Synthesis and Characterization of a new Schiff basses(3Z,3Z)-3,3' -((oxybis(4,1-phenylene))bis(azanylylidene))bis(indolin-2-one)

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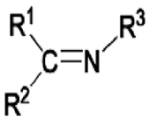
Abstract

The current effort entails the production and characterization of one schiff base compound, which includes the following: (3Z,3Z) -3,3' -((oxybis(4,1-phenylene))bis (azanylylidene))bis (oxybis(4,1-phenylene))bis(oxybis(4,1-phenylene))bis(oxybis(4,1-phenylene))bis (indolin-2-one) The novel compounds were created by ligand interactions with Co^{+2}, Ni^{+2}, and Cu^{+2} are transitional positive metal ions.. To describe the formula of these elemental composition analysis, ligands and related compounds (C.H.N), infrared (IR) spectra, 1H-NMR spectroscopy , mass spectra were utilized. The ligand complexes identified as octahedral structure, with the ligand coordinating with metals through Oxygen and Nitrogen atoms .

Keywords : Characterization , Synthesis , Schiff basses , azanylylidene

1.Introduction :

Hugo Schiff, a Nobel Laureate and German chemist, invented Schiff bases in 1864 [1]. They're the result of the condensing of primary amines and carbonyl compounds The structural counterpart of a ketone or aldehyde where the carbonyl group (C=O) has been substituted with an imine or azomethine group is bases of Schiff (also known as imine or azomethine) [2]. In coordination compounds, Schiff base ligands are significant, notably in the production of Schiff base complexes , since Schiff bases may form stable complexes with metal ions .



R˙ , R˝ and / or R˝ = alkyl or aryl

Fig. 1. structure of General bases of Schiff [4]

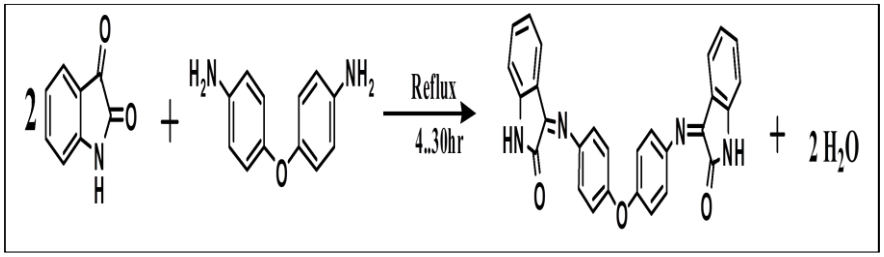
substantial that many bases of Schiff complexes are there? show remarkable active catalytic in a range of activities when the temperature is high (>100°C) and when there's a lot of wetness around. Several research on their application in homogeneous and heterogeneous catalytic reactions have already published in recent literature. [5, 6]. Schiff base ligands and their transition metals are becoming more and more utilized as accelerators in pharmacological systems, color dyes , polymers andFurthermore, these chemicals have been shown to behave as enzyme preparations [7]. Because of their exceptional

selectivity, sensibility, and stability for certain metal ions such as Ag(II), Al(III), Co(II), Cu(II), Gd(III), Hg(II), Ni(II), Pb(II), Y(III), and Zn, a wide range of Schiff base ligands have been used as cation carriers in biosensors (II). The catalytic activity of Schiff bases in the hydrogenation of olefins has been demonstrated in studies of their catalytic characteristics. One of the most fascinating applications of these compounds is their potential to act as efficient corrosion inhibitors. This occurs when a monolayer forms spontaneously on the surface to be covered [8]. The yearly number of articles published (about 500) [8] highlights the increasing interest in metal complexes including bases of Schiff ligands as ligands. Imines are widely distributed in many biological systems and are used in chemical processing and molecular catalysis, as well as pharmaceuticals, pharmacy, and chemistry, as well as technological advances, which illustrates why they are so popular. [9]

2.Preparations of compounds:

general procedure for preparing base of Schiff (Ligand)
(3*Z*,3*Z*)-3,3' -((oxybis(4,1-phenylene))biss(azanylylidene))biss(indolin-2-one)

In overall, the ligand was produced by combining (0.02 mole, 2.95gm) Isatin diluted in 30 ml 95 % ethanol after adding 3-5 drops glacial acetic acid with (0.01 mole, 2.00gm) 4,4'Diaminodiphenyl ether, For a period of time, the solution was refluxed (4.30 hours.) as well as the reaction ,progress was monitored using TLC with hexane: ethyl acetate 1: The solvent evaporates after completion, and the resulting compound is recrystallized with 100% methanol, yielding 82.5 percent yield and m.p (223-225 0C)[10,20,21,22] .



