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Synthesis, Analysis of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Metal Complex

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Abstract

In the present investigation synthesized new noble ligand (organic compound) 1 - {3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone derived from hydrazine and acceto-acetic ester . The 1 -{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone consist pyrazole and imidazole nitrogen derivatives, the 'N' atom and the oxygen atom of 'S' bonded with the metal Fe(III),Cu(II) and Re(II) to form complex . The structure was confirmed by using elemental analysis, UV-VIS, mass spectrometry, and NMR spectroscopy. This work covers results concerning the complexing properties of the new ligand towards Fe (III),Cu(II) and Re(II) ions. The formation of non-covalent complexes of 1:2 stoichiometry with the Fe (III),Cu(II) and Re(II) ions analysis have been confirmed by H-NMR,13CNMR and mass spectrometry.

Keywords: Pyrazol, imidazole, derivative, metal ion complexes; H-NMR, 13C-NMR

Introduction

The chemistry of metal complexes with ligands those containing oxygen and nitrogen as donor atoms have to attract for the research. So many organic ligands are known to coordinate to metal atom in two ways 1. Metal to ligand electron pair donation and 2. Ligand to metal donation of electrons, with under the different reaction conditions[1].

The drug (organic ligand) transition metal complexes of Manganese, cobalt, nickel, copper, and zinc are life-essential metallic elements and exhibit greater biological activity when associated with certain metal protein complexes[2-5], participating in oxygen transport, electronic transfer reactions, or the storage of ions [6-7]. Mn (II), Co (II), Ni (II), Cu (II), and Zn (II) complexes of the 4-chloro-2-{(E)-[(4-ophenyl)imino] methyl}phenol, has been synthesized [8-9]. The new Mn (II), Co (III), Ni (II), Cu (II), and Zn (II) complexes of the 4-chloro-2-{(E)-[(4-henyl) imino] methyl}phenol has been investigated and is now reported [8]. Evaluation results and revealed that the metal complexes are given six coordinated octahedral geometry, exhibited higher activity than the free other ligand[10-11-12].

Similarly the polymeric ligands also coordinate with d-block transition metal complexes has been synthesized and reported, which are good to their high thermal stability and enormous pharmacological activity along with potential applications as functional materials[16]. Owing to the high thermal stability of the polymeric ligand, they specific applications such as in waste water treatment, metal recovery, protective coatings, thermally stable materials, water disinfectants, antifouling paints, antimicrobial and surgical materials, gels and ointments for medical uses, and biological activity [13-14].

The polymers/copolymers/ tertiary polymeric material showing characteristics of various types of ligand with transition metal ions[15-20]. The chemical properties of benzothiazole based compounds have been investigated in several research fields in polymer field because of their high thermal stability and pharmacological activity[21-22], the organic chelate ring dramatically increasing the certain biological properties such as antibacterial [22], antiviral[23, anti]-fungal[24]and anti-tubercular[26] activities. These activities are probably due to the presence of the –N=C–S, N=N, C=S group present in the organic ligand[27].

The transition metal complexes of thiosemicarbazones ligand became largely appealing because of their broad profile of pharmacological activity that provides a diverse variety of compounds with different activities [28-30]. Some of the detected biological activities of the thiosemicarbazones and their complexes with transition metal ions are antibacterial, antifungal, antiarthritic, antimalarial, antitumor, antiviral and anti-HIV activities[31-35].

Thiosemicarbazone derivatives containing a 4-acyl-2-pyrazolin-5- one given an important class of organic compounds because of their structural chemistry and biological activities [36]. In the field of anticancer research, the pyrazolones exhibited promising antiproliferative activity against human myelogenous leukaemia HL-608[37].

The co-ordinating property of the 4-amino-2,3-dimethyl-1-phenyl- 3-pyrazolin-5-one ligand has been modified to give a flexible ligand system, formed by condensation with a variety of reagents such as aldehydes, ketones [38-40], thio-semicarbazides and carbazides, etc.[41-44].

All these study inspire us for this research, therefore; we are going to prepared new organic drug which has nitrogen, sulfur and other coordinating groups, which chelating the Fe, Cu, and Re metal ions and given different coloures and specific properties.

Experiment

Synthesis of ligand

In this preparation we are using AR grade chemicals, for this synthesis 25 ml of methyl-aceto-ethyl-acetate mix with the 20 ml of hydrazine hydrogen chloride in to the round bottom flask then the exothermic reaction is take place at room temperature (32^0C), and it produced compound 4-Ethoxy-4-hydrazino-butan-2-one with 12.2 gm. of yield.

After some time compound 4-Ethoxy-4-hydrazino-butan-2-one treated with the 4-imethylamino-3-hydroxymethyl-benzenesulfonic acid to given good yield 10.3 gm. of 3-(4-3-(3-Acetyl-3H-yrazol-4-yloxymethyl)-benzenesulfonic acid than it reacted with imidazole to give final product of yellow collared 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone at 140^0C with the gentle heating up to 5 hr.'s. and recover 12.32 gm.

Yield of drug, mechanism given in scheme and the structure which given for the drug according to spectra as follows:

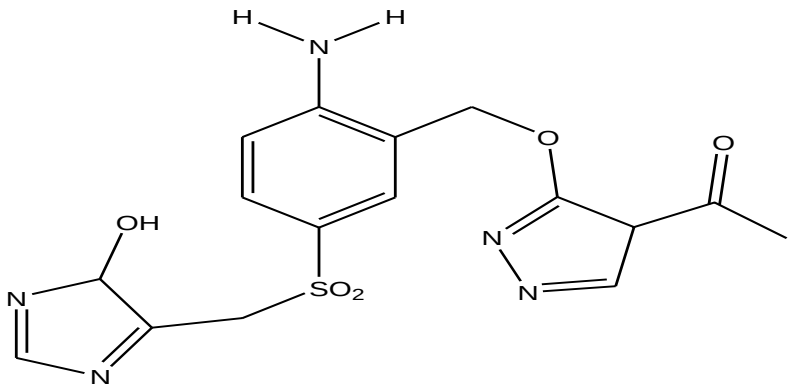


Figure 2.1: Structure of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone

Synthesis of metal complexes

Ethanolic solution of prepared ligand (0.02 mol) and Eethanolic solution of corresponding metal salts (0.02 mol) (MX2, where M= the Fe (III), Cu(II) and Re(IV) metal ions X=SO^4 /Cl /Acetate/NO_3) were mixed together with constant stirring in acidic media. The mixture was refluxed for 3 h at 85 ^oC. On cooling colored solid metal complexes were precipitated out. The products were filtered, washed with petroleum ether, than we get recrystallized complex.

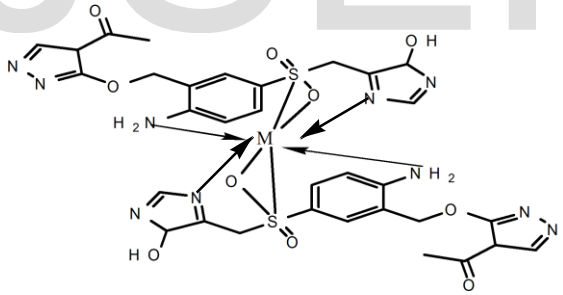


Figure 2.2: Structure of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone metal complex

Instrumentation

Infrared spectra of the ligand and its complexes were carried out by using KBr pellets in the range 4000-400 cm^{-1}on **Bucker model** of IR instrument. The electronic absorption was carried out by Shimadzu UV-1601 using alcohol as solvent. The Mass spectra were recorded by ESI technique on **VG AUTOSPEC** mass spectrometer instrument with **GLC**. The 1-H spectra were recorded on **Varian Gemini Unity** Spectrometer by employing TMS as internal standard, with KCl.

All the analysis done at SIRT, Bhopal and the Mass spectra analyzed at RGPV, Bhopal Pharmacy department.

