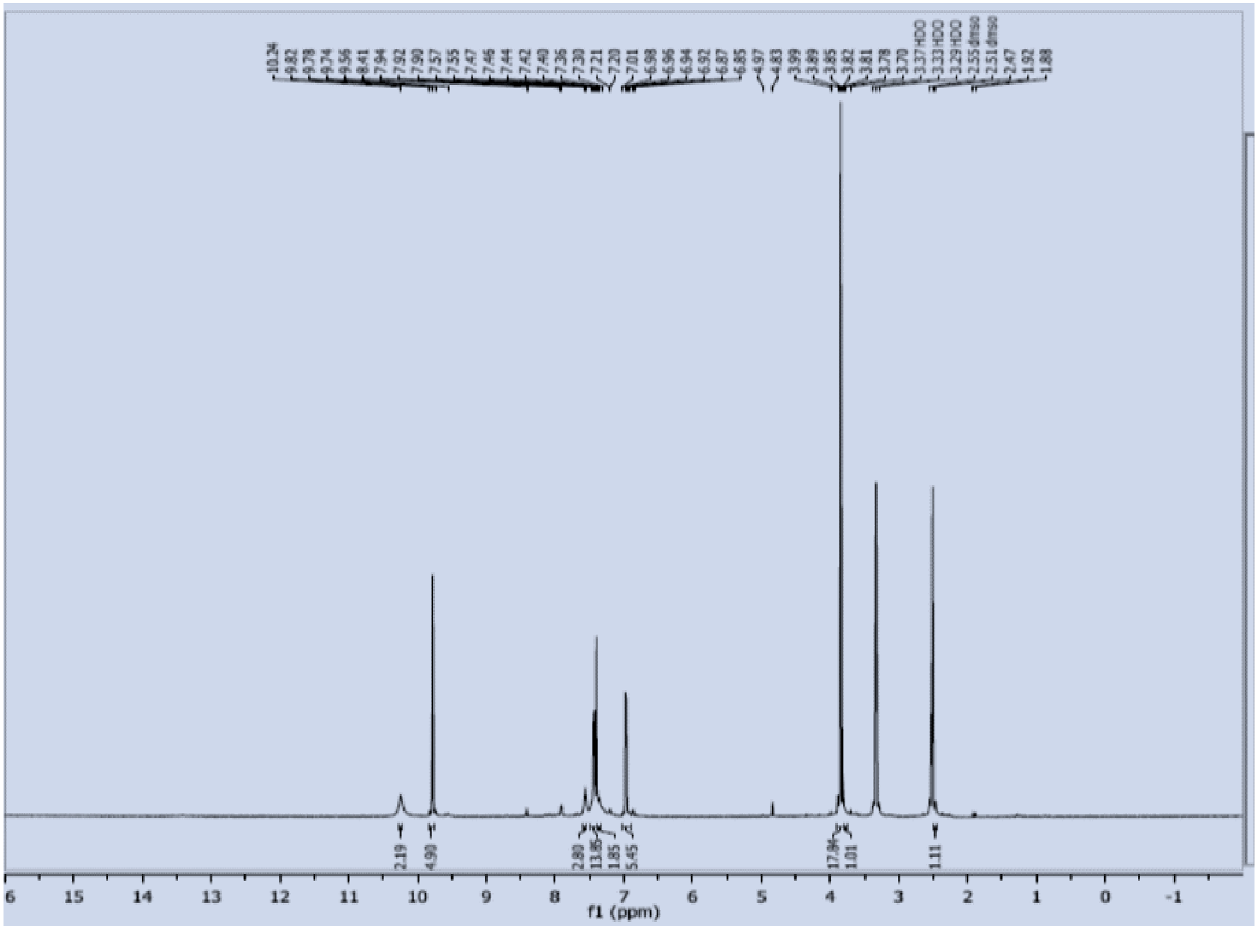

Fig. 3. ^{1}H-NMR spectrum of the new azo Schiff base

Infrared Spectra Studies of the Ligand and its Complexes

The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the Complexation, all data are listed in table (3).

