Information Horizons: AMERICAN Journal of Library And Information Science Innovation
Volume 3, Issue 11, 2025 ISSN (E): 2993-2777

Synthesis, Characterization and Thermal Analysis (TG, DTA and DSC) of Novel Schiff Base Derivatives From 4-Chloro-2-Fluoro Aniline and its Complexes with Copper (II) and Nickel (II) Ions

Haneen Shaker Sachit, Haider Abbas Mahdi
Department of Chemistry, College of Science, University of Thi-Qar, Iraq

Abstract. *Preparation of Schiff Bases from the Reaction of 4-Chloro-2-fluoroaniline with 3-Ethoxysalicyldehyde (Ligand 1) and 4-Methoxy salicyldehyde (Ligand 2) and Their Complexation with Copper (II) Chloride CuCl2.2H2O (1:2) and Nickel (II) Chloride NiCl2.6H2O (1:1). characterization on the basis their spectra of 1H-NMR, Fourier transform infrared (FTIR), and Differential scanning calorimetry to assess the thermal characteristics of the produced (TG, DTA andDSC). Spectral data of the ligands were found to be in a good agreement with their structures, and their complexes with Cu (II) and Ni (II) were synthesized.*

1. Introduction:

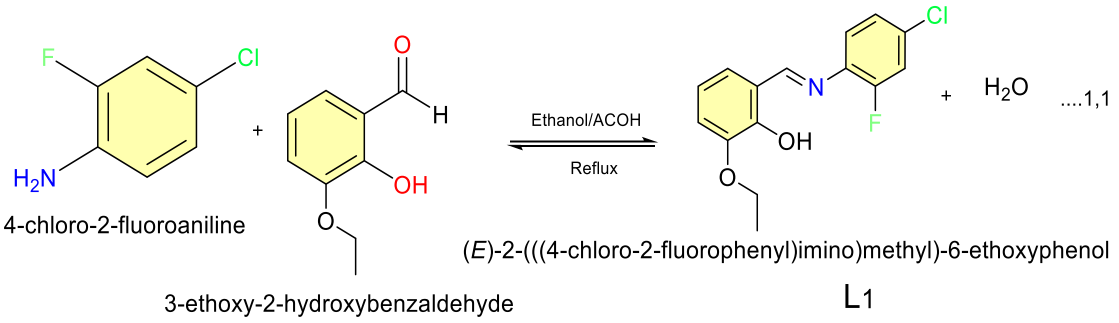
The first reported by Hugo Schiff in 1869[1], Schiff bases are condensation products of primary amines with carbonyl compounds (aldehyde or ketone) Schiff bases are an important class of organic compounds [2,3]. The common structural feature of these compounds is the azomethine group with the first general formula **RHC = N-R^1**, where **R** and **R^1** are alkyl, aryl, cyclo alkyl, or heterocyclic groups [4]. Structurally, a Schiff base (also known as imine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group **(C= O**) is replaced by an imine or azomethine group **(CH= N**) **[5**], Imines or ketamine are the names given to the bond formed by the reaction with the ketone, whilst azomethine or aldimine is the name given to the bond formed by the reaction with the aldehyde [6,7]. A wide variety of biological properties, such as antifungal [8,9], antibacterial [10,11], antimalarial [12], antioxidant [13,14], anticancer [15], antiviral [16], antiproliferative [17], and anti-inflammatory [18], have also been demonstrated for Schiff's bases. Schiff bases are frequently translucent, pigmented solids.[19] They are used to measure metal amounts and identify metals due to their precise melting points. carbonyl substances.[20] Because the carbon-nitrogen double bond in Schiff bases rotates more readily than the carbon-carbon double bond, stereoisomers can be used interchangeably. Because nitrogen is more electronegative than carbon, the azomethine bond becomes polarized.[21] Because of the double bond's electron-donating ability and the nitrogen atom's unshared electron pairs, all compounds with an azomethine group exhibit fundamental characteristics.[22] Schiff bases have less basic characteristics than their equivalent amines.[23] This is because, whereas the nitrogen atom in amines experiences sp3 hybridization, when thiamine structure is created, this hybridization changes to sp2 hybridization.[24] The C=N system's infrared stretch bands are often seen between 1610 and 1635 cm−1, whereas C=N are seen between 1665 and 1690 cm−1.[25]

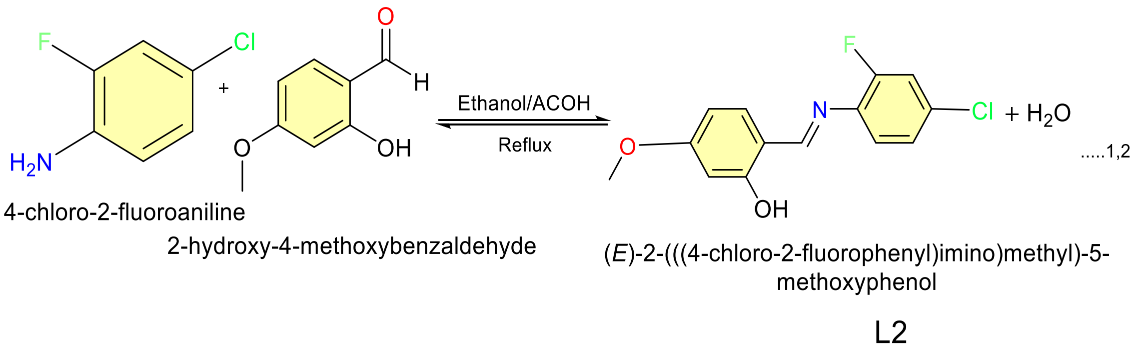
2. Experimental

All reagents and chemicals used in this study were in the analytical grade and purchased from (Sigma- Aldrich). The melting points of synthesized compounds were measured on the SMP31 melting point apparatus and on the FT.IR affinity (Shimadzu) spectrophotometer using KBr pellets.While their ^{1}H-NMR was recorded in DMSO-d_6 on the Bruker 400MHZ instrument, the internal standard is TMS. Work mass selective Detector 5973

1.2: Synthesis legands

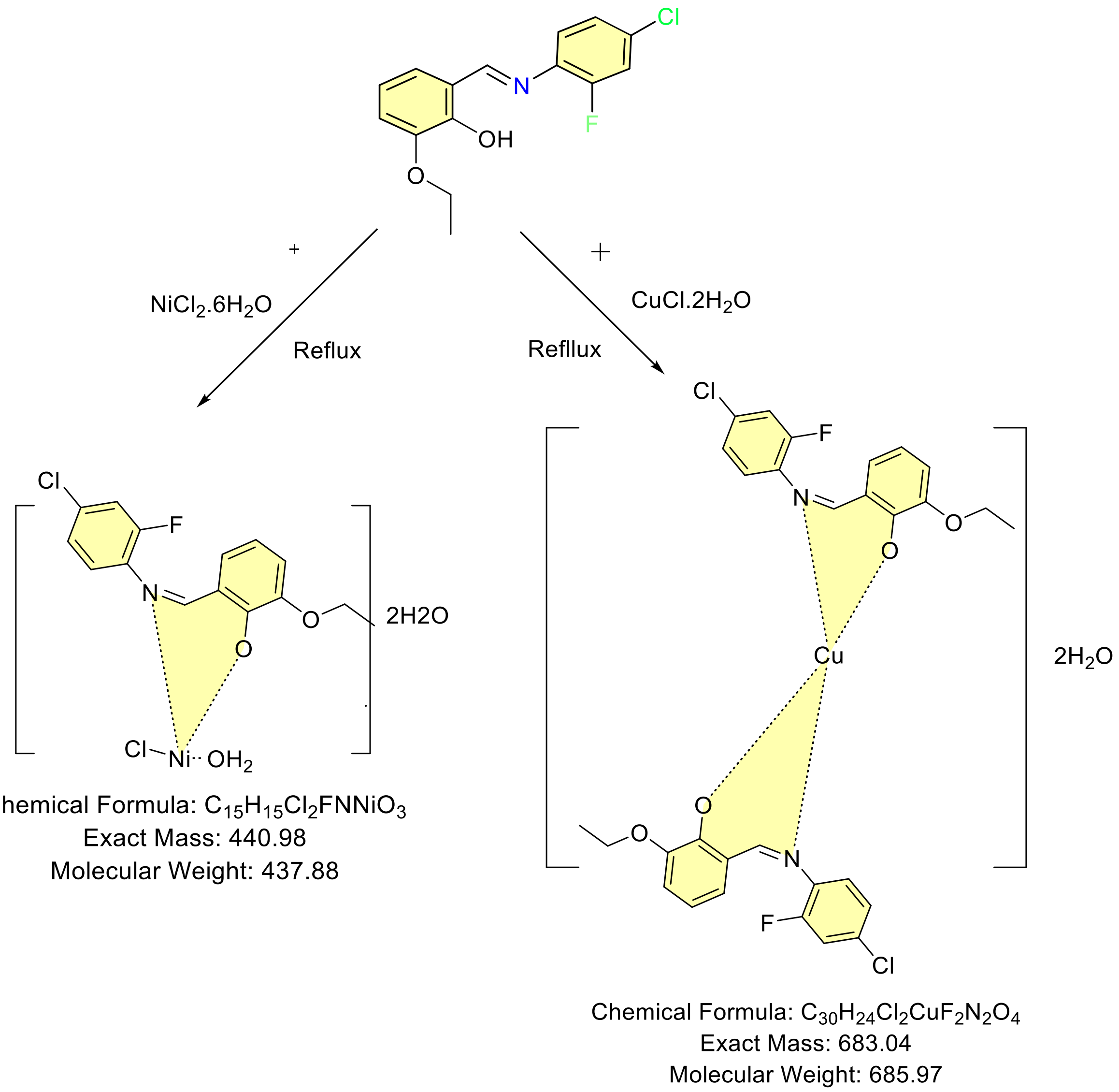
These ligands are prepared from dissolved amine(0.01mol,1.45g)of 4-chloro-2fluoro aniline Solute with (15ml)ethanol 99.9% and Aldehydes (0.01mol, 1.66g) (3-ethoxy Salicyldehyde) for ligand L1and (0,01mol,1.52g) (4-methoxy Salicyldehyde) for ligand L2 and Soluted with(15ml) ethanol99.9%.With add drops of glacial acetic acid to the aldehyde as a catalyst with continuous stirring for a period of (10min)After that, the amine is added to the aldehyde mixture with continuos stirring for several hours The interaction is followed in a way (TLC) after the end of the reaction is cooled to precipitate the product. The solution is filtered, dried and recrystallized with hot ethanol (99.9%) as shown in equation (1,1), (1,2)