Synthesis of transition metals complexes from shiff base

The ligand was combined (0.46g, 0.001mole) in (25 ml) of hot ethanol and (0.23g, 0.23g,0.17g 0.001mole) of every one of the salts CuCl2.2H2O, CoCl2.6H2O, and NiCl2.6H2O diluted in (10 milliliter) of hot ethanol then refluxed the mixture for 10 minutes (6-7 hr Thin layer chromatography was used to monitor the reaction (TLC), and the precipitate was filtered through filtrate, dried, and recrystallized using 100% ethanol, yielding 74.5, 71.3, and 67.5 percent, correspondingly, Cu(L) Cl_2, Co(L) Cl_2, and Ni(L)Cl_2 are the final chemicals[11,23,24,25].

Table (1) Physical properties of complexes Ligand No.

Symbol	**Formula**	**M.Wt.gm**	**Color**	**M.P °C**	**Yield %**
L	$C_{19}H_{16}N_2O_3$	458.5	Yellow	223-225	82.5
1	[Co(L)Cl_2]	587	Dark yellow	254	71.3
2	[Ni(L)Cl_2]	588	Green	294-296	67.5
3	[Cu(L)Cl_2]	591	Black	271-273	74.5

Results and discussion*3.*

Elemental microanalysis of Schiff base

Table (2) The practical and theoretical ratios of Schiff bases *CHN*.

symbol	practical			Theoretical		
	C %	H %	N %	C %	H %	N %
Ligand$C_{19}H_{16}N_2O_3$	73.28	3.84	12.31	73.35	3.96	12.22