The ligand spectrum showed an absorption beam at the frequency (1639) cm^{-1} that is due to ν(C=N) cm^{-1} bond of the imidazole ring [(11)], while this package showed a clear difference in the frequency locations in addition to the difference in the intensity and shape of the beams in the spectra Complexes where they appeared at frequencies between (1643-1645) cm^{-1}, which means that the consistency process occurred through the imidazole nitrogen atom with the metal ion, and the ligand spectrum showed a sharp absorption beam at the frequency (1460) cm^{-1} belonging to the azo group ν (N=N)[(12)] While the spectra of complexes showed a clear shift towards lower frequencies, they varied between (1446-1444) cm^{-1}, indicating The symmetry of the nitrogen atom also the ligand spectrum showed an absorption beam at the frequency (2979) cm^{-1} belonging to the sphincter ν (N-H)[(13)], whereas in the complexes this bundle appeared at frequencies between (3140-3209) cm^{-1}. The frequency (3176) cm^{-1} returns to ν (O-H) [(14)] bond while appeared in the spectra of complexes at frequencies between (3350-3383) cm^{-1}. The ligand spectrum showed a beam at the (1666) cm^{-1} frequency that returns to ν (C=N)[(15)] for the azomethine group. The ligand spectrum showed a beam at the (1298) cm^{-1} frequency that returns to ν ($O\text{-}CH_3$) while appeared in the spectra of complexes at frequencies between (1288-1290) cm^{-1}. for the azomethine group. Absorption beams appeared in the spectra of complexes at frequencies between (449-451) due to the association of ν (N-M) [(16)] Harmonicity while the ligand spectrum was devoid of these packages, which indicates that the coordination process between ligand and metal ions occurred through the atom nitrogen atom of the azo group and the nitrogen of the imidazole ring. The ligand spectrum is a beam at the (2954) cm^{-1} frequency that returns to the ν (C-H) aliphatic. In the spectra of complexes, this

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beam appeared at frequencies between (2827-2939) cm^{-1}. Also, a beam appeared at the (3943) cm^{-1} frequency that goes back to (C-H) [17] Aromatics and in the spectra of complexes appeared at the frequencies (3051-3066) cm^{-1}.

Table 3. IR spectra frequencies for the new azo Schiff base ligand and its metal complexes in cm^{-1}

Compound Formula	**υ(OH)**	**υ(NH)**	**υ(CH) Aro.**	**υ(CH) alph.**	**υ(C=N)**	**υ(N=N)**	**υ(OCH_3)**	**υ(M-N)**
L_2=$C_{29}H_{23}N_5O_2$	3176	2976	2943	2854	1666,1639	1460	1298	-----
[Cu(L_2)$_2$].Cl_2	3383	3140	3049	2827	1676,1643	1444	1288	449
[Zn (L_2)$_2$].Cl_2	3365	3140	3051	2939	1674,1643	1446	1288	451
[Cd (L_2)$_2$].Cl_2	3350	3209	3066	2837	1674,1645	1462	`1290	451