Synthesis Schiff base Complexes 2.2:

Schiff base complexes are prepared by dissolving (0.001 mol, 0.001 g) of the prepared ligands L1, L2, in (10ml) of absolute ethanol in a circular flask of (100 ml) with (0.001 mol) of salts of the elements also dissolved in (10ml) of ($CuCl_2.2H_2O$, $NiCl_2$.6H2O) and absolute ethanol the copper complexes were synthesized using a ratio 1:2 (metal:ligand) wereas nickel complexes synthesized using a ratio 1:1 and and then heat the mixture back for (2-3 hr.) The end of the reaction was followed up by the thin layer chromatography technique TLC, after which the mixture was cooled and separated by filtration with washing the product with cold ion-free water several times and left to dry completely. as shown in cheme(1-1)



Cheme(1-1) Synthesis Schiff base Complexes

3: Results and Discussion

All the physical properties and atomic data of the ligand and its complexes were gathered in the table (1)

Table (1) Physical properties of ligands and compleX

Chemical Formula	M.Wt	Color	°c m.p	Yield %
C15H13ClFNO2	293.72	orange	185.5	78
$C_{30}H_{28}Cl_2CuF_2N_2O_6$	685	brown	239.6	80
$C_{15}H_{18}Cl_2FNNiO_3$	438.9	green	205.2	70
C14H11ClFNO2	279.69	yallow	151.3	75
$C_{28}H_{22}Cl_4CuF_2N_2O_4$	696.8	brown	225.1	69
$C_{14}H_{19}Cl_3FNNiO_6$	494.3	green	196.1	72

3.1: FT-IR spectra

FT-IR of the synthesized ligands were gathered in the table (2). The FT-IR spectrum of ligands showed stretching characteristic vibration bands appeared at (3440-3749),(2970-3090),(2839-2928), (1581-1627), (1541-1599) and due to the υ (O-H)group, υ (C-H) aromatic group, υ (C-H) alaphtic group, υ (C=N)azomethine group, υ (C=C) [27] group respectively, as shown in the figures (1).

Table (2) Infrared spectra of Ligand and its metal complexes (υ cm^{-1})

No.	υ (O-H)	υ (C-H) aromatic	υ (C-H) alaphatic	υ (C=N) azomethane	υ (C=C)
L1	3440	3067	2928	1614	1599
[Cu(L1)$_2$]2H$_2$O		3062	2885	1612	1543
[Ni(L$_1$) Cl (H$_2$O)]2H$_2$O	3448	2970	2877	1627	1535
L2	3739	3090	2902	1615	1562
[Cu(L2)2] Cl$_2$	3741	3016	2839	1581	1541
[Ni(L2) Cl$_2$(H$_2$O)$_2$]2H$_2$O	3749	3015	2846	1620	1566