1.3.0. Drug yellow coloured 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone: Elemental analysis data for $C_{17}H_{19}N_5O_4S$ found: C 49.09%; H, 4.30%; N- 17.89% calculated: C, 49.10%; H, 4.39%; N, 17.68%. FT-IR (KBr, disc cm−1) 3423.2 υ (O-H), 1600.6, 1220.3 υ(C-O), 703.7 υ (H2O), 534.8 υ(H-N), 491.7 υ(N-N). UV-Vis λ_{max} (nm) at λ max (nm) 223.4, 270.2 and 358 nm. ^{1}H NMR): δ 7.50, 2.0(-OH), 3.23(C=O), 4 (-NH_2), 7.18–7.39 (m, 7ArH); ^{13}C NMR): COCH3 206 164–165(-NH_2), 162(N=N),193(-$COCH_3$),129 (O=(S)=O), 125(C-O),138.2(-C6H5). And the mass spectrum at the 100% abundance is 391 eg. The mass of compound is 391 and 389.3au along with the m+2 and M-2 degradation.

1.3.1. Iron (III) Complex: Yield: 65.03%, 0.1388 g, colour: grey, m.p > 380°C, and molar conductance 18 $Ohm^{-1}cm^2mol^{-1}$. Elemental analysis data for $C_{17}H_{19}Fe(III)N_5O_4S$ found: C, 52.88%; H, 3.13%; N, 4.92% calculated: C, 52.74%; H, 4.50%; N, 4.76%. FT-IR (KBr, disc cm−1) 3429.0 υ (O-H), 1601. 1215.7 υ(C-O), 701.0 υ (H2O), 532.6 υ(Fe-N), 491.1 υ(Fe-O). 1H NMR): δ 7.50, 2.0(-OH), 3.23(C=O), 4 (-NH2), 7.18–7.39 (m, 7ArH); 13C NMR): COCH3 206 164–165(-NH2), 162(N=N),193(-COCH3),129 (O=(S)=O), 125(C-O),138.2(-C6H5).UV-Vis λ_{max} (nm) 221.4, 251.8, and 342.1. And the mass of complex is 838.3au. the structure as follows:

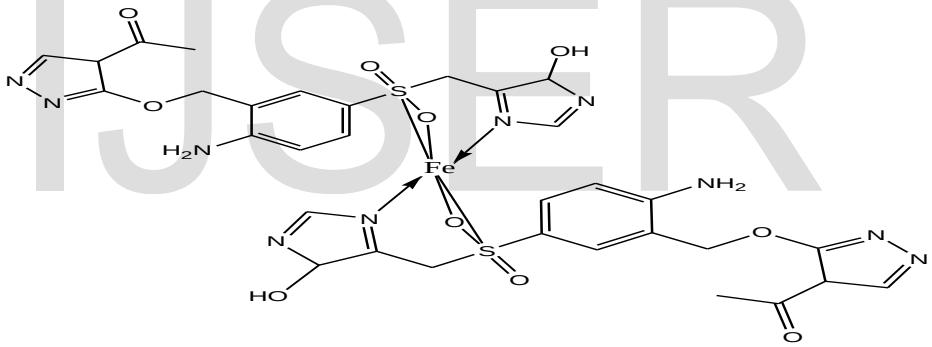


Figure 2.3: Structure of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Iron (III) complex

1.3.2. Copper (II) Complex: Yield: 61.05%, 0.2362 g, colour: red brown, m.p > 392°C, and molar conductance 22 $Ohm^{-1}cm^2mol^{-1}$. Elemental analysis data for $C_{17}H_{19}Cu(II)N_5O_4S$ found: C, 52.66%; H, 3.40%; N, 4.75% calculated: C, 52.70%; H, 3.38%; N, 4.73%. FT-IR (KBr, disc cm−1) 3420.7 υ(O-H), 1595., 1214.8 υ(C-O), 697.9 υ(H2O), 527.4 υ(Cu-N), 489.2 υ(Cu-O). UV-Vis λ_{max} (nm) 245.2, 315.1 and 422.9. 1HNMR (ppm d6-DMSO, 400 MHz): δ 7.50, 2 7.12–7.15 (m, 7ArH); 13C NMR (ppm d6-DMSO): 124–118.32(C-O). And the mass of complex through mass spectra analysis 846.58 au.

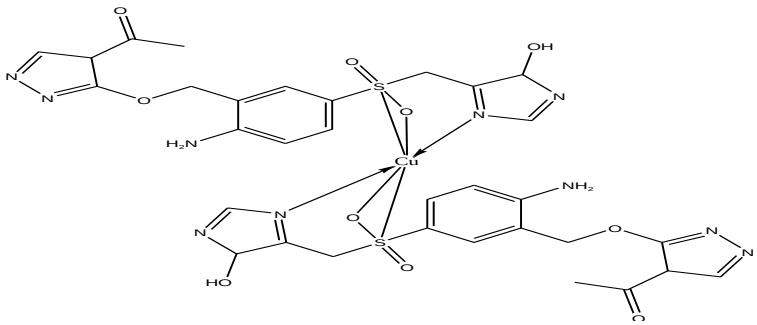


Figure 2.4: Structure of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Copper (II) complex

1.3.3. Re (II) Complex: Yield: 73.91%, 0.2672 g, colour: brown, m.p > 394°C, and molar conductance 24 $Ohm^{-1}cm^{2}mol^{-1}$. Elemental analysis data for C17H19Re (II)N_5O_4S found: C, 52.41%; H, 3.34%; N, 4.72% calculated: C, 52.47%; H, 3.39%; N, 4.69%. FT-IR (KBr, disc cm−1) 3455.6 υ(O-H), 1599.7, 1213.9 υ(C-O), 695.8 υ(H2O), 536.1 υ(Re-N), 490.8 υ(Re-O). 1H NMR): δ 7.50, 2.0(-OH), 3.23(C=O), 4 (-NH2), 7.18–7.39 (m, 7ArH); 13C NMR): COCH3 206 164–165(-NH2), 162(N=N),193(-COCH3),129 (O=(S)=O), 125(C-O),138.2(-C6H5).UV-Vis λ_{max} (nm) 243.1, 267.1 and 345.5. According to the mass spectra the mass of metal-drug complex is 968.21 au.