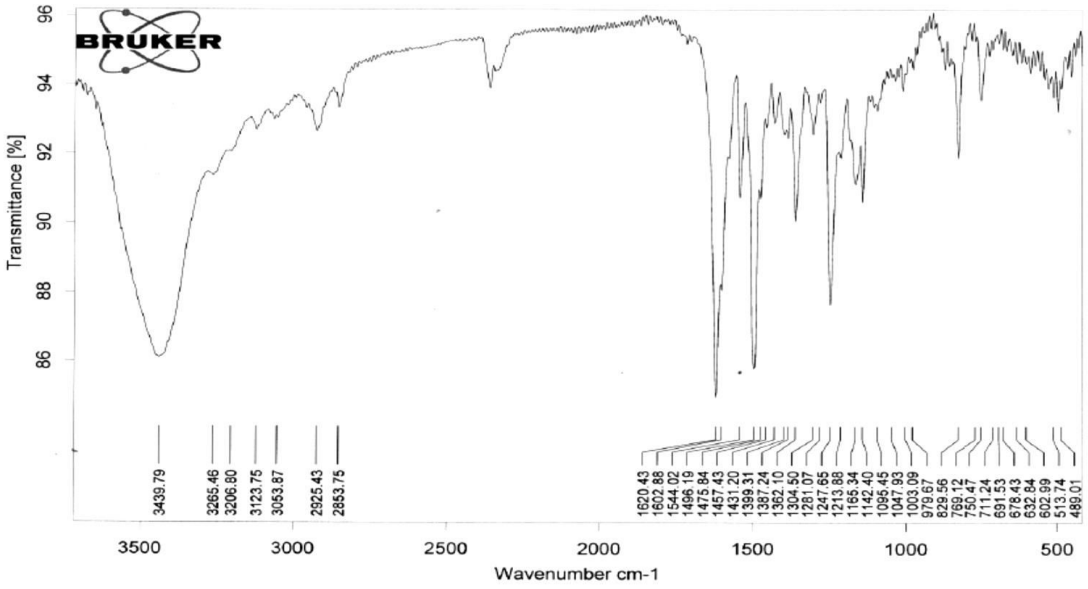
3.1 Infra-Red Spectroscopy Study

Infrared Spectra of bases of schiff

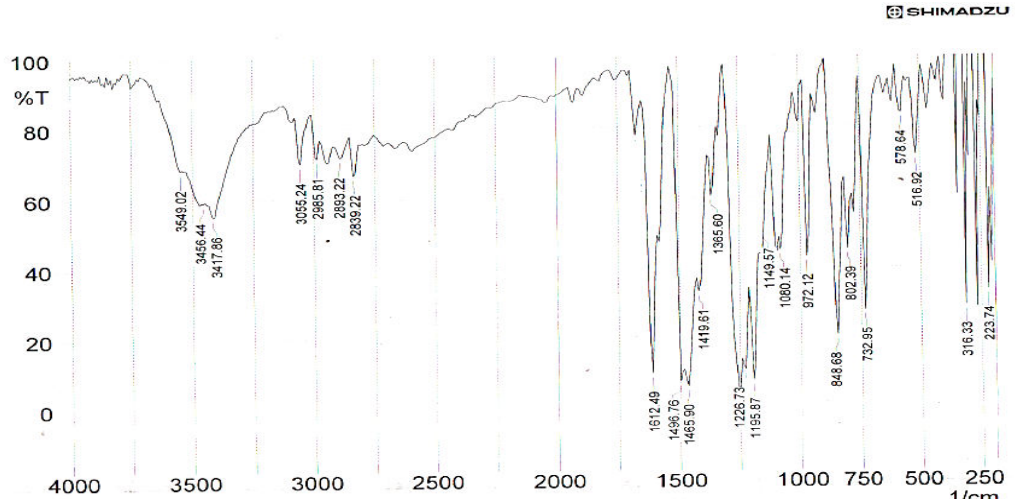
The FT-IR spectra of bases of Schiff molecule are showedat Tables 1-3. The distinctive absorption bands in the spectral region in the spectral region (1608-1624 cm-1) attributed stretch of the azomethene group (C=N) are found in bases of Schiff . Back to the stretch of the bond, it also owns bands in the range (3202-3551 cm-1) (O-H) On the other hand, these Schiff bases have strong bands in the rear to extend of the aromatic rings' bond (C=C) range (1531-1577 cm-1). As well as all Schiff bases with the bands at the range that have been prepared (2895-2995 cm-1).backing to the stretch for an aromatic group (C-H), and consists a band at (3075 cm-1) back to the stretch group (N-H), and consists a band at (1000-1200 cm-1) back to the stretch group (N-H) back to the stretch group (N-H) back to the stretch group (N-H) back to the stretch group (N-H) back to the stretch group (N-H) back to the stretch group (N-H) back to the stretch (C-O-C). Complexes spectra indicating the appearance of additional bands that were not present in the spectrum of those bands are (617-691cm-1), (432-462), and (401-421cm-1) return to stretching vibration (M-N), (M-O), and (M-Cl) correspondingly, confirming the complexity processes[13,14,15,26,27]

Table (3): FT-IR peaks value of the Schiff bases compounds.

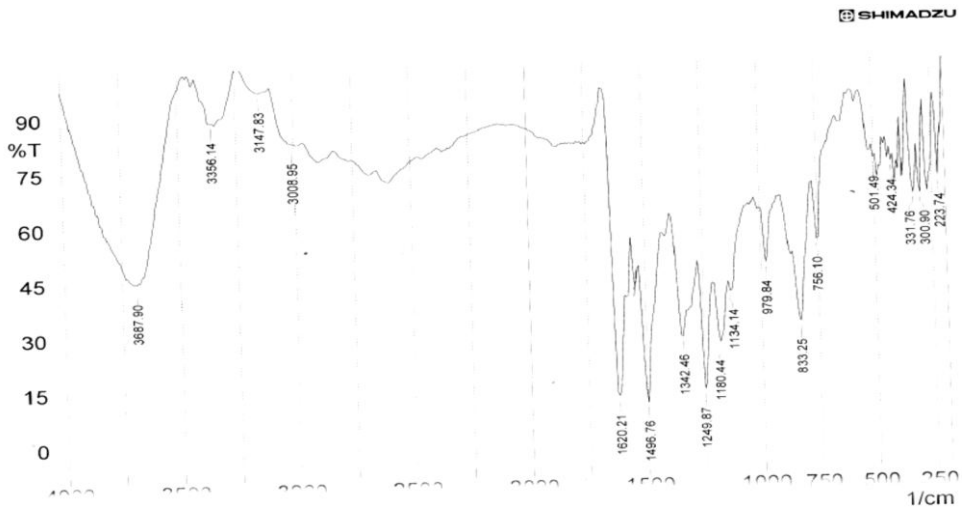
symbol	C-H (Ar)	C=N	N-H	C=C (Ar)	C-O-C (Ether)	M-O	M-N	M-Cl
Ligand$C_{19}H_{16}N_2O_3$	**3075**	**1612**	**3255 3178**	**1589**	**1195**	**—**	**—**	**—**
[Cu(L_1)Cl_2]	**2962**	**1616**	**3400**	**1449**	**1161**	**462**	**513**	**402**
[Co(L_1)Cl_2]	**2995**	**1613**	**3433**	**1492**	**1097**	**433**	**537**	**400**
Ni(L_1)Cl_2]	**2924**	**1642**	**3430**	**1548**	**1100**	**420**	**558**	**370**