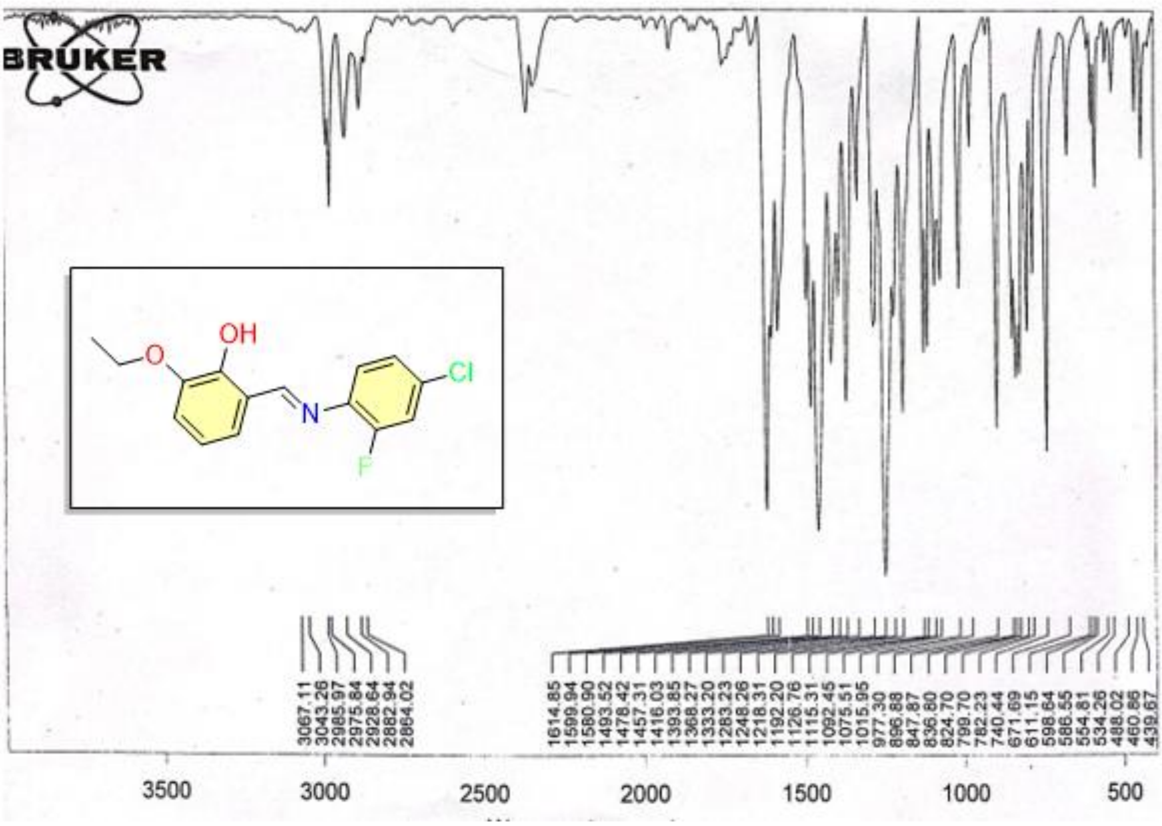


Fig. (1) FTIR spectrum of L1

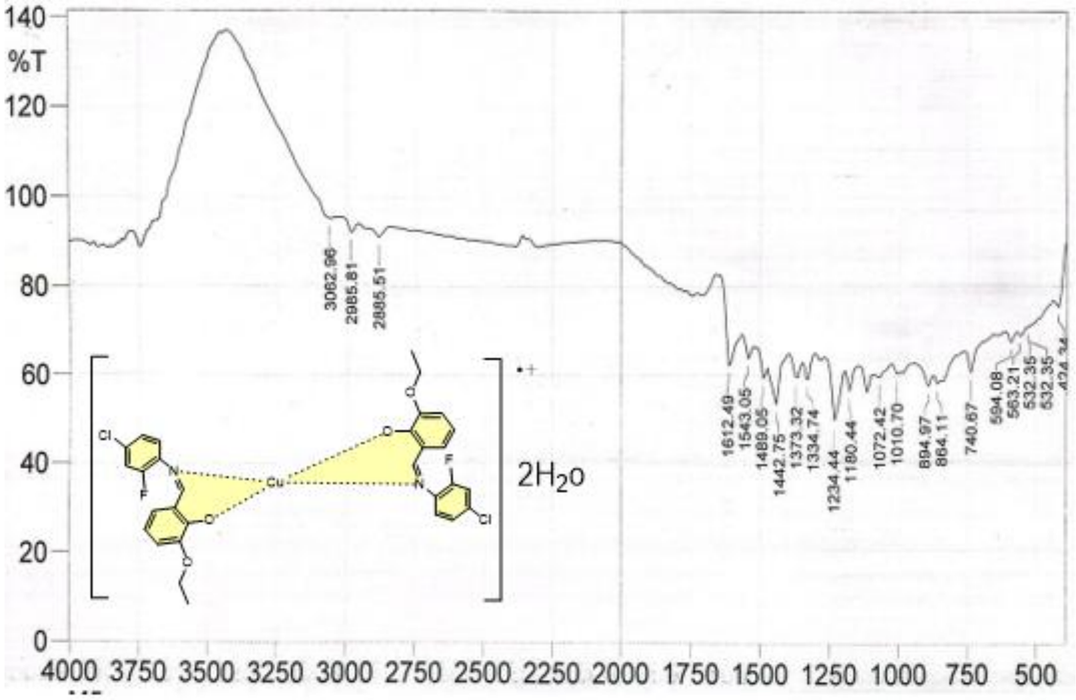


Fig. (2) FTIR spectrum of [cu(L1)$_2$]2H$_2$0

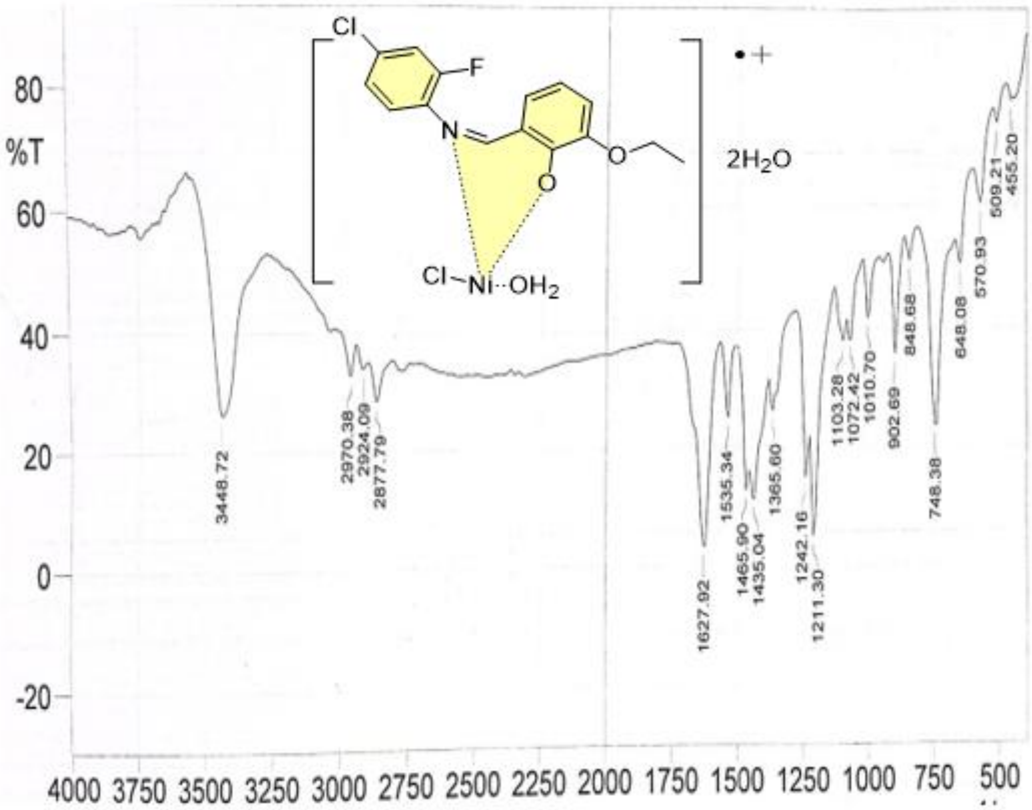


Fig. (3) FTIR spectrum of [Ni(L1) Cl (H$_2$O)]2H$_2$O

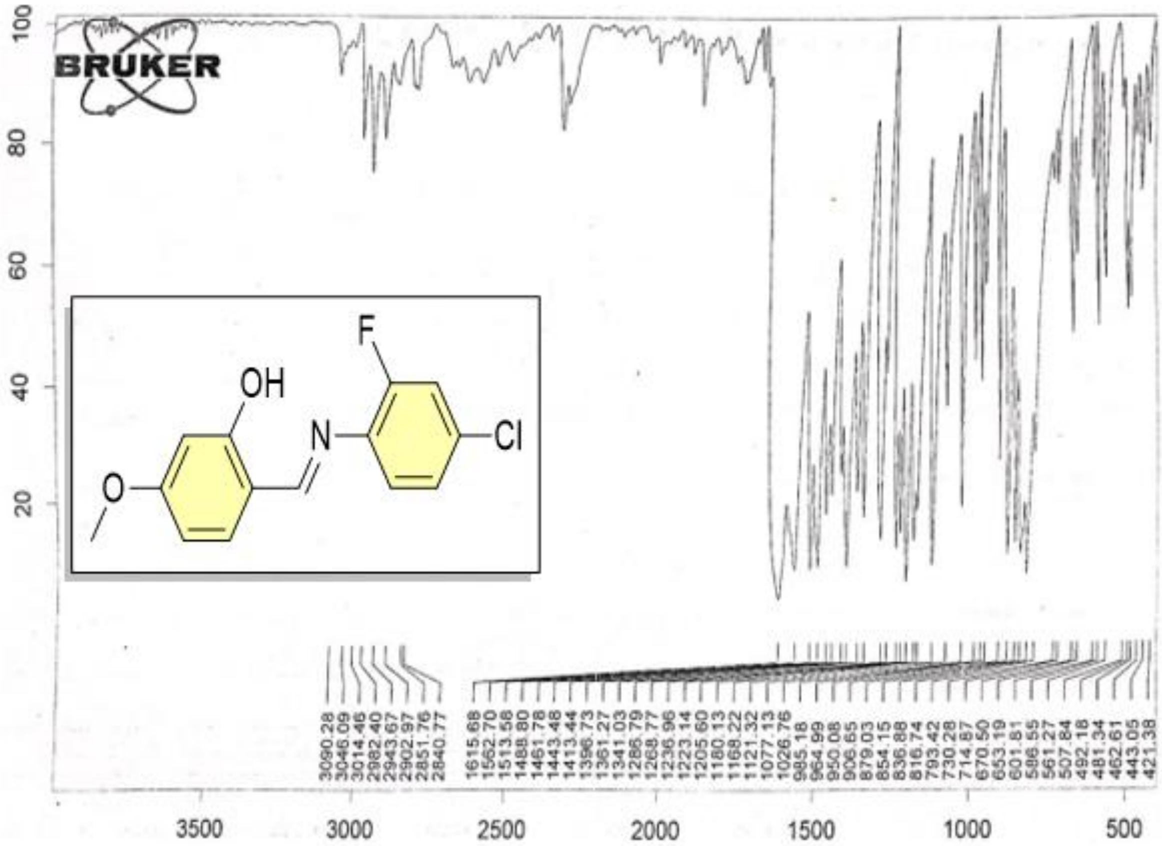


Fig (4) FTIR spectrum of L2

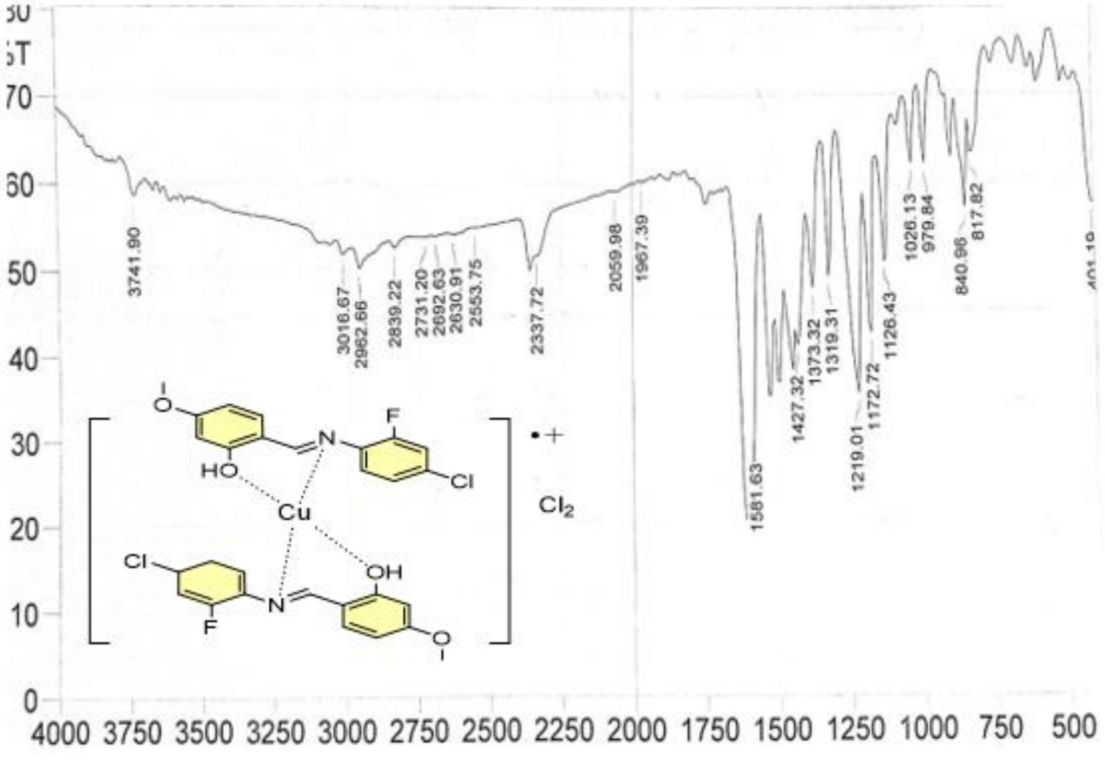


Fig (5) FTIR spectrum of $[Cu(L_2)_2]Cl_2$

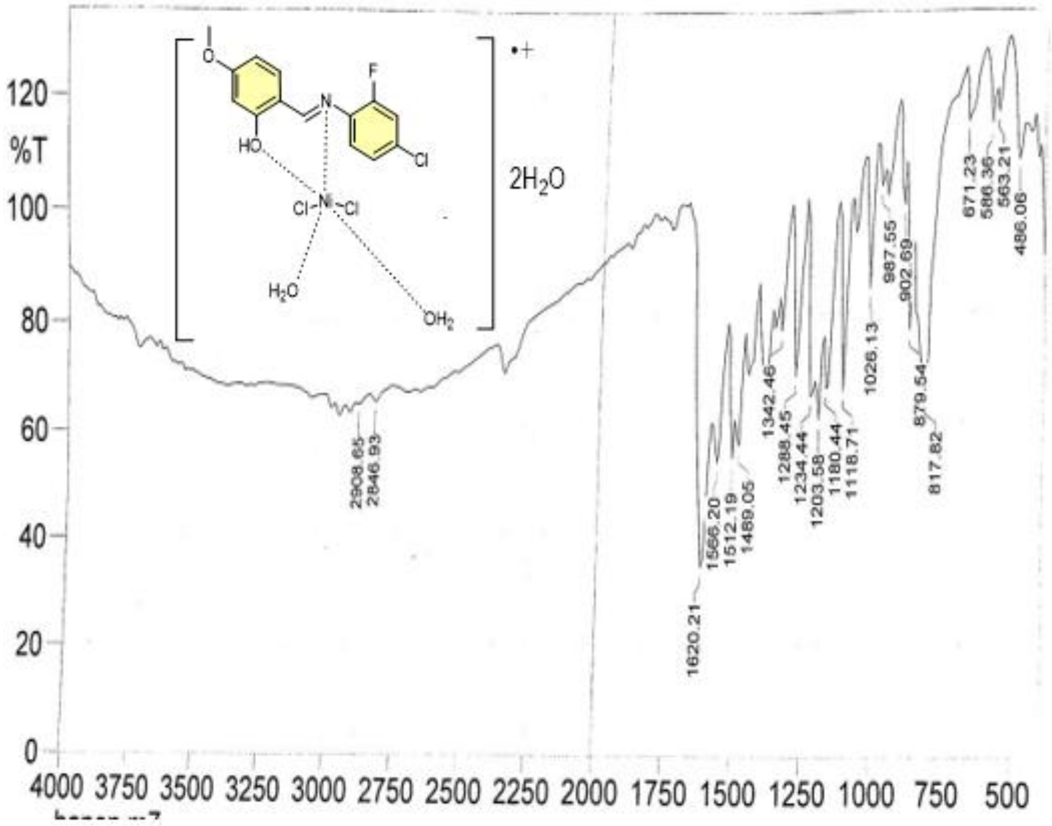
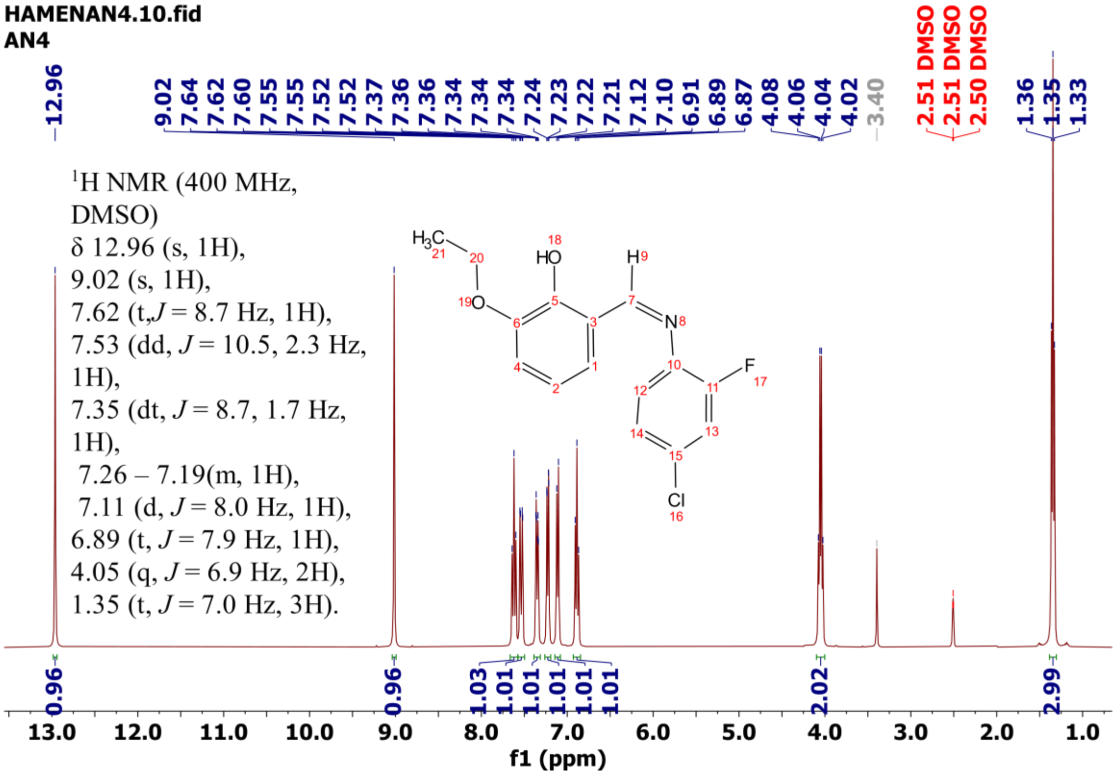


Fig (6) [Ni(L_2) $(Cl)_2(H_2O)_2$]$2H_2O$

3.2:^{1}H-NMR Spectral

The ^{1}H-NMR spectrum of the ligand (L1) was appeared two signals at (1.35) ppm and (4.05) ppm and due to the proton of (CH_3) and (CH_2) respectively, melti signals at (7.19-7.95) ppm due to the aromatic group [28], while the signal of the azomethine groups at (9.02) ppm, the signal of phenolic groups at (12.96) ppm. As shown in the figure (7)

The ^{1}H-NMR spectrum of the ligand (L2) was appeared two signals at (3.81) ppm due to the proton of (OCH_3), melti signals at (6.50-7.61) ppm due to the aromatic group, while the signal of the azomethine groups at (8.93) ppm, the signal of phenolic groups at (13.36) ppm. As shown in the ^{1}H-NMR data and figure (8)[28]