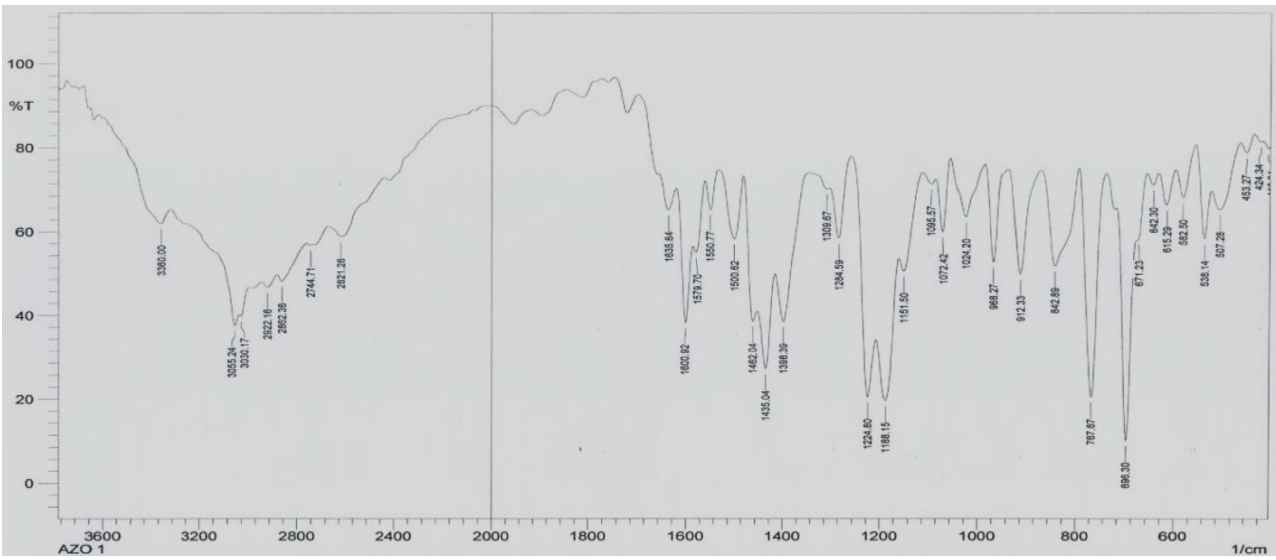

Fig. 4. IR-spectra of the Azo compound

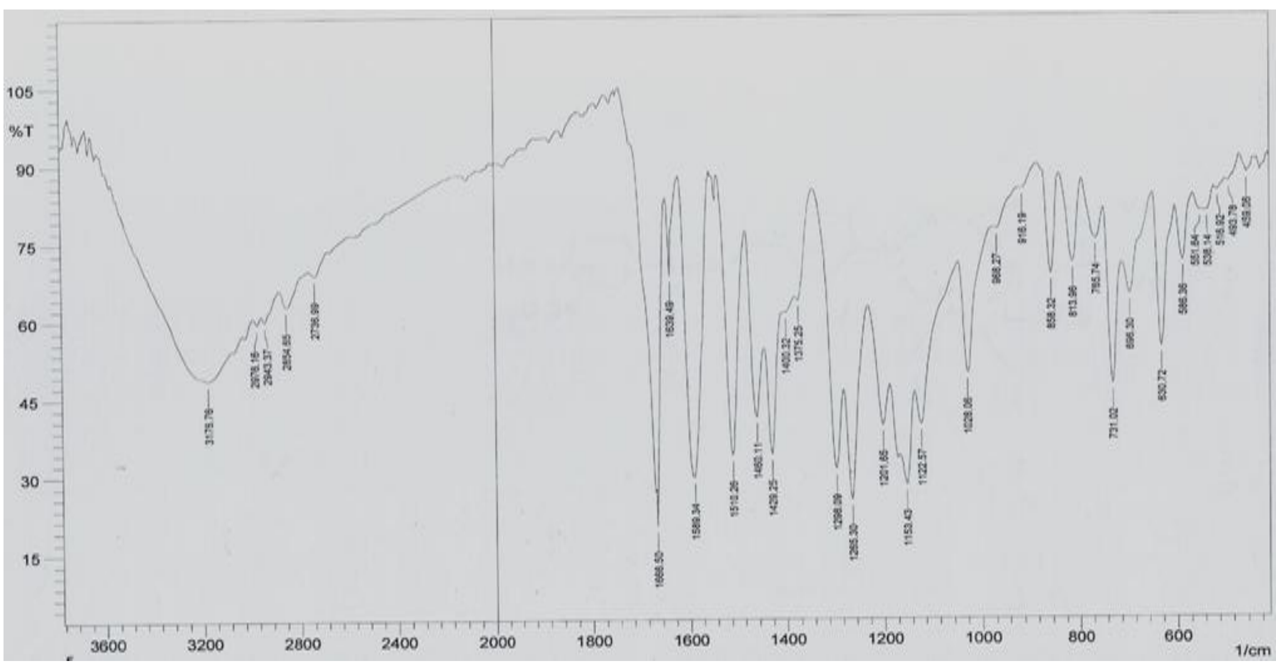