Figure(1) IR spectra of the ligand($C_{19}H_{16}N_2O_3$)



Figure(2) IR spectra of the complex[$Cu(L)Cl_2$]



Figure(3) IR spectra of the complex[$Co(L)Cl_2$]$2H_2O$

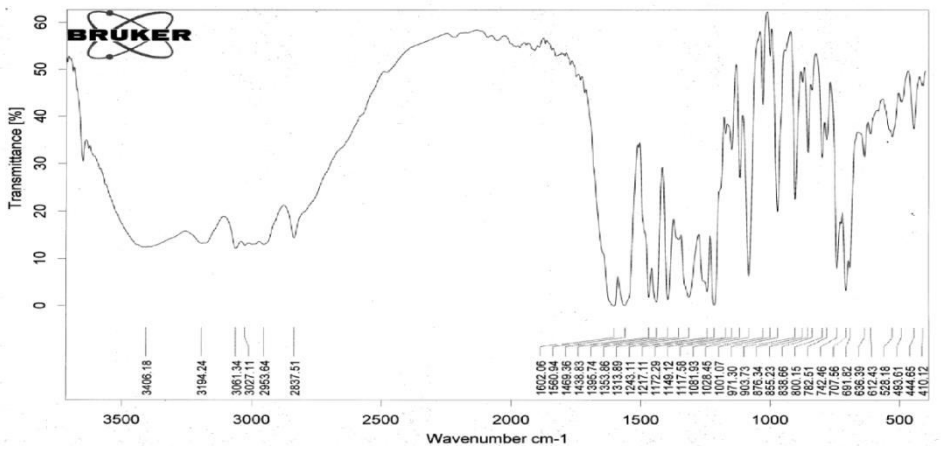
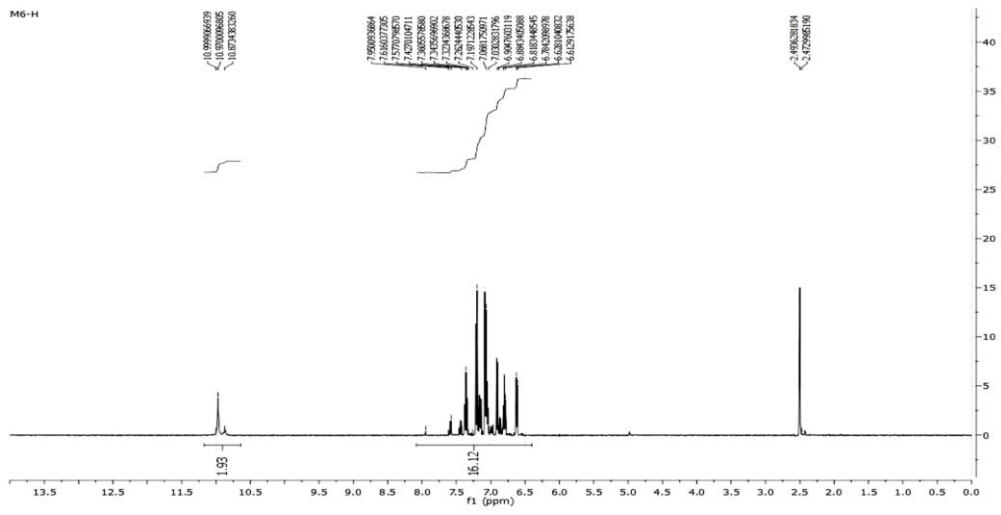


Figure (4) IR spectra of the complex [$Ni(L)Cl_2$]

3.2 H- NMR spectra of Schiff base

The 1H-NMR spectra of the produced Schiff base displays multiplet signal at molecular shift () (6.61- 7.40 ppm) owing to aromatic ring protons (Ar-H), and the emergence of a singlet signal at (10.97 ppm) due to the symmetrical protons of a group (-NH) in Isatin. And for the DMSO-d6 solvent, spectra revealed a signal at 2.5 ppm[16,17,27,28].