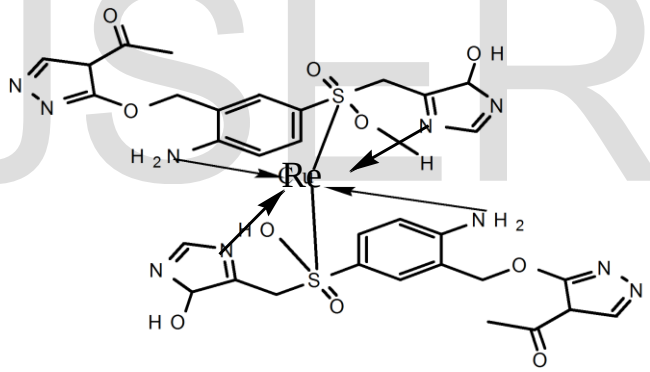
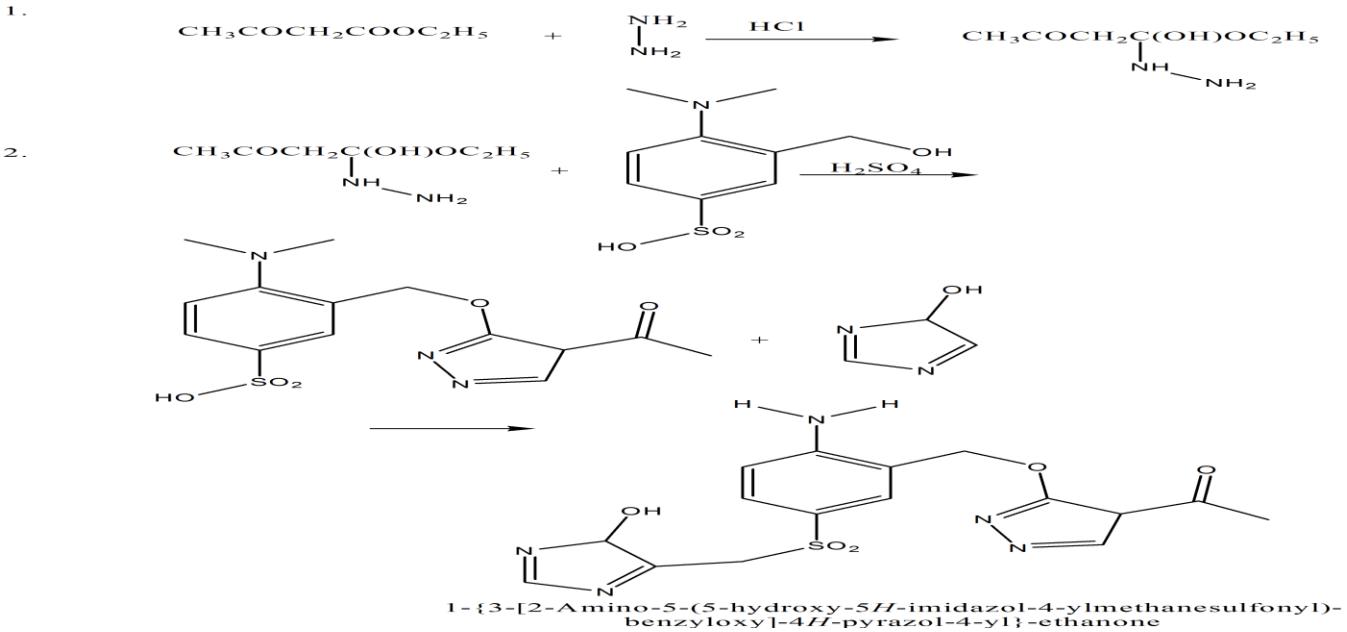
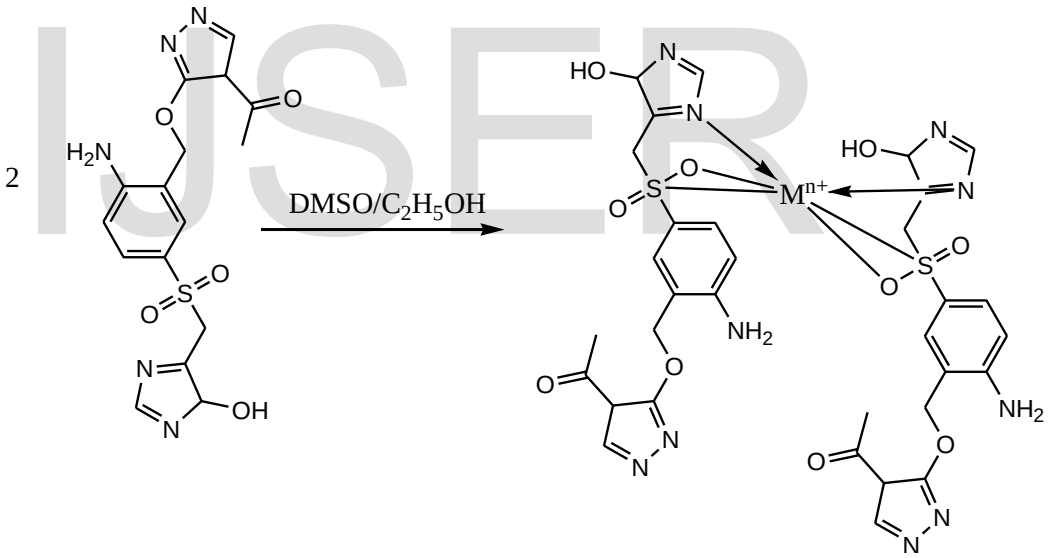


Figure 2.5: Structure of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Re (II) complex

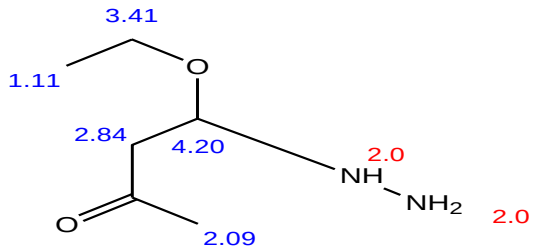


Scheme: 2.1 Mechanism scheme for the ligand synthesis

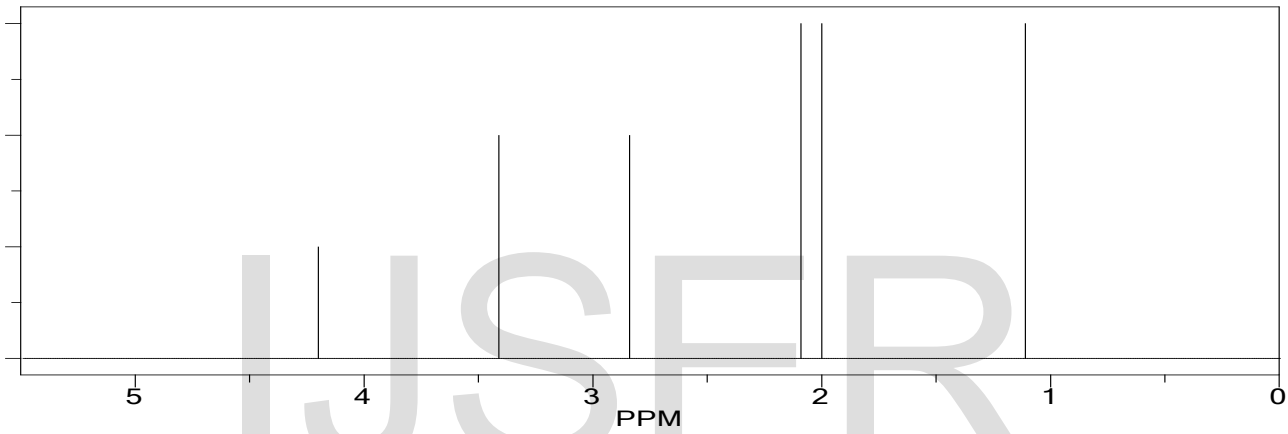


Scheme: 2.2 Mechanism scheme for the synthesis of ligand metal complex

ChemNMR H-1 Estimation



Estimation Quality: blue = good, magenta = medium, red = rough

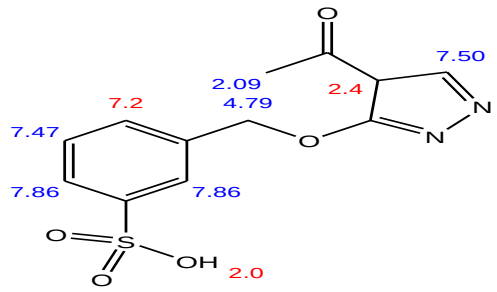


Protocol of the H-1 NMR Prediction:

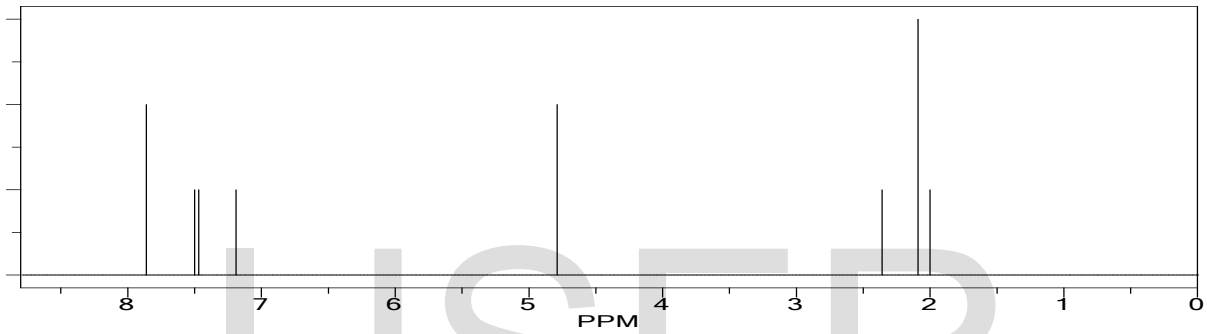
Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
NH	2.0	2.00	amine
NH2	2.0	2.00	amine
CH3	2.09	0.86	methyl
		1.23	1 alpha -C(=O)C
CH2	2.84	1.37	methylene
		1.12	1 alpha -C(=O)-C
		0.13	1 beta -O-C
		0.22	1 beta -N
CH	4.20	1.50	methine
		1.35	1 alpha -O-C
		1.13	1 alpha -N
		0.22	1 beta -C=O
CH3	1.11	0.86	methyl
		0.25	1 beta -O-C
CH2	3.41	1.37	methylene
		0.00	1 alpha -C
		2.04	1 alpha -O-C