Fig. 5. IR-spectra of the Ligand

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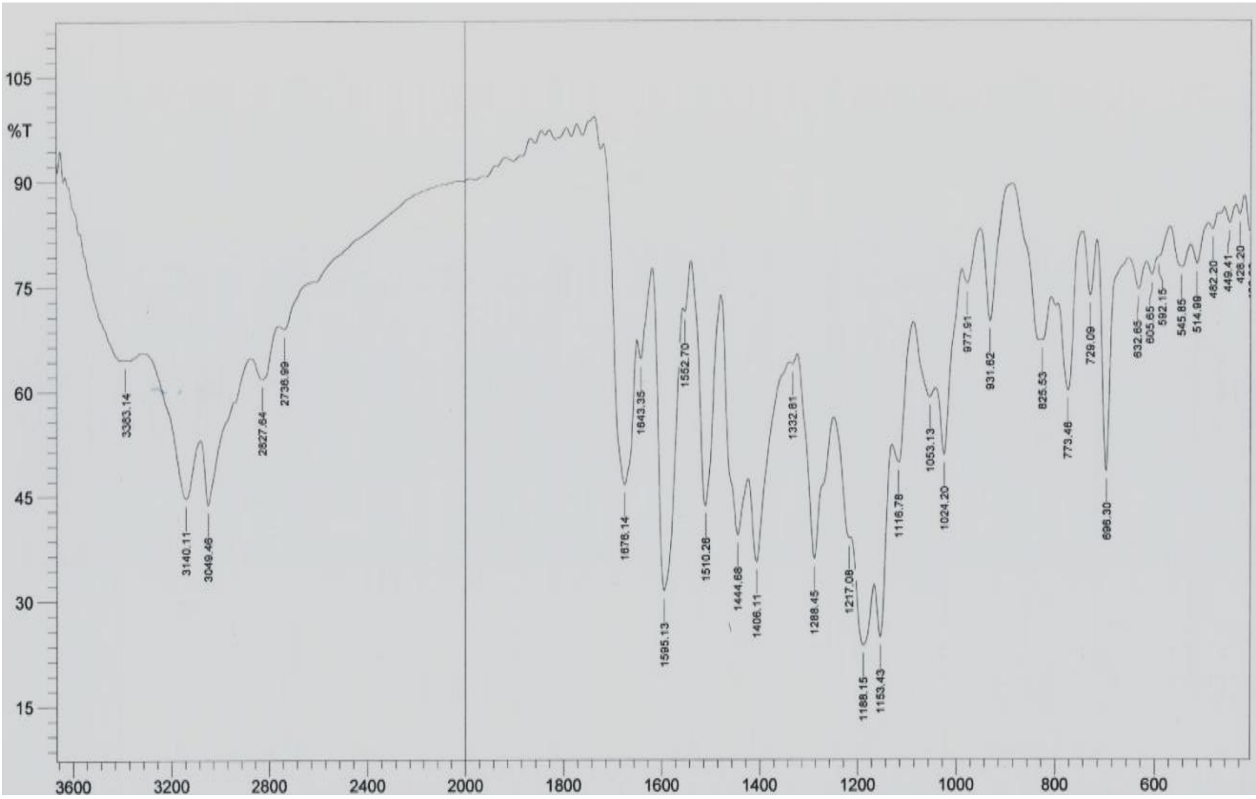