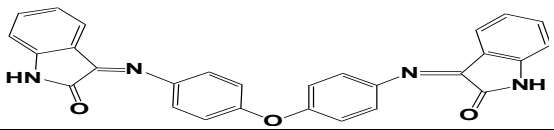


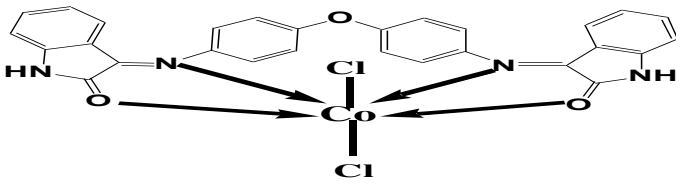
Figure(5) ^{1}H – NMR spectrum data of the prepared ligand.

3.3*Massspectrum of Schiff bases with their complexes*
Mass spectra of a ligand

Categorizing mass spectra of the ligand presence of molecular ion (M+.) at (458 m/z) as the spectra revealed a partial ion at (76 m/z) due to the benzene ring also describes the spectrum presence of peaks 430, 402,286, 210, 117, 76 m/z, and 65 m/z owing to [C27H18N4O2] [18,19,28,29].

Scheme(1) Includes the important peaks which attributed to thefragmentation ofLigand

	**m/z**
$C_{28}H_{18}N_4O_3$	**458**
$[C_{27}H_{18}N_4O_2]^{+\cdot}$,	**430**
$[C_{26}H_{18}N_4O]^{+\cdot}$	**402**
$[C_{19}H_{13}N_2O]^{+\cdot}$	**286**
$[C_{13}H_9N_2O]^{+\cdot}$	**210**
$[C_7H_5N_2]^{+\cdot}$	**117**
$[C_6H_4]^{+\cdot}$	**76**

	**m/z**

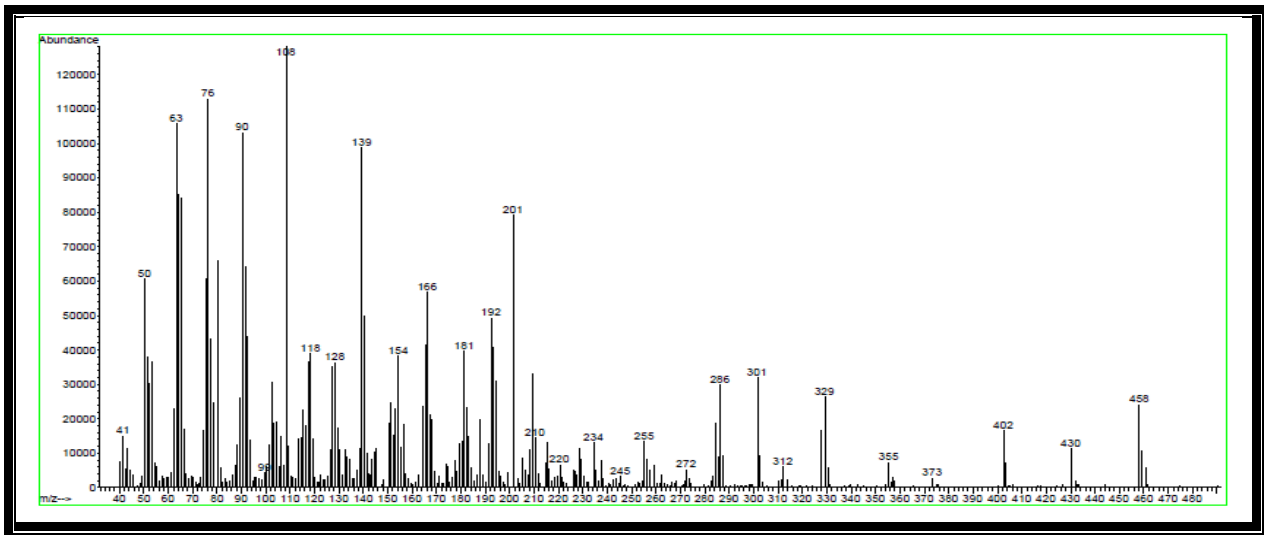


Figure (6) mass spectra of Ligand

Co[$(Cl_2)^{+\cdot}L_5$)	587
Co[$(Cl)^{+\cdot}L_5$)	552
Co[$()^{+\cdot}L_5$)	517
$[L_5]^{+\cdot}$	458