^{1}H NMR (400 MHz, DMSO)
δ 12.96 (s, 1H),
9.02 (s, 1H),
7.62 (t,*J* = 8.7 Hz, 1H),
7.53 (dd, *J* = 10.5, 2.3 Hz, 1H),
7.35 (dt, *J* = 8.7, 1.7 Hz, 1H),
7.26 – 7.19(m, 1H),
7.11 (d, *J* = 8.0 Hz, 1H),
6.89 (t, *J* = 7.9 Hz, 1H),
4.05 (q, *J* = 6.9 Hz, 2H),
1.35 (t, *J* = 7.0 Hz, 3H).

Fig (7) ^{1}H-NMR spcteum of L1

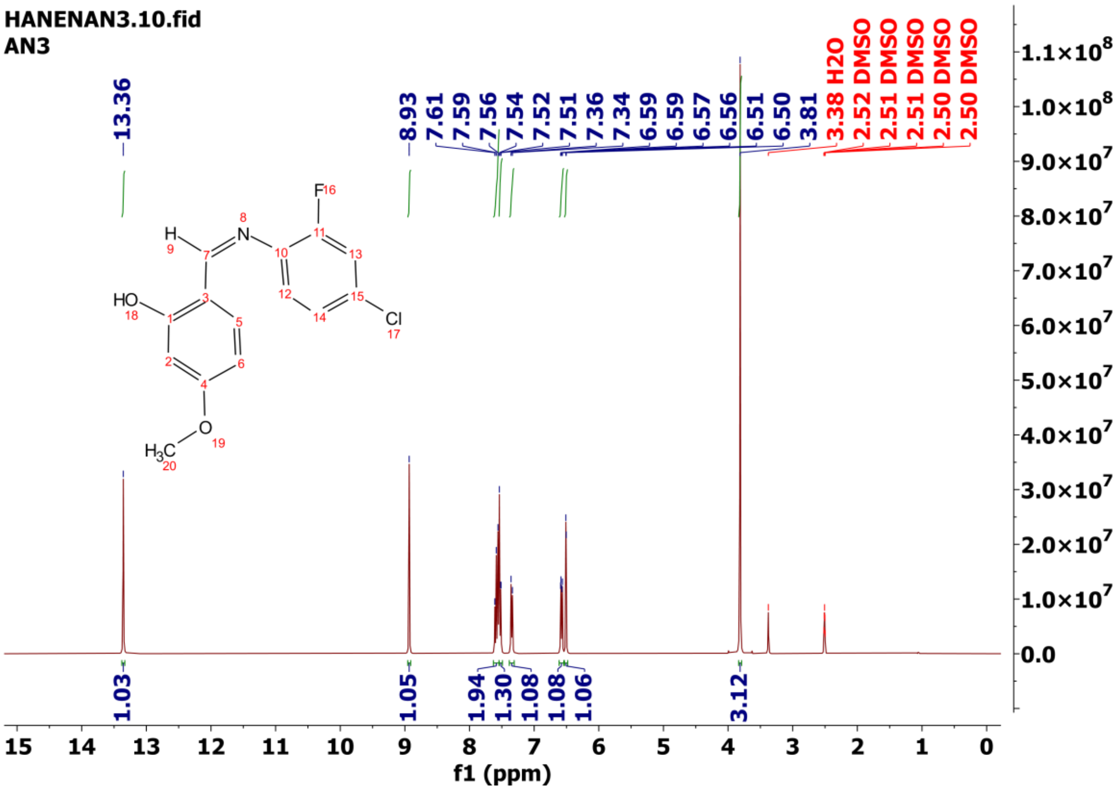


Fig (8)^1 H-NMR spcteum of L2

3.3: The mass spectra

Mass spectrometry has been successfully used to investigate molecular species; The pattern of mass spectrum gives an impression of the successive degradation of the target compound with the series of peaks corresponding to the various fragments. Their intensity gives an idea of the stability of Fragments [29], the stoichiometry of compounds was compared using mass spectra obtained at room temperature (21) °C in Table (3) and figures (5-10). Each synthesized compounds matched the molecular ion fragment and supported the proposed structure.