Figure 2.6: ^{1}H-NMR of 4-Ethoxy-4-hydrazino-butan-2-one

ChemNMR H-1 Estimation



Estimation Quality: blue = good, magenta = medium, red = rough

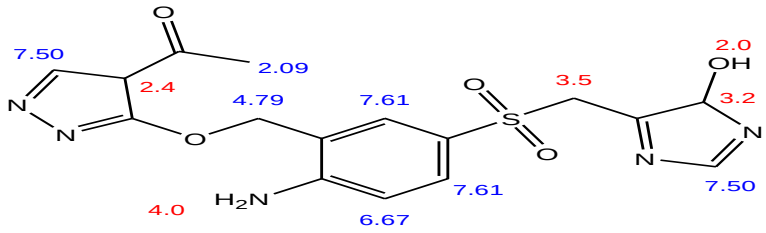


Protocol of the H-1 NMR Prediction:

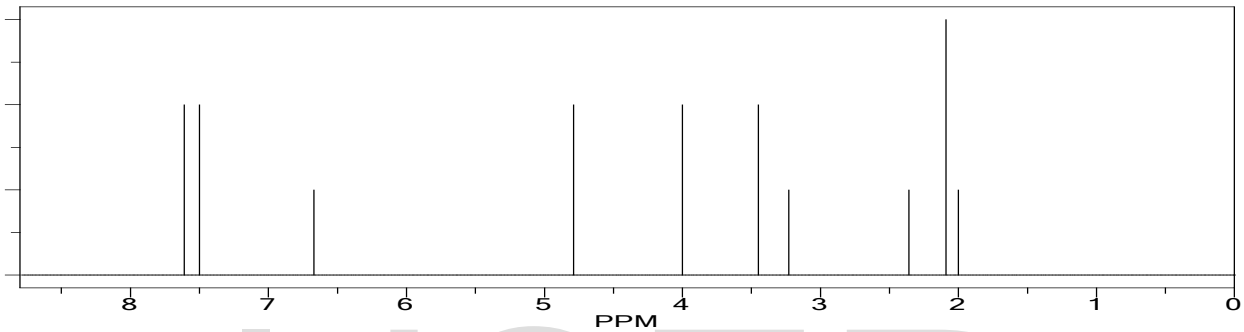
Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	7.47	7.26	1-benzene
		0.28	1 -S(=O)(=O)-R
		-0.07	1 -C-O
CH	7.86	7.26	1-benzene
		0.67	1 -S(=O)(=O)-R
		-0.07	1 -C-O
CH	7.86	7.26	1-benzene
		0.67	1 -S(=O)(=O)-R
		-0.07	1 -C-O
CH	7.2	7.26	1-benzene
		?	1 -S(=O)(=O)-R
		-0.07	1 -C-O
			-> 1 increment(s) not found
OH	2.0	2.00	alcohol
CH2	4.79	1.37	methylene
		1.22	1 alpha -1:C*C*C*C*C*C*1
		2.20	1 alpha -O
CH	7.50	7.50	aldimine
CH	2.4	1.50	methine
		0.86	1 alpha -C=O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
CH3	2.09	0.86	methyl
		1.23	1 alpha -C(=O)C

Figure 2.7: ^{1}H-NMR 3-(4-acetyl-4H-pyrazol-3-yloxymethyl)-benzene sulphonic acid

ChemNMR H-1 Estimation



Estimation Quality: blue = good, magenta = medium, red = rough

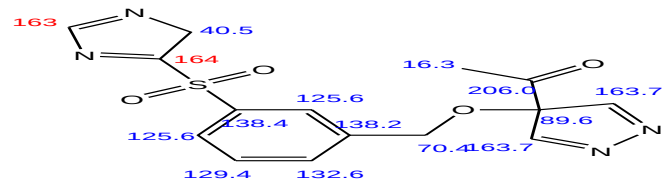


Protocol of the H-1 NMR Prediction:

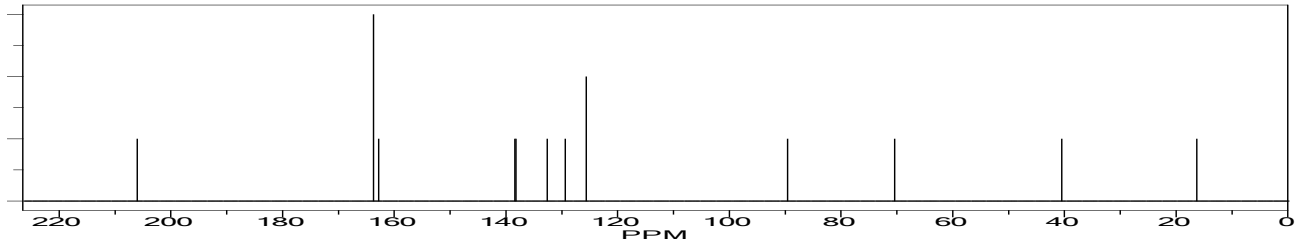
Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH3	2.09	0.86	methyl
		1.23	1 alpha -C(=O)C
CH	2.4	1.50	methine
		0.86	1 alpha -C=O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
CH	7.50	7.50	aldimine
CH2	4.79	1.37	methylene
		1.22	1 alpha -1:C*C*C*C*C*C*1
		2.20	1 alpha -O
CH	6.67	7.26	1-benzene
		-0.07	1 -C-O
		-0.80	1 -N
		0.28	1 -S(=O)(=O)-R
CH	7.61	7.26	1-benzene
		-0.07	1 -C-O
		-0.25	1 -N
		0.67	1 -S(=O)(=O)-R
CH	7.61	7.26	1-benzene
		-0.07	1 -C-O
		-0.25	1 -N
		0.67	1 -S(=O)(=O)-R
CH2	3.5	1.37	methylene
		2.08	1 alpha -S(=O)(=O)
		?	1 unknown alpha substituent(s)
			-> 1 increment(s) not found
CH	7.50	7.50	aldimine
CH	3.2	1.50	methine
		1.73	1 alpha -O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
OH	2.0	2.00	alcohol
NH2	4.0	4.00	aromatic C-NH