Fig. 6. IR-spectra of Cu (II) complex

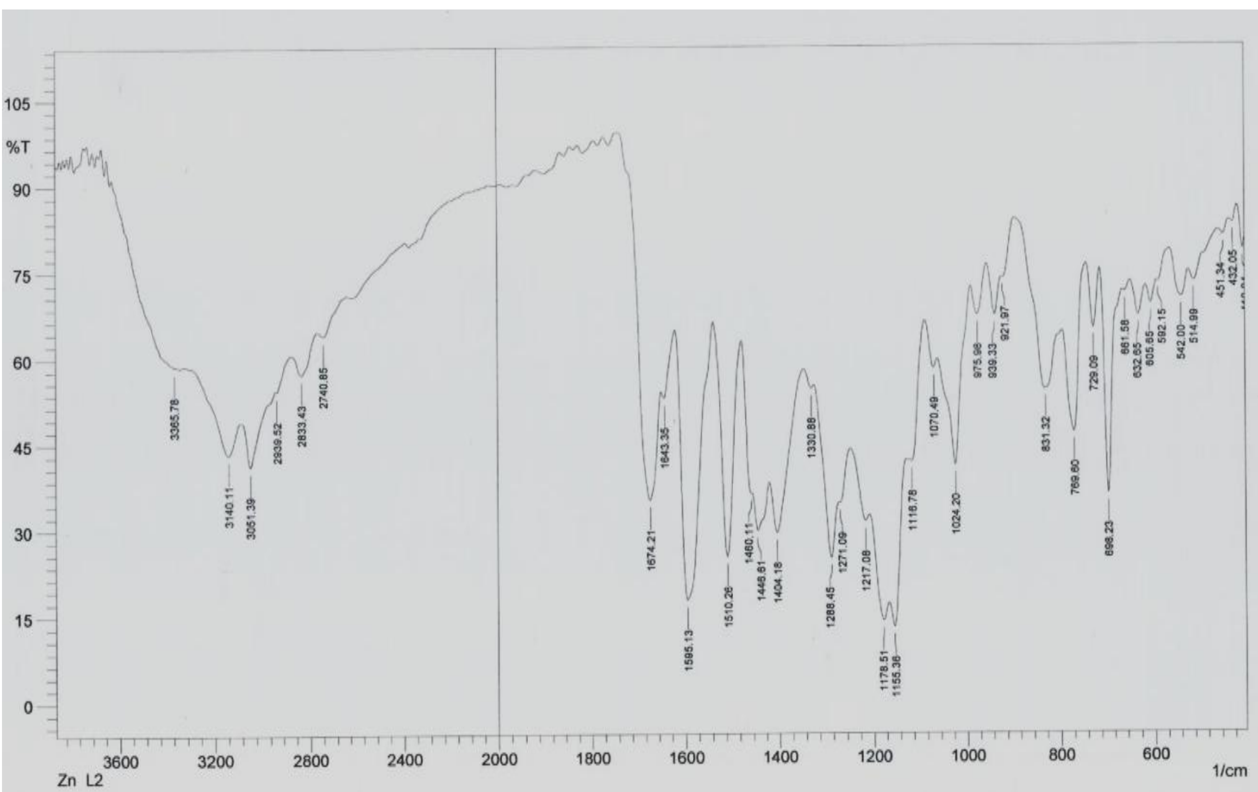

Fig. 7. IR-spectra of Zn (II) complex

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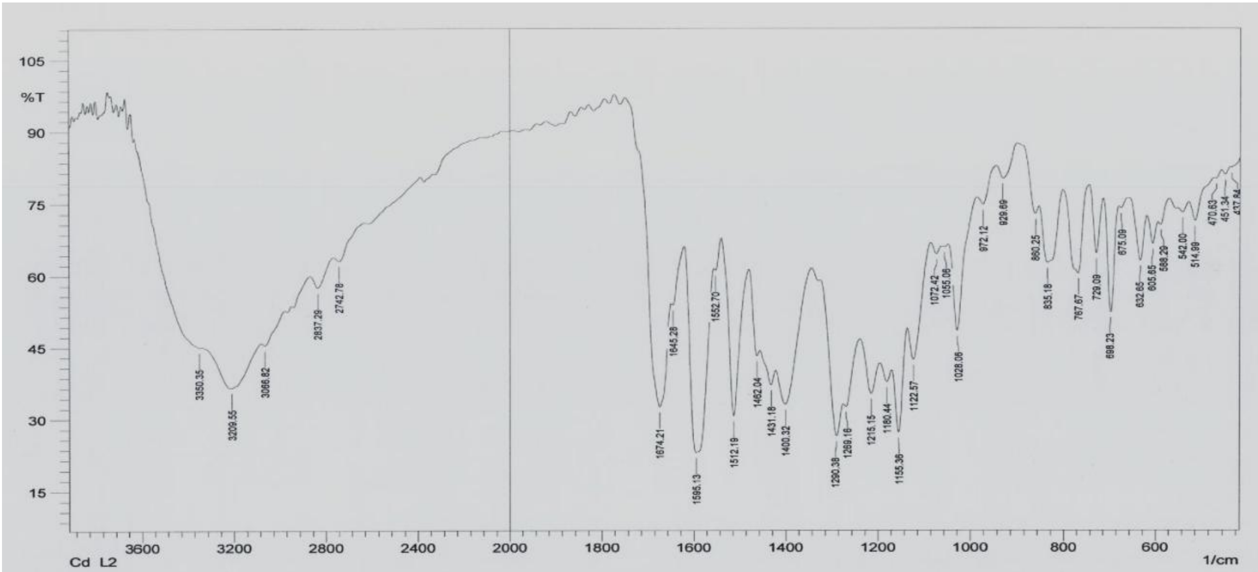

Fig. 8. IR-spectra of Cd (II) complex

Magnetic Susceptibility

The results of the magnetic sensitivity measurements are listed in the table (4) where the magnetic moment value of the magnetic moment of Cu(II) Complex reach (1.76B.M), which indicates the presence of the paramagnetic characteristic resulting from the presence of a single electron for the Cu(II) ion in its complexes[18]. As for the complexes of both Zn(II), and Cd(II) they have shown Di magnetic properties due to the fullness of the plane (nd) in the electrons[19].

Measurement of Molar Conductivity

From the results obtained, it is clear that the molar electrical conductivity measurements for solutions of Chelate complexes of ions under study with the new ligand and with concentration of (1×10^{-3}) molar per complex at the laboratory temperature and using ethanol as solvent , were ranged from (10.58-14.88S. $cm^2.mol^{-1}$) and listed in table (4), We find the lack of ionic properties of all these complexes. These results are identical to what was stated in the literature for metallic complexes devoid of ionic properties [20].

Table 4. Molar conductivity and Magnetic susceptibility values for the complexes in ethanol solution.

compounds	μ_{eff} (B.M)	Λ_M($S.cm^2 . mol^{-1}$)
$[Cu(L_2)_2]Cl_2$	1.76	10.58
$[Zn(L_2)_2]Cl_2$	Dia	8.60
$[Cd(L_2)_2]Cl_2$	Dia	14.88

Electronic Spectra

The electronic absorption spectra are very useful in the estimation of effects equipped thru other approaches of structural exploration. The UV-Vis spectra of new azo Schiff base ligand (L) fig(9) table (5) showed two absorption peaks may be attributed to charge transfer(C.T) bands at the frequency (280mn)($33112cm^{-1}$) and (432nm)($23148cm^{-1}$)[21] which were allotted to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. As for the octahedral copper (II) complex spectrum, it showed one absorption peak, at frequency (906nm)($10245cm^{-1}$)[22] and this indicate that the copper(II) complex took the octahedral shape deformed. As for electronic spectra of the zinc(II) complex, and mercury(II) complex with new azo Schiff base ligand (L), they does not possess type (d-d) electronic transmissions because of the fullness of the five (d) orbitals. As new peaks appeared in the metal ion complexes that were not visible in the ligand spectrum, this indicates the consistency of the metal ion with the new ligand due to the charge transfer (C.T).

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the spectrum of the free ligand is red-shifted in complexes due to ligand to metal charge transfer (LMCT) transition, suggesting an octahedral geometry around metal(II) in the complexes as showed in Fig.(10), (11) and (12).

Table 5. Shows the electronic spectra of ligand and its metal complexes in ethanol solvent.