Table (4)- Mass spectra of synthesized compound

Compound	Calculated mass	Obtain mass (m/z)	Peak assigned
L1	293	293	M^+
$[Cu(L1)_2]2H_2O$	685	687	$[M+2H]^+$
$[Ni(L_1) Cl (H_2O)]2H_2O$	438	440	$[M+2H]^+$
L2	279	279	M^+
$Cu(L2)_2] Cl_2$ [	696	694	$[M-2H]^+$
$[Ni(L2) Cl_2(H2O)_2]2H_2O$	494	492	$[M-2H]^+$

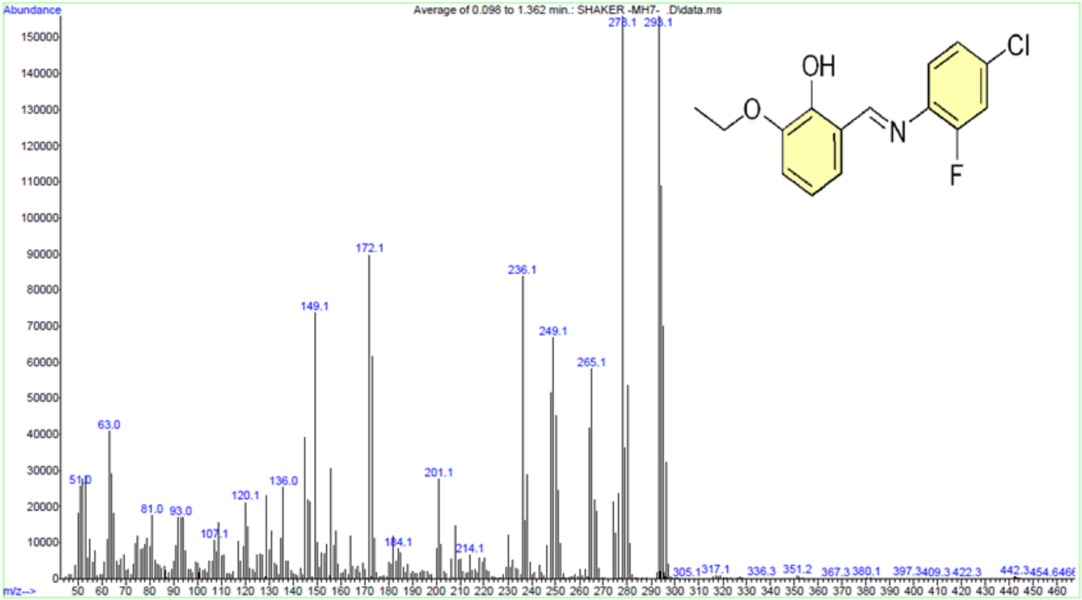


Fig (9) mass spctrum of legand L1

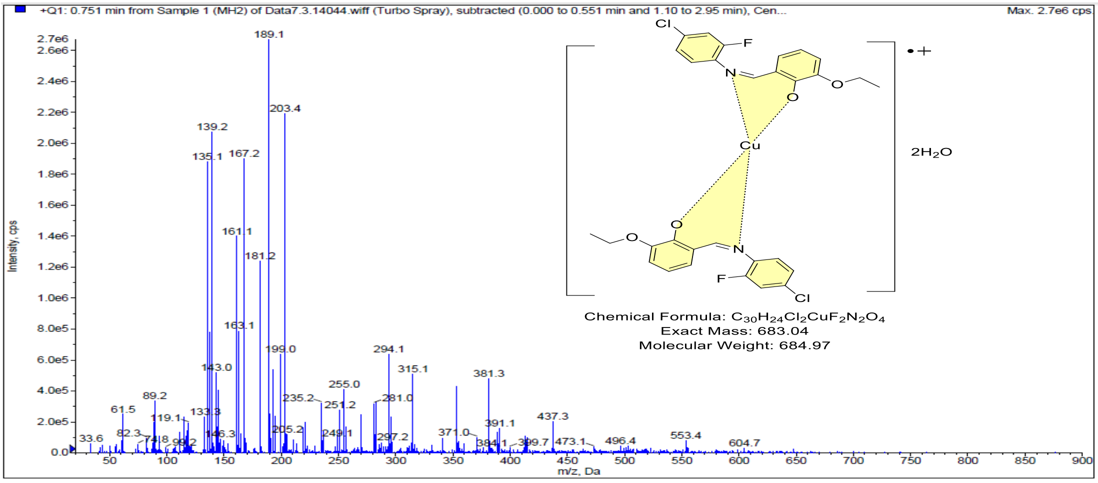


Fig. (10) mass spctrum of complex $[Cu(L1)_2]2H_2O$

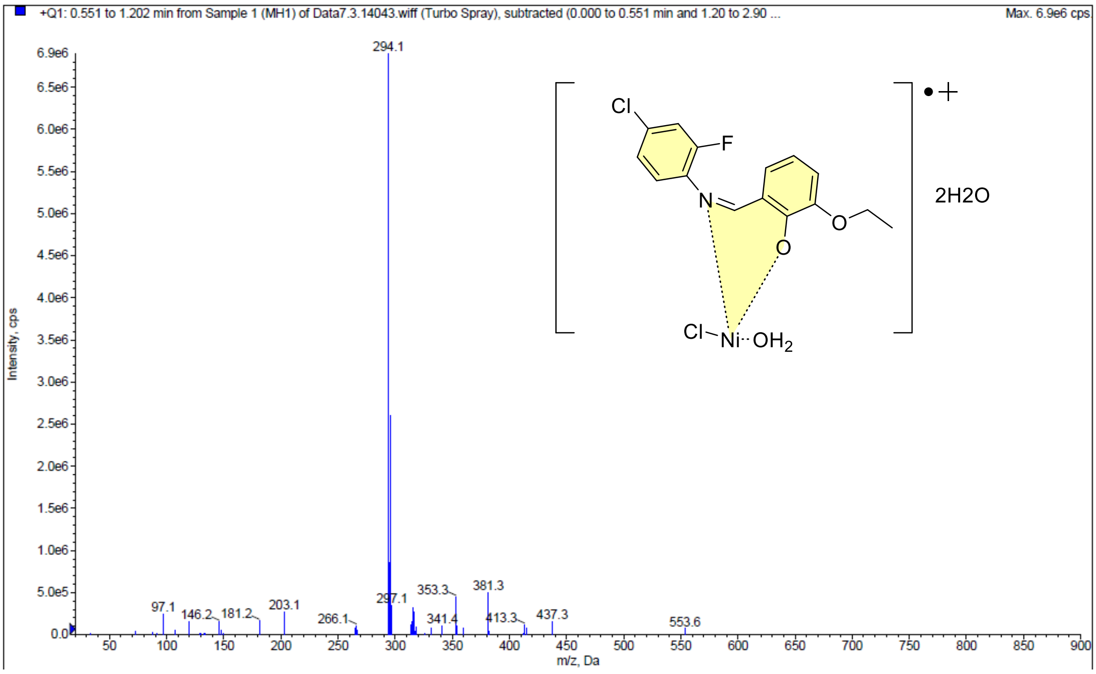


Fig. (11) mass spctrum of complex [Ni(L1) Cl (H_2O)]$2H_2O$

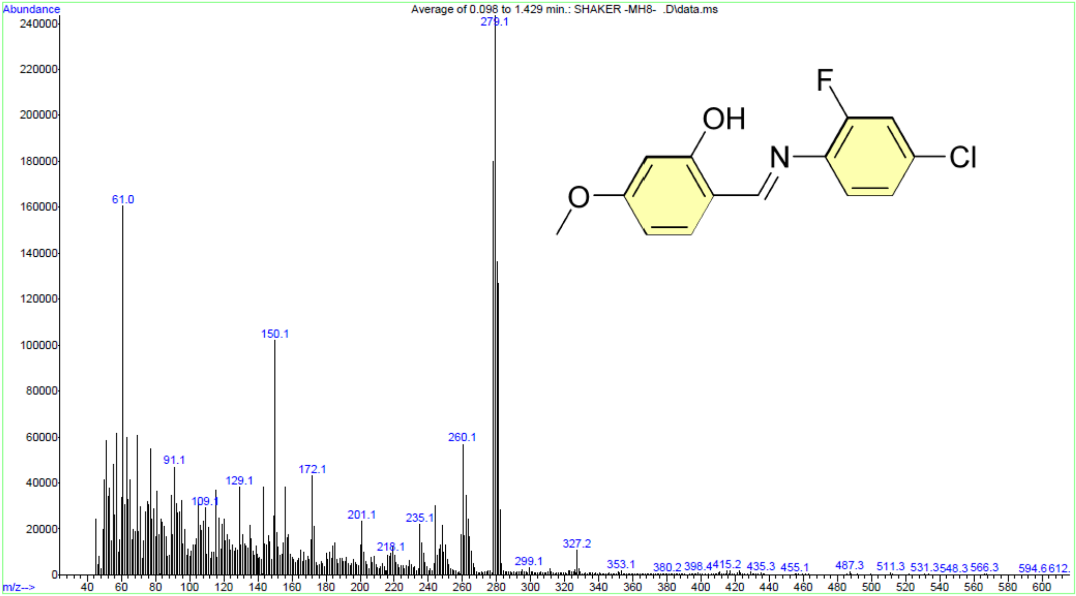


Fig. (12) mass spctrum of ligand L2

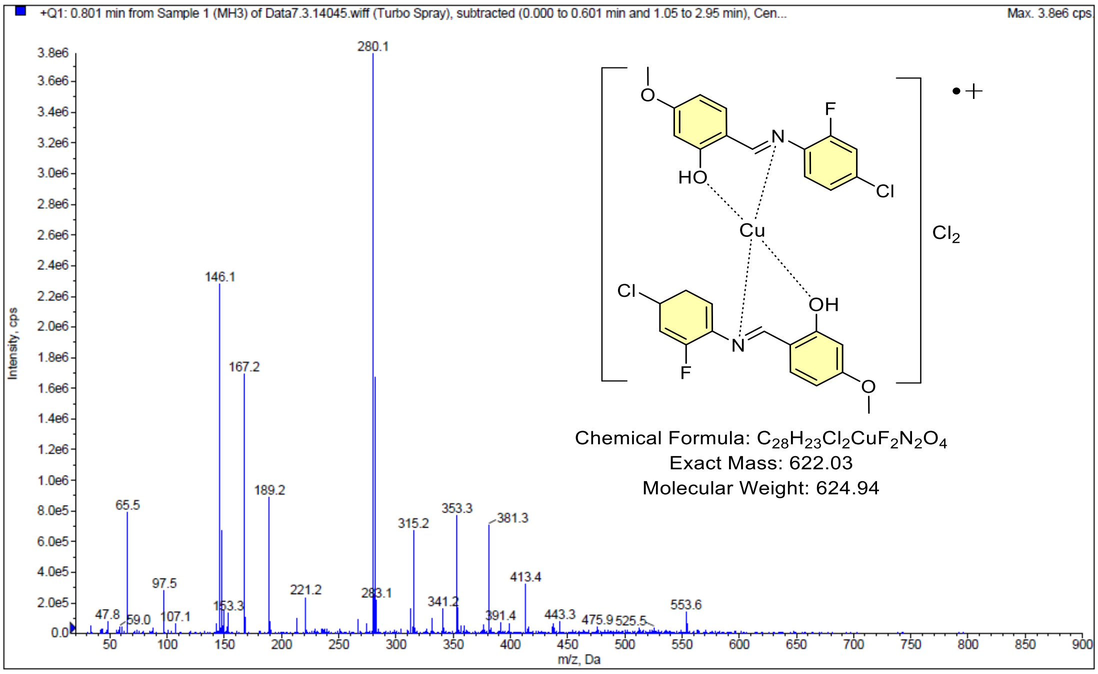
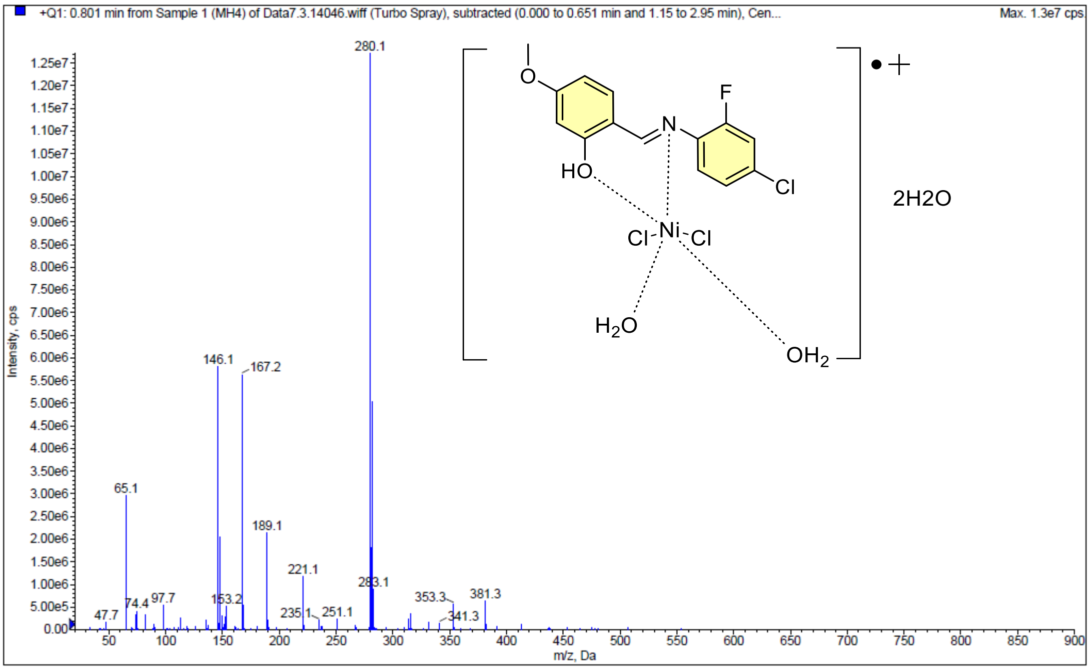


Fig. (13) mass spctrum of complex $[Cu(L2)_2]\ (Cl)_2$



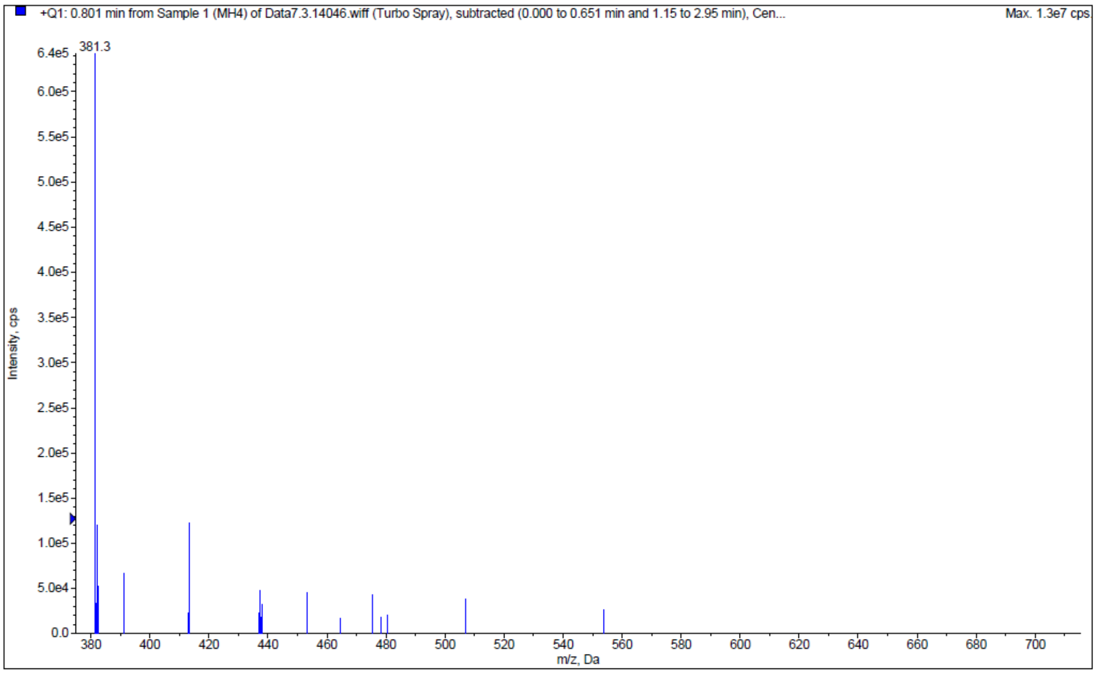


Fig. (14) mass spctrum of complex [Ni(L_2) $CL_2(H_2O)_2$]$2H_2O$

3.4: Magnetic Susceptibility Copper (II) Complexes (Cu^{2+})

The results of magnetic susceptibility measurements, presented in Table 3, indicate that the copper (II) complexes exhibit paramagnetic properties. This behavior can be attributed to the presence of one unpaired electron in the d^9 configuration of Cu (II). The electronic configuration follows the (e^4 t_2^5) arrangement, resulting in an effective magnetic moment (μ_eff) value of approximately (1.73 BM). Comparatively, the magnetic moments for the complexes was faound to be higher than the theoretical spin-only value (1.73 BM), specifically (2.60,1.45 BM), the expected (tetrahedral) geometry for this complex, supports the possibility of sp^3 hybridization around the copper complex.