Figure 2.8: ^{1}H-NMR 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone

ChemNMR C-13 Estimation



Estimation Quality: blue = good, magenta = medium, red = rough



Protocol of the C-13 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
C	206.0	193.0	1-carbonyl
		13.0	2 -C
CH3	16.3	-2.3	aliphatic
		29.3	1 alpha -C(=O)-C
		-1.8	2 gamma -C=N
		-6.2	1 gamma -O
		0.3	1 delta -C
CH	163.7	162.8	1-imine
		0.9	1 -C
		0.0	1 -R from N-imine
C	89.6	-2.3	aliphatic
		29.8	2 alpha -C=N
		29.3	1 alpha -C(=O)-C
		49.0	1 alpha -O
		9.4	1 beta -C
		-2.6	1 gamma -1:C*C*C*C*C*C*1
		-15.0	steric corrections
		-8.0	gamma corrections
CH	163.7	162.8	1-imine
		0.9	1 -C
		0.0	1 -R from N-imine
CH2	70.4	-2.3	aliphatic
		24.3	1 alpha -1:C*C*C*C*C*C*1
		49.0	1 alpha -O
		9.4	1 beta -C
		-4.8	2 gamma -C=N
		-2.7	1 gamma -C(=O)-C
		0.0	1 delta -S(=O)=O
		-2.5	steric corrections
C	138.2	128.5	1-benzene
		8.7	1 -C-O-C
		1.0	1 -S(=O)(=O)
CH	132.6	128.5	1-benzene
		-0.9	1 -C-O-C
		5.0	1 -S(=O)(=O)
CH	129.4	128.5	1-benzene
		-0.1	1 -C-O-C
		1.0	1 -S(=O)(=O)
CH	125.6	128.5	1-benzene
		-0.9	1 -C-O-C
		-2.0	1 -S(=O)(=O)
C	138.4	128.5	1-benzene
		-0.1	1 -C-O-C
		10.0	1 -S(=O)(=O)
CH	125.6	128.5	1-benzene
		-0.9	1 -C-O-C
		-2.0	1 -S(=O)(=O)
CH	163	162.8	1-imine
		?	1 unknown substituent(s)
		0.0	1 -C from N-imine
			-> 1 increment(s) not found
C	164	162.8	1-imine
		0.9	1 -C
		?	1 unknown substituent(s)
		0.0	1 -R from N-imine
			-> 1 increment(s) not found
CH2	40.5	-2.3	aliphatic
		14.9	1 alpha -C=N
		40.0	1 alpha -N=C
		1.0	1 beta -S(=O)=O
		-2.6	1 gamma -1:C*C*C*C*C*C*1
		-2.5	steric corrections
		-8.0	gamma corrections

Figure 2.9: ^{13}C-NMR 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone

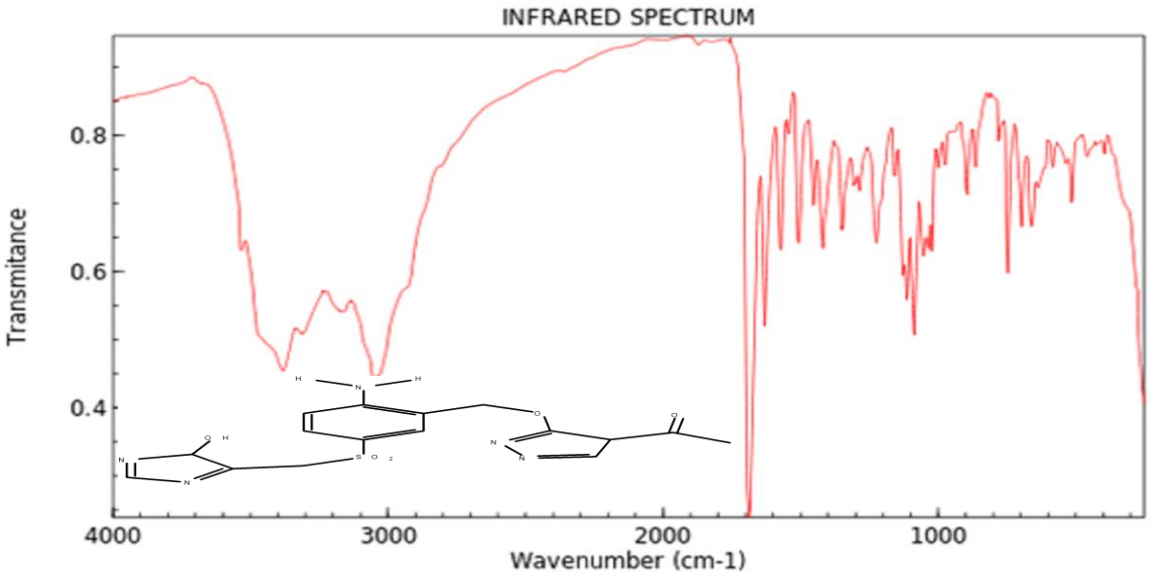


Figure 2.10: IR Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone

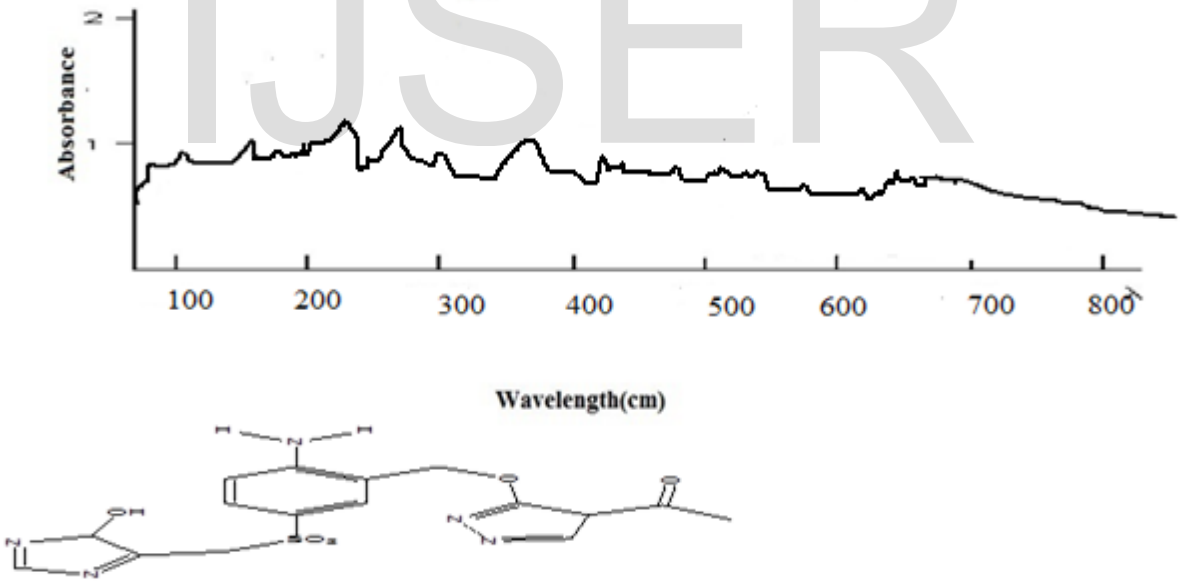


Figure 2.11: UV-VIS Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone

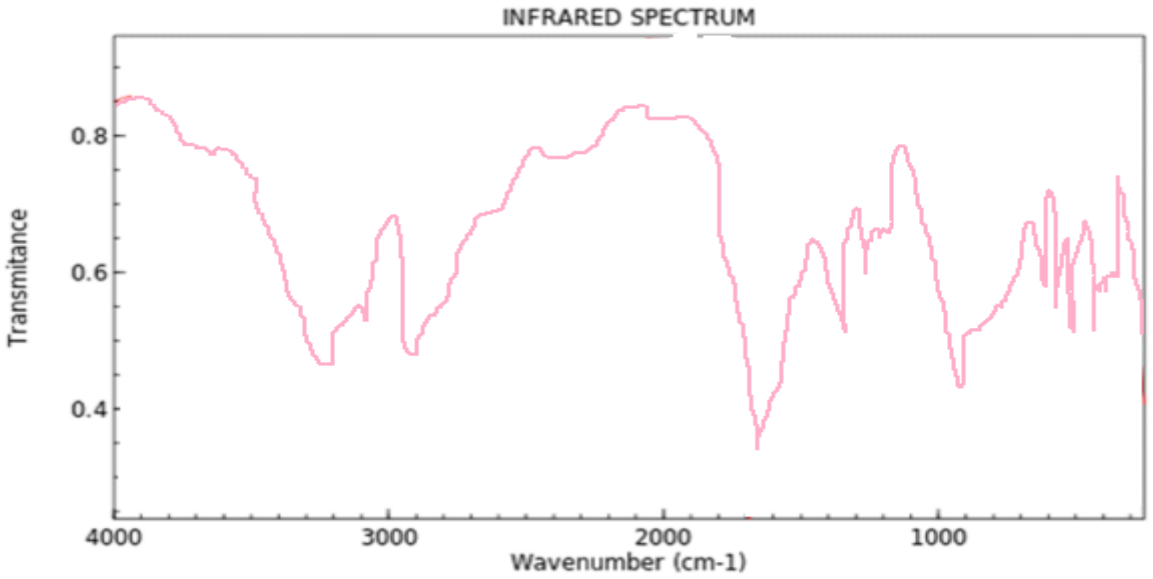


Figure 2.12: IR Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Iron (II) complex