Compound	Assigument	Absorption band (nm)cm^{-1}	Proposed Structure
L=($C_{23}H_{23}N_5O_2$)	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	(280 nm)34482 (432nm)2348	……….
[$Cu(C_{23}H_{23}N_5O_2)_2$]Cl_2	$^2B_1g\rightarrow^2A_1g$	(906 nm)10245	oh
[$Zn(C_{23}H_{23}N_5O_2)_2$]Cl_2	M→L,CT		oh
[$Hg(C_{23}H_{23}N_5O_2)_2$]Cl_2	M→L,CT		oh

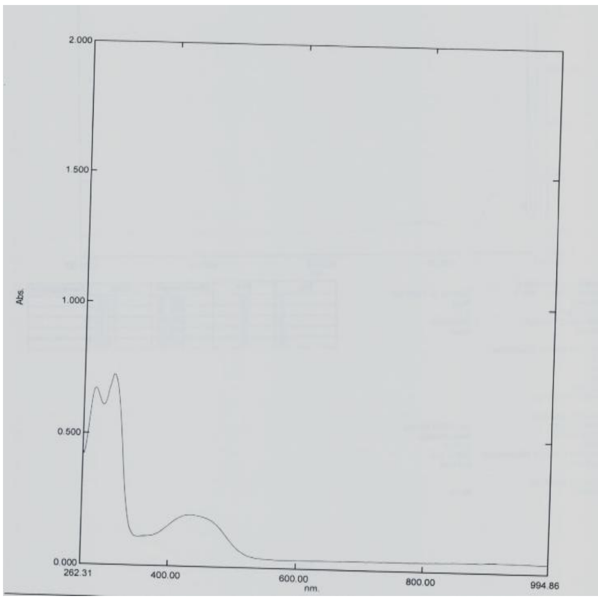

Fig. 9. UV-Vis spectra of new Ligand

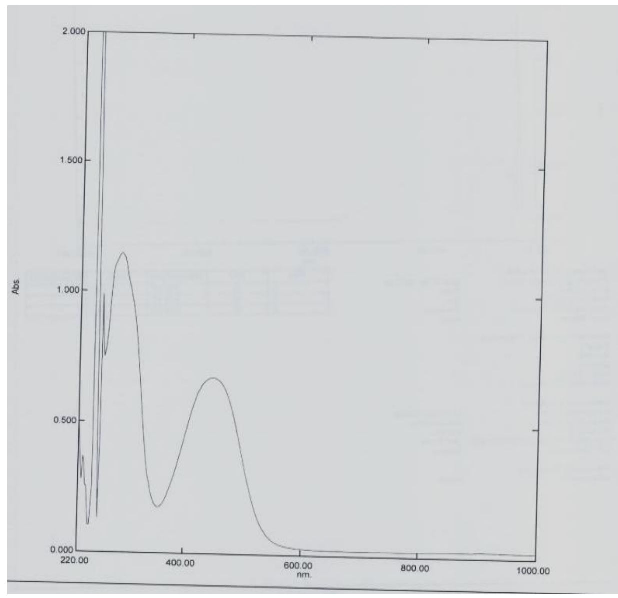

Fig. 10. UV-Vis spectra of Cu(II)complex

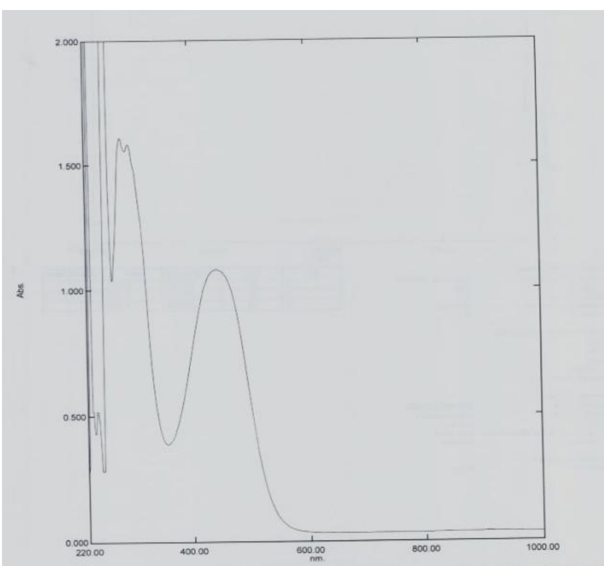

Fig. 11. UV-Vis spectra of Zn(II) complex

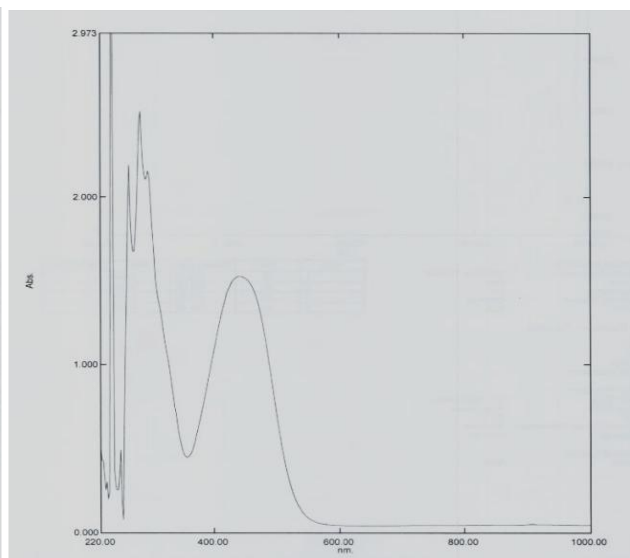

Fig. 12. UV-Vis spectra of Hg(II)complex

Proposed Structural

From the results reached it is possible to proposed the octahedral structure of all metal complexes with new Azo Schiff base ligand(L). The Proposed Structural of metallic complexes can be illustrated in the Fig (13).