3.5: Magnetic Susceptibility Nickel (II) Complexes (Ni^{2+})

The electronic configuration of Ni is [Ar] $4s^2$ $3d^8$, corresponding to a d^8 low-spin system, supports the possibility of dsp^2 hybridization with squerplaner around the nickel complex [Ni(L1) Cl (H2O)]$2H_2O$. Experimental magnetic susceptibility values confirm that the complex [Ni(L2) Cl_2(H2O)$_2$]$2H_2O$ exhibit paramagnetic behavior is consistent with an (octahedral) geometry around the Ni^{2+}center, and the hybridization is likely d^2sp^3. [29]

Table 3. The results of magnetic susceptibility measurements for complexes

NO	Chemical formula	M.wt	Xg $\times10^{-4}$	Xm $\times10^{-4}$	μ eff B.M	Geometry
1	[Cu(L1)$_2$]$2H_2O$	685	0.0013	8.89	1.45	SP^3
2	[Cu(L2)$_2$] Cl_2	696	0.041	2.85	2.60	SP^3
3	[Ni(L1) Cl (H2O)]$2H_2O$	438	0.00	0.00	0.00	d SP^2
4	[Ni(L2) Cl_2(H2O)$_2$]$2H_2O$	478	0.096	4.99	3.45	d^2 SP^3

3.6: Molar Electrical Conductivity

The molar conductivity values of the complexes depend on the number of ions outside the coordination sphere and these values can provide us with good information about the structural formula of the complexes because it is obvious from the molar conductivity values of the prepared complexes that all these complexes behave like non electrolyte compounds due to the presence of ions inside the coordination sphere, except for the Copper complex [Cu(L2)$_2$] Cl_2.. The results obtained are consistent with the molecular and steric formulas of the prepared complexes [30] as shown in Table 3.3 .

Table 3.4. Molar conductivity values of complexes prepared in DMSO solvent at concentration 0.001 M at temperature25Ċ

NO.	Comples	Λ m (s.cm^{-2}. mole^{-1})	Electrolyte ratio
1	[Cu(L1)2]2H2O	6.59	non-Electrolyte
2	[Ni(L1) Cl $(H_2O)_2$]$2H_2O$	8.34	non-Electrolyte
3	[Cu(L2)2] Cl_2	45.15	Electrolyte
4	[Ni(L2) $Cl_2(H_2O)_2$]$2H_2O$	12.7	non-Electrolyte

Thermal Analysis

The thermal behavior of the ligand and the complex has been investigated using thermogravimetric techniques in the temperature range from ambient to 900 ºC at heating rate of 20 ºC/min. The decomposition temperature and the weight losses of the ligand and the complexes were calculated from TGA data. The ligand is stable up to 185 ºC and its decomposition starts at 377 ºC and is completed at 680 ºC. Thermogravimetric studies of the Ni(II) complex showed no weight loss up to 190 and 231 ºC respectively, indicating absence of the lattice water molecules in the complexes [32]. Weight loss occurred in three steps, On the other hand in the Ni(II) complex, the step (1) 7.55% (calc. 7.0%) weight loss occurred in the (190-231) ºC the step (2) 57.11% (calc. 57.0%) weight loss occurred in the range and second, (231-461) ºC. the step (3) 26.3% (calc. 26.0%) weight loss occurred in the range and third, (461-726) ºC[31]

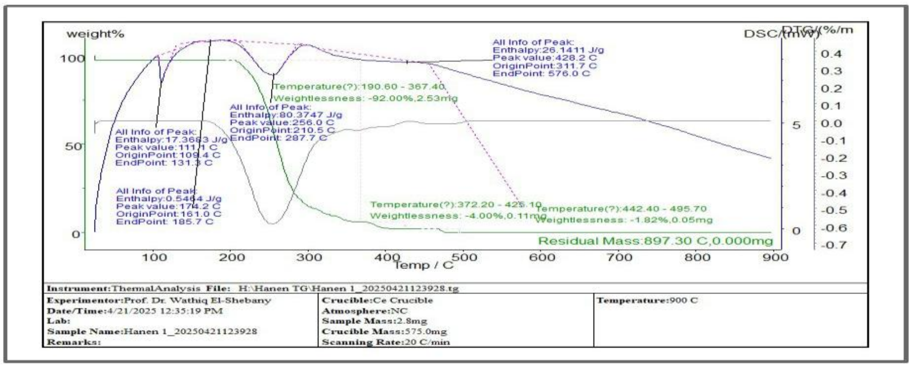


Fig. (15) spctrum Thermal Analysis of ligand L1

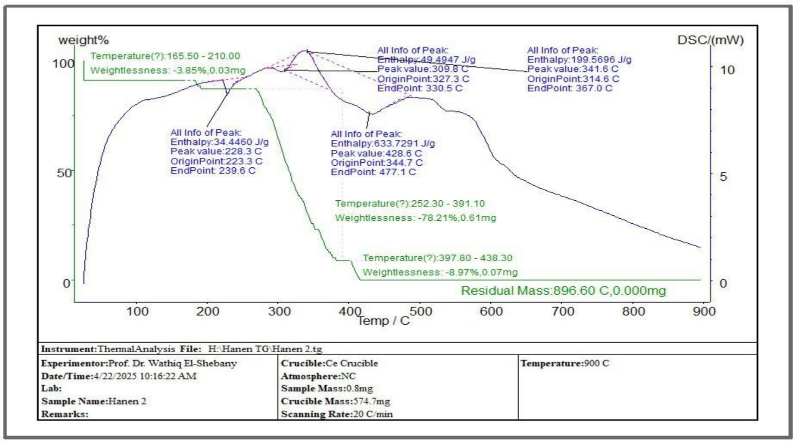
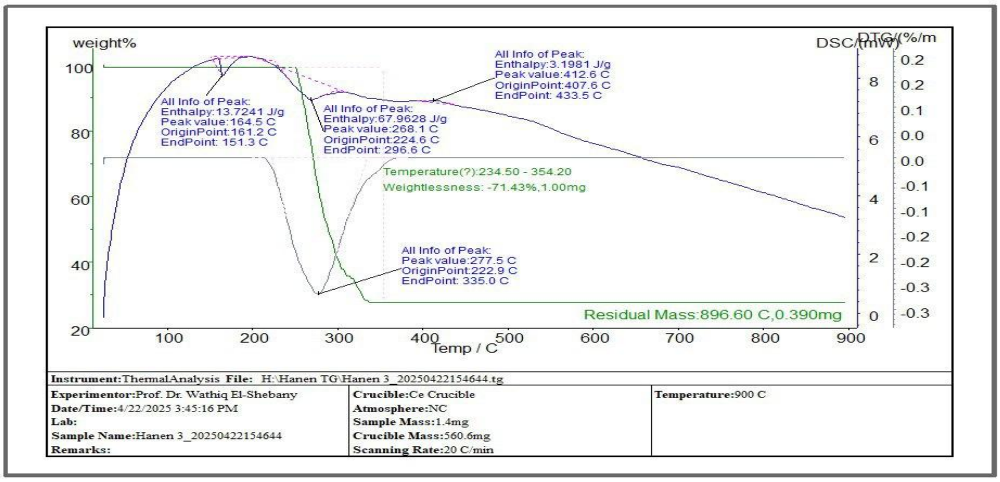


Fig. (16) spctrum Thermal Analysis of complex [Cu$(L1)_2$]2H2O



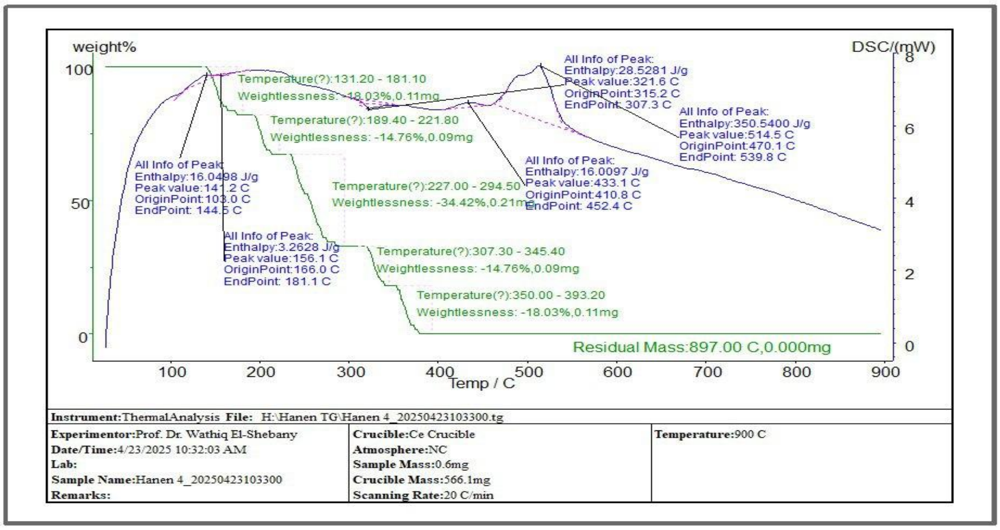
Instrument: ThermalAnalysis **File:** H:\Hanen TG\Hanen 3_20250422154644.tg

Experimentor: Prof. Dr. Wathiq El-Shebany
Date/Time:4/22/2025 3:45:16 PM
Lab:
Sample Name: Hanen 3_20250422154644
Remarks:

Crucible: Ce Crucible
Atmosphere:NC
Sample Mass:1.4mg
Crucible Mass:560.6mg
Scanning Rate:20 C/min