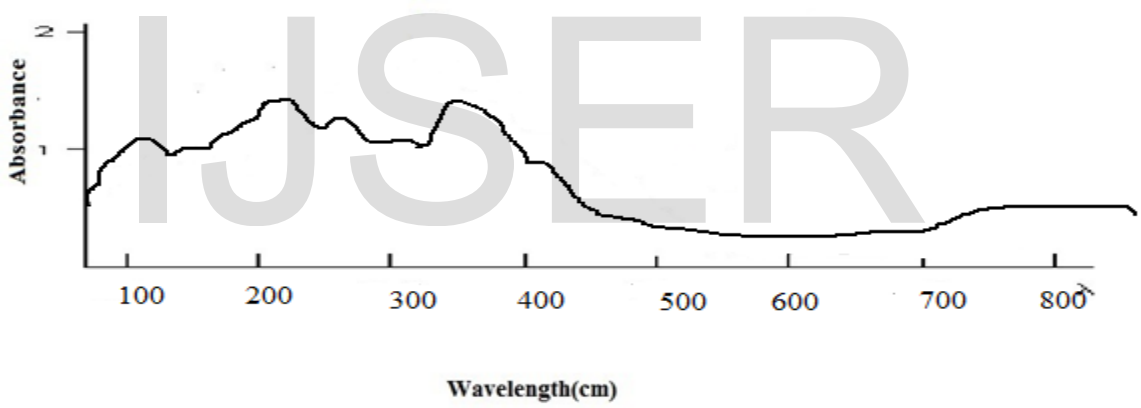


Figure 2.13: UV-VIS Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Iron (II) complex

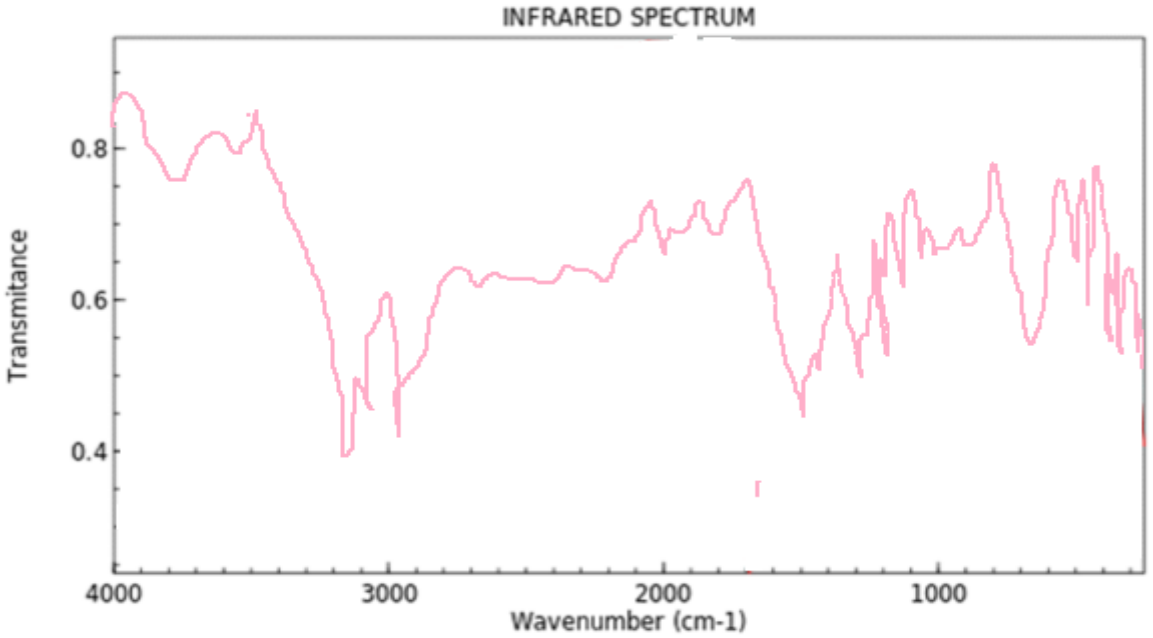


Figure 2.14: IR Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Cooper (II) complex

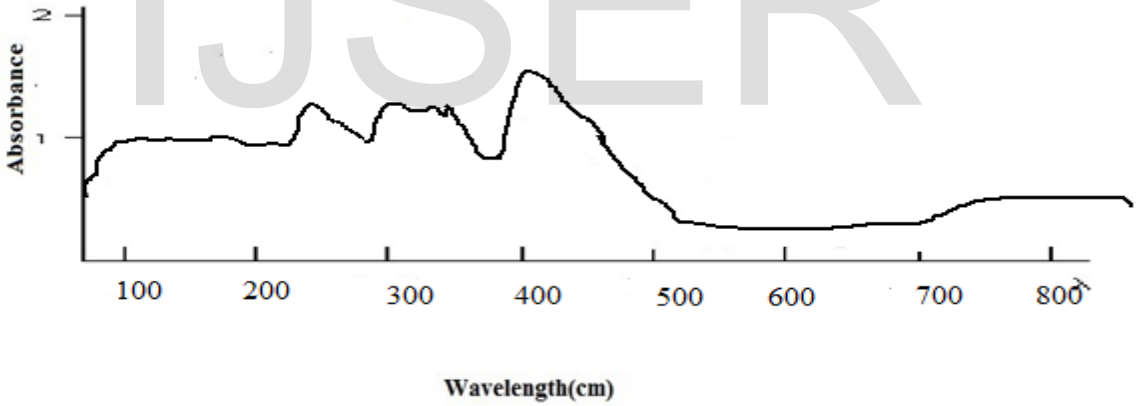


Figure 2.15: UV-VIS Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Cooper (II) complex

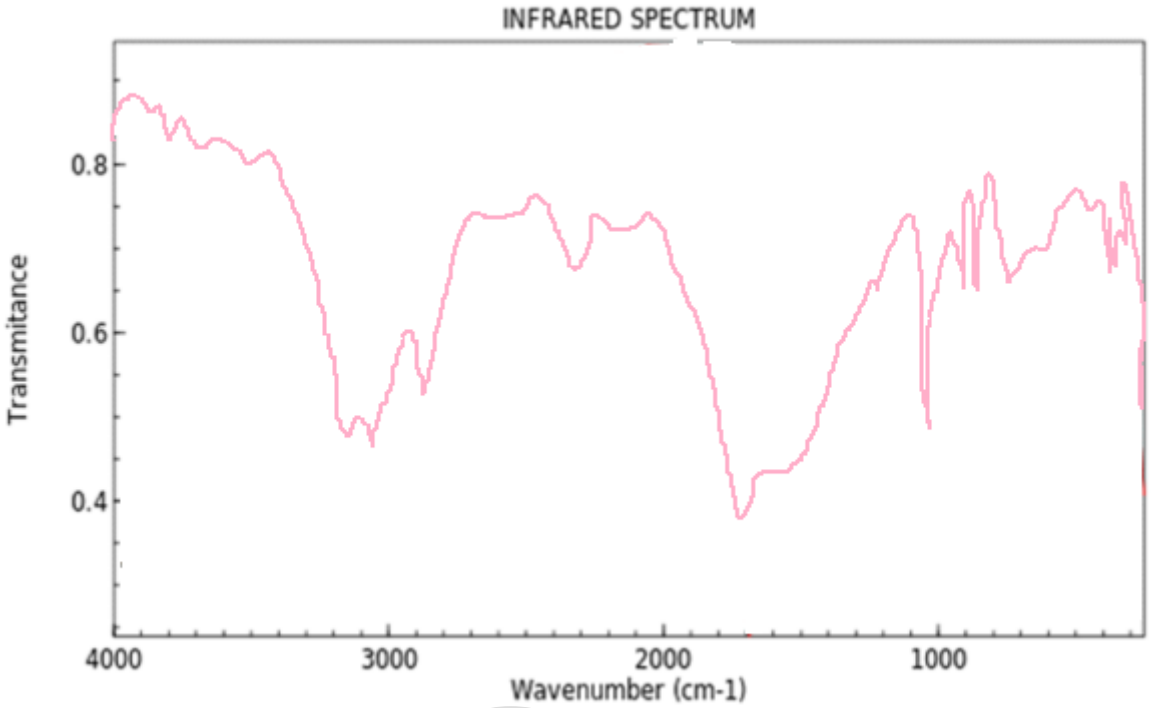


Figure 2.16: IR Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Re (II) complex