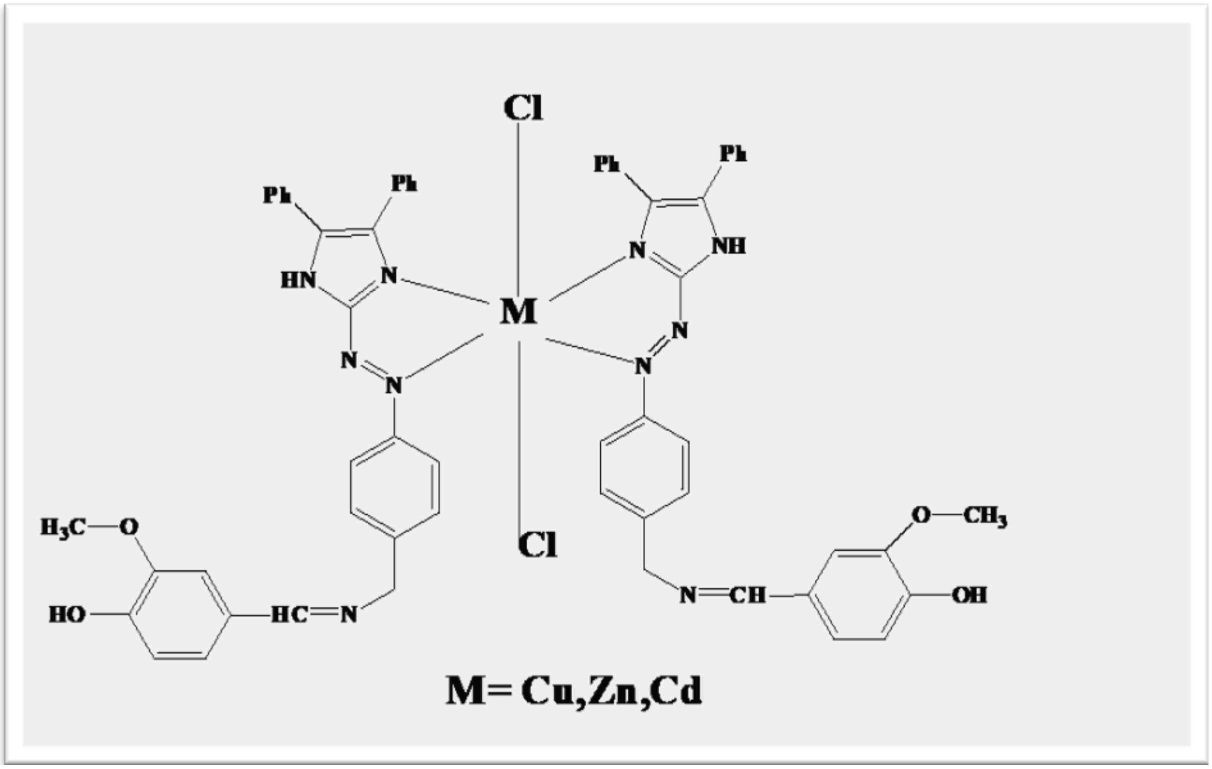

Fig. 13. Proposed Structural of Cu(II), Zn(II) and Cd(II) complexes

References

[1] Kajal, A.; Bala, S.; Kamboj, S.; Sharma, N.; Saini, V. Schiff Bases: A Versatile Pharmacophore. *Journal of Catalysts* 2013, *2013*, 1–14, http://doi.org/10.1155/2013/893512.

[2] Docking Study of New Substituted Schiff Base Derivatives. *Pharmaceutical Chemistry Journal* 2018, *52*, 424-437, http://doi.org/10.1007/s11094-018-1835-0.

[3] Malik, A.; Goyat, G.; Verma, K.K.; Garg, S. Synthesis, Spectral and Antimicrobial Studies of Some O-Vanillin-2-aminopyridine Schiff Base Complexes of Organyltellurium(IV). *Chem. Sci. Trans*. 2018, *7*, 329–337, https://doi.org/10.7598/cst2018.