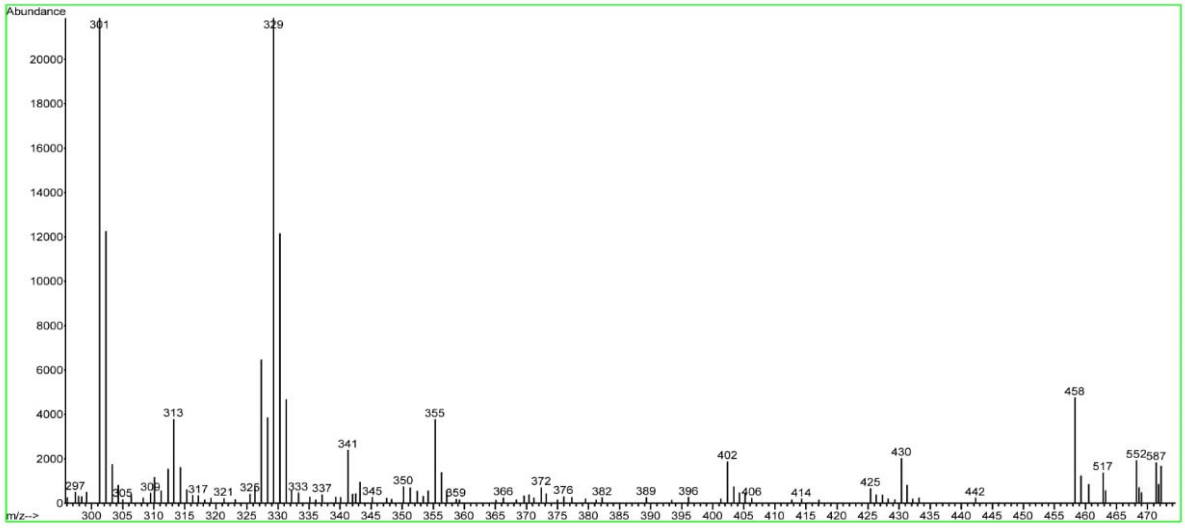
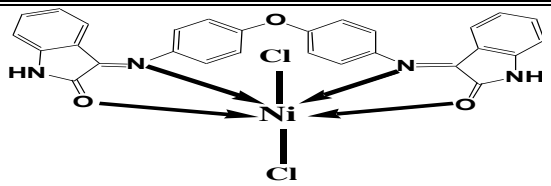
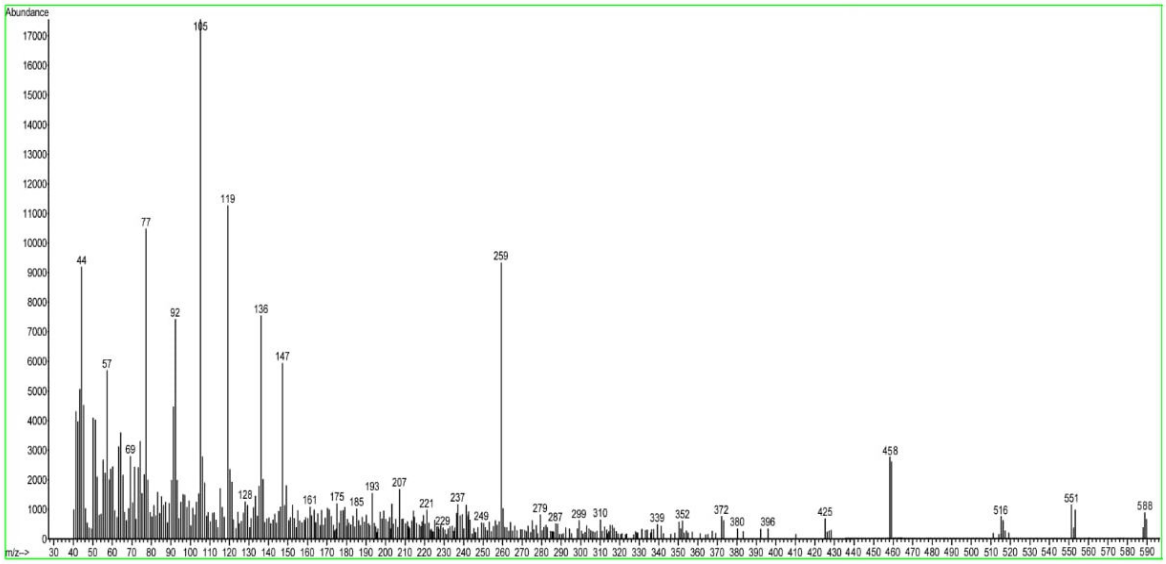