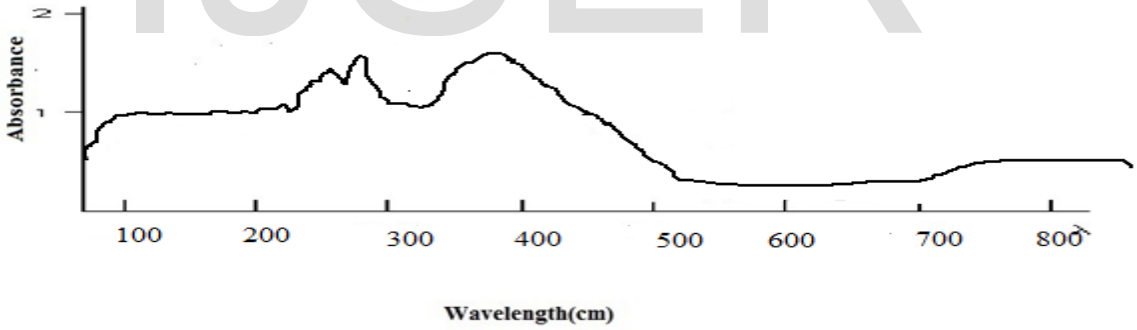
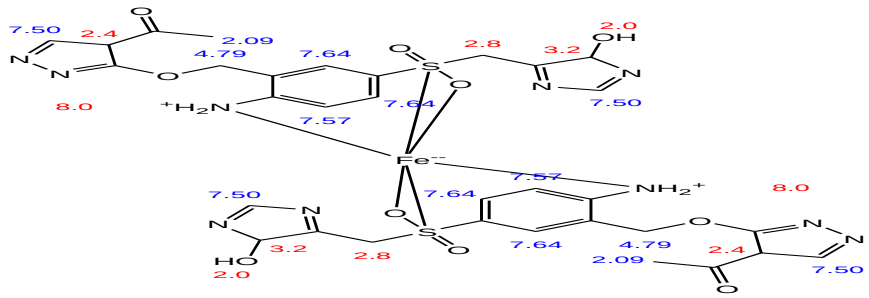
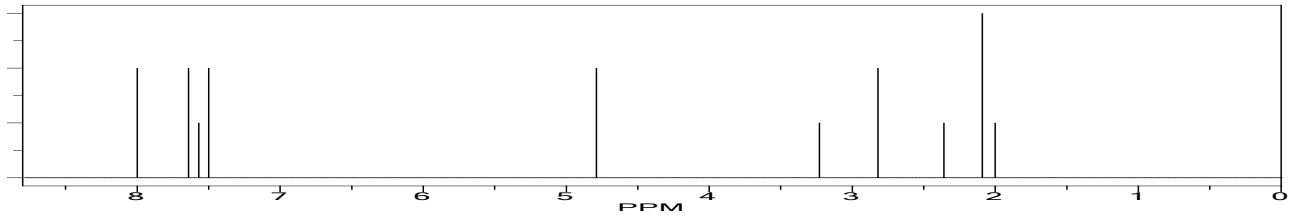


Figure 2.17: UV-VIS Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Re (II) complex

ChemNMR H-1 Estimation



Estimation Quality: blue = good, magenta = medium, red = rough



Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH3	2.09	0.86	methyl
		1.23	1 alpha -C(=O)C
CH	2.4	1.50	methine
		0.86	1 alpha -C=O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
CH	7.50	7.50	aldimine
CH2	4.79	1.37	methylene
		1.22	1 alpha -1:C*C*C*C*C*C*1
		2.20	1 alpha -O
CH	7.57	7.26	1-benzene
		-0.07	1 -C=O
		0.16	1 -Np
		0.22	1 -S(=O)-R
CH	7.64	7.26	1-benzene
		-0.07	1 -C=O
		0.06	1 -Np
		0.39	1 -S(=O)-R
CH	7.64	7.26	1-benzene
		-0.07	1 -C=O
		0.06	1 -Np
		0.39	1 -S(=O)-R
CH2	2.8	1.37	methylene
		1.45	1 alpha -S(=O)-1:C*C*C*C*C*C*1
		?	1 unknown alpha substituent(s)
			-> 1 increment(s) not found
CH	7.50	7.50	aldimine
CH	3.2	1.50	methine
		1.73	1 alpha -O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
OH	2.0	2.00	alcohol
NH2+	8.0	8.00	aromatic C-NH+
CH3	2.09	0.86	methyl
		1.23	1 alpha -C(=O)C
CH	2.4	1.50	methine
		0.86	1 alpha -C=O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
CH	7.50	7.50	aldimine
CH2	4.79	1.37	methylene
		1.22	1 alpha -1:C*C*C*C*C*C*1
		2.20	1 alpha -O
CH	7.57	7.26	1-benzene
		-0.07	1 -C=O
		0.16	1 -Np
		0.22	1 -S(=O)-R
CH	7.64	7.26	1-benzene
		-0.07	1 -C=O
		0.06	1 -Np
		0.39	1 -S(=O)-R
CH	7.64	7.26	1-benzene
		-0.07	1 -C=O
		0.06	1 -Np
		0.39	1 -S(=O)-R
CH2	2.8	1.37	methylene
		1.45	1 alpha -S(=O)-1:C*C*C*C*C*C*1
		?	1 unknown alpha substituent(s)
			-> 1 increment(s) not found
CH	7.50	7.50	aldimine
CH	3.2	1.50	methine
		1.73	1 alpha -O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
OH	2.0	2.00	alcohol
NH2+	8.0	8.00	aromatic C-NH+

Figure 2.18: ^{1}H-NMR Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Fe (II) complex