Temperature:900 C

Fig. (17) spctrum Thermal Analysis of ligand L2



Instrument: ThermalAnalysis **File:** H:\Hanen TG\Hanen 4_20250423103300.tg

Experimentor: Prof. Dr. Wathiq El-Shebany
Date/Time:4/23/2025 10:32:03 AM
Lab:
Sample Name: Hanen 4_20250423103300
Remarks:

Crucible: Ce Crucible
Atmosphere:NC
Sample Mass:0.6mg
Crucible Mass:566.1mg
Scanning Rate:20 C/min

Temperature:900 C

Fig. (18) spctrum Thermal Analysis of complex [Ni(L2) (H_2O)]2H_2O

REFERENCES

1. Hussain, Z., Yousif, E., Ahmed, A. and Altaie, A. Synthesis and characterization of Schiff's bases of sulfamethoxazole. *Org. Med. Chem. Lett.*, 2014, *4*, 1.
2. Subasi, N.T. Overview of Schiff bases. In: *Schiff Base in Organic, Inorganic and Physical Chemistry*, IntechOpen, London, 2022.
3. Safaei-Ghomi, J., Zahedi, S. and Basharnavaz, H. Synthesis and characterization of ionic liquid supported on Fe3O4 nanoparticles and a DFT study of 1, 3-dipolar cycloaddition for the synthesis of isoxazolidines in the presence of ionic liquid-Fe3O4. *Polycycl. Aromat. Compd.*, 2020, *40*, 574–584.
4. Hania, M.M. Synthesis of some imines and investigation of their biological activity. E-J. Chem., 2009, 6, 629–632.
5. Canpolat, E. and Kaya, M. Studies on mononuclear chelates derived from substituted Schiff Base ligands: Synthesis and characterization of a new 5-methoxysalicyliden-p-aminoacetophenoneoxime and its complexes with Co(II), Ni(II), Cu(II), and Zn(II). Russ. J. Coord. Chem., 2005, 31, 790–794
6. Samanta, B., Chakraborty, J., Choudhury, C.R., Dey, S.K., Dey, D.K., Batten, S.R., Jensen. P., Yap, G.P.A. and Mitra, S. New Cu(II) complexes with polydentate chelating Schiff base ligands:

Synthesis, structures, characterisations and biochemical activity studies. Struct. Chem., 2007, 18, 33–41.

7. Samanta, B., Chakraborty, J., Choudhury, C. R., Dey, S. K., Dey, D. K., Batten, S. R.,... & Mitra, S. New Cu (II) coplexes with polydentate chelating Schiff base ligands: Synthesis, structures, characterisations and biochemical activity studies. Structural Chemistry,2007, 18, 33-41
8. He, S. X., Yu, H. H., Huang, C., Chen, D. M., & Zhu, B. X. Metallomacrocycle or 1D chain: Synthesis, structures, and antifungal activities of zinc (II) and silver (I) complexes based on two reduced Schiff base ligands. Journal of Molecular Structure, 2023, 1271,136073.
9. Dong, Y., Li, M., Hao, Y., Feng, Y., Ren, Y., & Ma, H. Antifungal Activity, Structure-Activity Relationship and Molecular Docking Studies of 1, 2, 4-Triazole Schiff Base Derivatives. Chemistry & Biodiversity,2023, 20(3), e202201107.
10. Devi, P., Singh, K., & Kubavat, B.Synthesis, spectroscopic, quantum, thermal and kinetics, antibacterial and antifungal studies: Novel Schiff base 5-methyl-3-((5-bromosalicylidene) amino)-pyrazole and its transition metal complexes. Results in Chemistry, 2023, 5, 100813.
11. Mekky, A. H., Mohammad, Z. A. A., & Auribi, S. M. Synthesis and biological activity of monocyclic spiro azetidine-2-one. J. Educ. Pure Sci, 2(1), 67-74 Tople, M. S., Patel, N. B., Patel, P. P., Purohit, A. C., Ahmad, I., & Patel, H. (2023). An in silico-in vitro antimalarial and antimicrobial investigation of newer 7-chloroquinoline based Schiff-bases. Journal of Molecular Structure,2012, 1271, 134016.
12. AL-Rubaie, L. A.Synthesis and Theoretical Study of new Schiff base derivatives. University of Thi-Qar Journal of Science,2014, 4(3), 119-122.
13. Gueye, M. N., Dieng, M., Thiam, I. E., Lo, D., Barry, A. H., Gaye, M., & Retailleau, P. Lanthanide (III) complexes with tridentate Schiff base ligand, antioxidant activity and X-ray crystal structures of the Nd (III) and Sm (III) complexes. South African Journal of Chemistry,2017, 70, 8-15.
14. Hosny, S., Ragab, M. S., & Abd El-Baki, R. F.Synthesis of a new sulfadimidine Schiff base and their nano complexes as potential anti-COVID-19 and anti-cancer activity. Scientific Reports,2023, 13(1), 1502.
15. Abdel-Rahman, L. H., Abdelghani, A. A., AlObaid, A. A., El-ezz, D. A., Warad, I., Shehata, M. R., & Abdalla, E. M.Novel Bromo and methoxy substituted Schiff base complexes of Mn (II), Fe (III), and Cr (III) for anticancer, antimicrobial, docking, and ADMET studies. Scientific reports, 2023,13(1), 3199.
16. Al-Wahaibi, L. H., El-Sheref, E. M., Hammouda, M. M., & Youssif, B. G. One-Pot Synthesis of 1-Thia-4-azaspiro [4.4/5] alkan-3-ones via Schiff Base: Design, Synthesis, and Apoptotic Antiproliferative Properties of Dual EGFR/BRAFV600E Inhibitors. Pharmaceuticals,2023, 16(3), 467
17. El-Lateef, A., Hany, M., Elbastawesy, M. A., Abdelghani Ibrahim, T. M., Khalaf, M. M., Gouda, M.,... & Morcoss, M. M. Design, Synthesis, Docking Study, and Antiproliferative Evaluation of Novel Schiff Base–Benzimidazole Hybrids with VEGFR-2 Inhibitory Activity. Molecules, 2023,28(2), 481. x
18. Alyamani, N. M.New Schiff Base–TMB Hybrids: Design, Synthesis and Antiproliferative Investigation as Potential Anticancer Agents. Symmetry,2023, 15(3), 609.
19. Kumar, B., Devi, J., & Manuja, A. Synthesis, structure elucidation, antioxidant, antimicrobial, anti-inflammatory and molecular docking studies of transition metal (II) complexes derived from heterocyclic Schiff base ligands. Research on Chemical Intermediates,2023, 49(6), 2455 2493.
20. Gung, B. W., & Taylor, R. T. Parallel combinatorial synthesis of azo dyes: a combinatorial experiment suitable for undergraduate laboratories. Journal of chemical education, 2004,81(11), 1630

21. Sun, T., Cheng, D., Chai, Y., Gong, J., Sun, M. and Zhao, F. High contrast mechanofluorochromic behavior of new tetraphenylethene-based Schiff base derivatives. *Dyes. Pigm.*, 2019, *170*, 107619
22. Sakthivel, A., Jeyasubramanian, K., Thangagiri, B. and Raja, J.D. Recent advances in Schiff base metal complexes derived from 4-amoniantipyrine derivatives and their potential applications. *J. Mol. Struct.*, 2020, *1222*, 128885.
23. Issa, R.M., Awad, M.K. and Atlam, F.M. DFT theoretical studies of antipyrine Schiff bases as corrosion inhibitors. *Mater. Corrosion*, 2010, *61*, 709–714.
24. Oliveri, I.P., Maccarrone, G. and Di Bella, S. A Lewis basicity scale in dichloromethane for amines and common nonprotogenic solvents using a zinc(II) Schiffbase complex as reference Lewis acid. *J. Org. Chem.*, 2011, *76*, 8879–8884.
25. Wang, C., Qiao, Z., Tian, Y., Yang, H., Cao, H. and Cheetham, A.K. Alcohol imination catalyzed by carbon nanostructures synthesized by C (sp2)-C (sp3) free radical coupling. *Iscience*, 2023, *26*, 106659.
26. Smith, P.A.S. *The Chemistry of Open-Chain Organic Nitrogen Compounds*. New York: Benjamin, 1965.
27. Affat, S., Al – Shamkhawy, S. ., & Snigur, D. Cloud Point Extraction Coupled to Flame Atomic Absorbance Spectroscopy for Cobalt (II) determination with Azo Azomethine Dye. University of Thi-Qar Journal of Science,2024, 11(1), 124-130.
28. Abdul-Hassan, W.S., Hasan, H.M. and Mekky, A.H. Ab initio calculations and structure of three acyclic bis(acetyl acetone)imine derivatives. J. Thi-Qar Sci., 2012, 3, 149–157.
29. El-Saied, F. A., El-Bahnasawy, R. M., Azzem, M. A., and El-Sawaf, A. K., 1994, Synthesis, characterization and electrochemical properties of $β$-diketone complexes of ruthenium (III), Polyhedron, 13 (11), 1781–1786.
30. Feltham, R.D. and Hayter, R.G., 875. The electrolyte type of ionized complexes. Journal of the Chemical Society (Resumed), pp.4587-4591. 1964.
31. Refat, M. S., El-Deen, I. M., Zein, M. A., Adam, A. M. A., and Kobeasy, M. I., 2013, Spectroscopic, structural and electrical conductivity studies of Co (II), Ni (II) and Cu (II) complexes derived from 4-acetylpyridine with thiosemicarbazide, International Journal of Electrochemical Science, 8 (7), 9894–9917.