Figure (7) mass spectra of Ligand $[Co(L_1)Cl_2]2H_2O$

	**m/z**
Ni[$(Cl_2)^{+\cdot}L_5$)	588
Ni[$(Cl)^{+\cdot}L_5$)	551
Ni[$()^{+\cdot}L_5$)	516
$[L_5]^{+\cdot}$	458



[Ni(L)Cl_2]2H_2OFigure (8) mass spectra of Ligand

References

1. Brodowska, K., Sykuła, A., Garribba, E., Łodyga-Chruścińska, E., & Sójka, M. (2016). Naringenin Schiff base: antioxidant activity, acid–base profile, and interactions with DNA. *Transition Metal Chemistry*, *41*(2), 179-189

2. Xia, L., Xia, Y. F., Huang, L. R., Xiao, X., Lou, H. Y., Liu, T. J., ... & Luo, H. (2015). Benzaldehyde Schiff bases regulation to the metabolism, hemolysis, and virulence genes expression in vitro and their structure–microbicidal activity relationship. *European journal of medicinal chemistry*, *97*, 83-93.

3. Nair, M. S., Arish, D., & Joseyphus, R. S. (2012). Synthesis, characterization, antifungal, antibacterial and DNA cleavage studies of some heterocyclic Schiff base metal complexes. *Journal of Saudi Chemical Society*, *16*(1), 83-88**.**

4. Zeng, W., Lee, S., Son, M., Ishida, M., Furukawa, K., Hu, P., ... & Wu, J. (2015). Phenalenyl-fused porphyrins with different ground states. *Chemical Science*, *6*(4), 2427-(4)2433

5. Montazerozohori, M., & Musavi, S. A. (2008). Synthesis and spectral characterization of a new symmetric bidentate Schiff-base and its zinc complexes. *Journal of Coordination Chemistry*, *61*(24), 3934-3942.

6. Katyal, M., & Dutt, Y. (1975). Analytical applications of hydrazones. *Talanta*, *22*(2), 151-166.

7. Shemirani, F., Mirroshandel, A. A., Niasari, M. S., & Kozani, R. R. (2004). Silica gel coated with Schiff's base: Synthesis and application as an adsorbent for cadmium, copper, zinc, and nickel determination after preconcentration by flame atomic absorption spectrometry. *Journal of Analytical Chemistry*, *59*(3), 228-233.

8. Gupta, V. K., Singh, A. K., & Gupta, B. (2006). A cerium (III) selective polyvinyl chloride membrane sensor based on a Schiff base complex of N, N′-bis [2-(salicylideneamino) ethyl] ethane-1, 2-diamine. *Analytica chimica acta*, *575*(2), 198-204.

9. Fătu, D., & Popescu, V. (2003). The thermal behaviour of some Co (II) complex combinations with schiff bases. *Journal of thermal analysis and calorimetry*, *71*(2), 521-529.

10. Ganjali, M. R., Tavakoli, M., Faridbod, F., Riahi, S., Norouzi, P., & Salavati-Niassari, M. (2008). Interaction Study of a new Bis-Bidentate Schiff's Base with some metal ions and its application in fabrication of Sm (III) potentiometric membrane sensor. *Int. J. Electrochem. Sci*, *3*, 1559-1573.

11. Afatt, S. S., & Mahdi, H. A. (2012). Synthesis and Characterization of a new Schiff Base {N-(2-{[(4-bromophenyl) imino] methyl} phenyl) acetamide} and its complexes with some transition metal. *Journal of College of Education for Pure Science*, *2*(4), 110-117.

12. FA, S. Synthesis, Spectral and Thermal Characterization of Selected Metal Complexes Containing Schiff Base Ligands with Antimicrobial Activities.

13. Ejidike, I. P., & Ajibade, P. A. (2015). Synthesis, characterization and biological studies of metal (II) complexes of (3E)-3-[(2-{(E)-[1-(2, 4-dihydroxyphenyl) ethylidene] amino} ethyl) imino]-1-phenylbutan-1-one Schiff base. *Molecules*, *20*(6), 9788-9802.

14. Kamble, R. R., Sudha, B. S., & Bhadregowda, D. G. (2008). Expeditious synthesis of 1, 3, 4-oxadiazole derivatives via sydnones. *Journal of the Serbian Chemical Society*, *73*(2), 131-138.