[4] Kalaiarasi, G.; Dharani, S.; Puschmann, H.; Prabhakaran, R. Synthesis, structural characterization, DNA/protein binding and antioxidant activities of binuclear Ni(II) complexes containing ONS chelating ligands bridged by 1,3-bis(diphenylphosphino)propane. *Inorganic Chemistry Communications* 2018, *97*, 34-38, http://doi.org/10.1016/j.inoche.2018.09.004.

[5] Luo, H.; Xia, Y.; Sun, B.; Huang, L.; Wang, X.; Lou, H. Pan, W. Zhang, X. Synthesis and Evaluation of in Vitro Antibacterial and Antitumor Activities of Novel N,N-Disubstituted Schiff Bases. *Biochem. Res. Int.* 2017, *2017*, http://doi.org/10.1155/2017/6257240.

[6] Al-Shemary, R.K. Design, Synthesis and Biological Evaluation of Schiff Bases and Their Co(II), Cu(II), Ni(II) Chelates from Derivative Containing Indole Moiety Bearing-Triazole. *Eur. Chem. Bull.* 2017, 6, 433-439. http://doi.org/10.17628/ecb.2017.6.433-439.

[7] More, G.; Bootwala, S.Z.; Mascarenhas, J.; Aruna, K. Anti-Microbial And Anti-Tubercular Activity Evaluation of Newly. *International Journal of Pharmaceutical Sciences and Research* 2018, *9*, 3029-3035, http://doi.org/10.13040/IJPSR.0975-8232.9(7).3029-35.

[8] Mahmood Yousif Al-Labban, H.; Mohammed Sadiq, H.; Abduljabbar Jaloob Aljanaby, A. Synthesis, Characterization and study biological activity of some Schiff bases derivatives from 4-amino antipyrine as a starting material. *Journal of Physics: Conference Series* 2019, *1294*, 0–8, http://doi.org/10.1088/1742-6596/1294/5/052007.

[9] Shreekanta, S.A.; Venkatesh, T.V.; Naik, P.P. Murugendrappa, N. Bulk Electroorganic Synthesis of Schiff Bases and Their Electrical Behaviour. *IOSR Journal of Applied Chemistry* 2013, *3*, 31–35.

[10] Bader, N. Applications of Schiff's bases chelates in quantitative analysis: A review. *Rasayan Journal of Chemistry* 2010, *3*, 660-670.

[11] Alorabi, Q.A.; Abdelbaset, M.; Zabin, A.S. Colorimetric Detection of Multiple Metal Ions Using Schiff Base 1-(2-Thiophenylimino)-4-(N-dimethyl)benzene. *Chemosensors* 2020, *8*, http://doi.org/10.3390/CHEMOSENSORS8010001.

[12] Uddin, M.N.; Khandaker, S.; Moniruzzaman; Amin, M.S.; Shumi, W.; Rahman, M.A.; Rahman, S.M. Synthesis, characterization, molecular modeling, antioxidant and microbial properties of some Titanium(IV) complexes of schiff bases. *Journal of Molecular Structure* 2018, *1166*, 79-90, http://doi.org/10.1016/j.molstruc.2018.04.025.

[13] Al Zoubi, W.; Al-Hamdani, A.A.S.; Kaseem, M. Synthesis and antioxidant activities of Schiff bases and their complexes: a review. *Applied Organometallic Chemistry* 2016, *30*, 810-817,

[14] Rabab Mahdi Ubaid Mahmood, Synthesis, Spectral Investigation and Microbial Studying of Pyridine-Heterocyclic Compounds., *European Journal of Molecular & Clinical Medicine*, *2020,* Volume 7, Issue 11, Pages 4444-4453.

[15] S.M. Al-Hassany; Ph.D., College of Science, University of Babylon, (2013).

[16] C. Spinu and A. Kriza; (2000), *J. Acta chem. Slov.*, 47, 179-185.

[17] Rabab Mahdi Ubaid Mahmood, Rajaa Abdul Ameer Ghafil., Synthesis and Characterization some Imidazolidine Derivatives and Study the Biological Activity, *Annals of R.S.C.B.*, ISSN: 1583-6258, Vol. 25, Issue 3, 2021, Pages. 569 - 584 .

[18] Dilek, C., Oguz, Y.S., and Selahattin, S.; (2014), Inte, J. of *Sci. Rest. Innovation tech.*, 1 (2), 52 – 72.

[19] M.M. Hamia.,(2009), *E.J. of Chem.*, 6(51), 508.

[20] C. Anitha, C.D.Sheela, P. Tharmaraj, and R. Shanmugakala; (2013), *International J. of Inorganic Chem.*,1.

[21] D.D. Nasrinl, M.A. Alam, M.N. Hossain, and M. Nazimuddin; (2012) *Chem. J.*, 3 (1),13.

[22] Sk. Jasimuddin, P. Byabartta, G. Mostafa, T.H. Lu, and C. Sinha; (2004), *J. Polyhedron.*, 23, 727-733.