15. Nassar, M. Y., Ahmed, I. S., Dessouki, H. A., & Ali, S. S. (2018). Synthesis and characterization of some Schiff base complexes derived from 2, 5-dihydroxyacetophenone with transition metal ions and their biological activity. *Journal of Basic and Environmental Sciences*, *5*, 60-71.

16. Fatoni, A., Hariani, P. L., Hermansyah, H., & Lesbani, A. (2018). Synthesis and Characterization of Chitosan Linked by Methylene Bridge and Schiff Base of 4, 4-Diaminodiphenyl Ether-Vanillin. *Indonesian Journal of Chemistry*, *18*(1), 92-101.

17. Rosu, T., Negoiu, M., Pasculescu, S., Pahontu, E., Poirier, D., & Gulea, A. (2010). Metal-based biologically active agents: Synthesis, characterization, antibacterial and antileukemia activity evaluation of Cu (II), V (IV) and Ni (II) complexes with antipyrine-derived compounds. *European Journal of Medicinal Chemistry*, *45*(2), 774-781.

18. Parsaee, Z., & Mohammadi, K. (2017). Synthesis, characterization, nano-sized binuclear nickel complexes, DFT calculations and antibacterial evaluation of new macrocyclic Schiff base compounds. *Journal of Molecular Structure*, *1137*, 512-523.

19. Hasan, M. R., Hossain, M. A., Salam, M. A., & Uddin, M. N. (2016). Nickel complexes of Schiff bases derived from mono/diketone with anthranilic acid: Synthesis, characterization and microbial evaluation. *Journal of Taibah University for Science*, *10*(5), 766-773.

20. Alsafee, B. A. H. (2014). Preparation and characterisation of some transition metal complexes of new 4-[(5-ethyl-1, 3, 4-oxadiazol-2-yl) sulfanyl] aniline. *The Swedish Journal of Scientific Research*, *1*(6), 11-23.

21. Hassan, B. A., Nasera, H. N., & Abdulridha, M. M. (2019). Synthesis and antimicrobial evaluation of fused heterocyclic compound [1, 2, 4] triazolo [4, 3-b][1, 2, 4, 5] tetra zine. *International Journal of Research in Pharmaceutical Sciences*, *10*(2), 1254-1258.

22. Hamed, L. D. F. M., Lectu, A., & Hassan, B. A. The non-antibacterial activity of sulfonamide derivatives

23. Abdulridha, M. M., Hassan, B. A., & Hamed, F. M. (2018). Synthesis And Antibacterial Evaluation Of 1, 3, 4-Thiadiazole Containing 1, 3, 4-Oxadiazole Bearing Schiff Bases. *International Journal Of Pharmaceutical Research*.

24. Alsafee, B. A. H. (2017). Synthesis, Identification and Antibactrial Activity of Some New Heterocyclic Compounds Contaning 1, 3, 4-Thiadiazole and 1, 3, 4-Oxadiazole Bearing Schiff Base. *Iraqi National Journal Of Chemistry*, *17*(2).

25. Hasan, B. A. H., Hussein, U. A. R., Salih, H. A., Abbas, A. T., & Mtuasher, S. M. (2017). Antimicrobial activity of ethanolic and aqueous extracts of pomegranate peel against Extended Spectrum Beta-Lactamase producing bacteria. *University of Thi-Qar Journal*, *12*(4), 1-14.

26. Alsafee, B. A. H., & Abdulridha, M. M. (2016). Synthesis and characterization of Cu (II) and Fe (II) metal complexes of oxazepine derivative via Schiff base [Fe (HPOHBOT) Cl2] and [Cu (HPOHBOT) Cl2]. *African Journal of Pharmacy and Pharmacology*, *10*(35), 728-736.

27. Alsafee, B. A. H. (2015). Preparation and characterization of some transition metal complexes of 4-amino-N-(5-sulfanyl-1, 3, 4-thiadiazol-2-yl) benzenesulfonamide. *International Journal of Scientific & Engineering Research*, *6*(1), 37-45.

28. Alsafee, B. A. H. (2014). Preparation and characterisation of some transition metal complexes of new 4-[(5-ethyl-1, 3, 4-oxadiazol-2-yl) sulfanyl] aniline. *The Swedish Journal of Scientific Research*, *1*(6), 11-23.

29. Hasan, B. A., & Abdulridha, M. M. PREPARATION AND CHARACTERISATION OF SOMETRANSATION METAL COMPLEXES OF NEW [BUTANAL (5-ETHYL-1, 3, 4-OXADIA-ZOL-2-YL) HYDRAZONE].