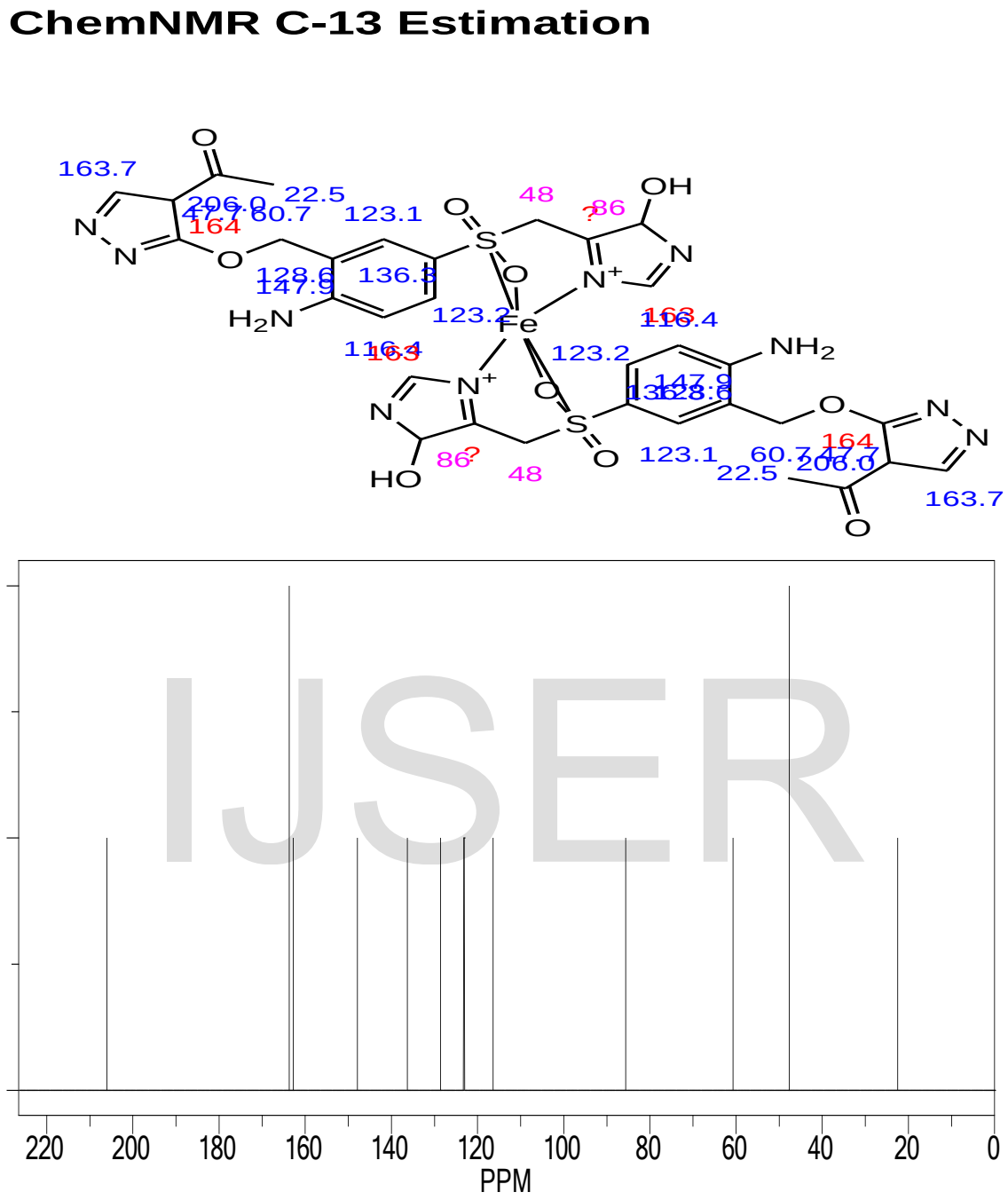
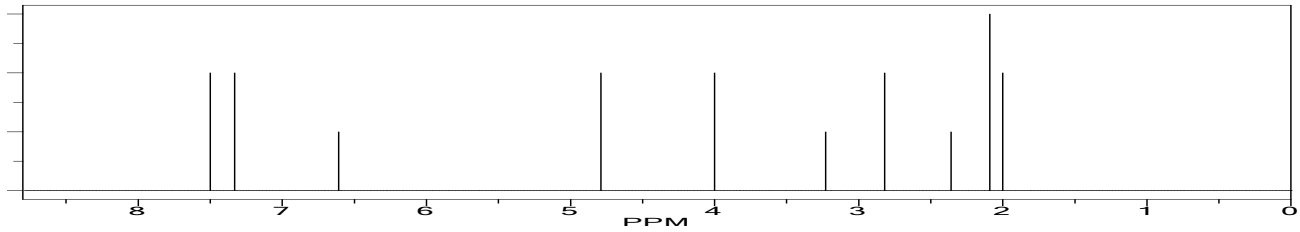


Figure 2.19: ^{13}C-NMR Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Fe (II) complex

ChemNMR H-1 Estimation

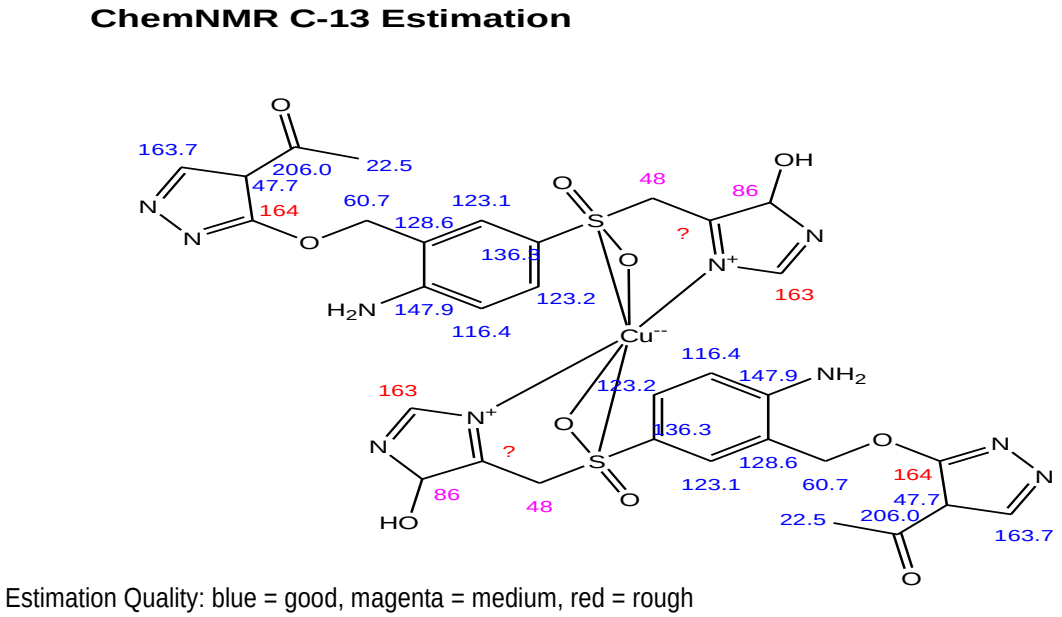
Estimation Quality: blue = good, magenta = medium, red = rough



Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH3	2.09	0.86	methyl
		1.23	1 alpha -C(=O)C
CH	2.4	1.50	methine
		0.86	1 alpha -C=O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
CH	7.50	7.50	aldimine
CH2	4.79	1.37	methylene
		1.22	1 alpha -1:C*C*C*C*C*C*1
		2.20	1 alpha -O
CH	6.61	7.26	1-benzene
		-0.07	1 -C-O
		-0.80	1 -N
		0.22	1 -S(=O)-R
CH	7.33	7.26	1-benzene
		-0.07	1 -C-O
		-0.25	1 -N
		0.39	1 -S(=O)-R
CH	7.33	7.26	1-benzene
		-0.07	1 -C-O
		-0.25	1 -N
		0.39	1 -S(=O)-R
OH	2.0	2.00	alcohol
CH2	2.8	1.37	methylene
		1.45	1 alpha -S(=O)-1:C*C*C*C*C*C*1
		?	1 unknown alpha substituent(s)
			-> 1 increment(s) not found
CH	7.50	7.50	aldimine
CH	3.2	1.50	methine
		1.73	1 alpha -O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
OH	2.0	2.00	alcohol
NH2	4.0	4.00	aromatic C-NH
CH3	2.09	0.86	methyl
		1.23	1 alpha -C(=O)C
CH	2.4	1.50	methine
		0.86	1 alpha -C=O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
CH	7.50	7.50	aldimine
CH2	4.79	1.37	methylene
		1.22	1 alpha -1:C*C*C*C*C*C*1
		2.20	1 alpha -O
CH	6.61	7.26	1-benzene
		-0.07	1 -C-O
		-0.80	1 -N
		0.22	1 -S(=O)-R
CH	7.33	7.26	1-benzene
		-0.07	1 -C-O
		-0.25	1 -N
		0.39	1 -S(=O)-R
CH	7.33	7.26	1-benzene
		-0.07	1 -C-O
		-0.25	1 -N
		0.39	1 -S(=O)-R
CH2	2.8	1.37	methylene
		1.45	1 alpha -S(=O)-1:C*C*C*C*C*C*1
		?	1 unknown alpha substituent(s)
			-> 1 increment(s) not found
CH	7.50	7.50	aldimine
CH	3.2	1.50	methine
		1.73	1 alpha -O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
OH	2.0	2.00	alcohol
NH2	4.0	4.00	aromatic C-NH
OH	2.0	2.00	alcohol

Figure 2.20: ^{1}H-NMR Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Cu (II) complex



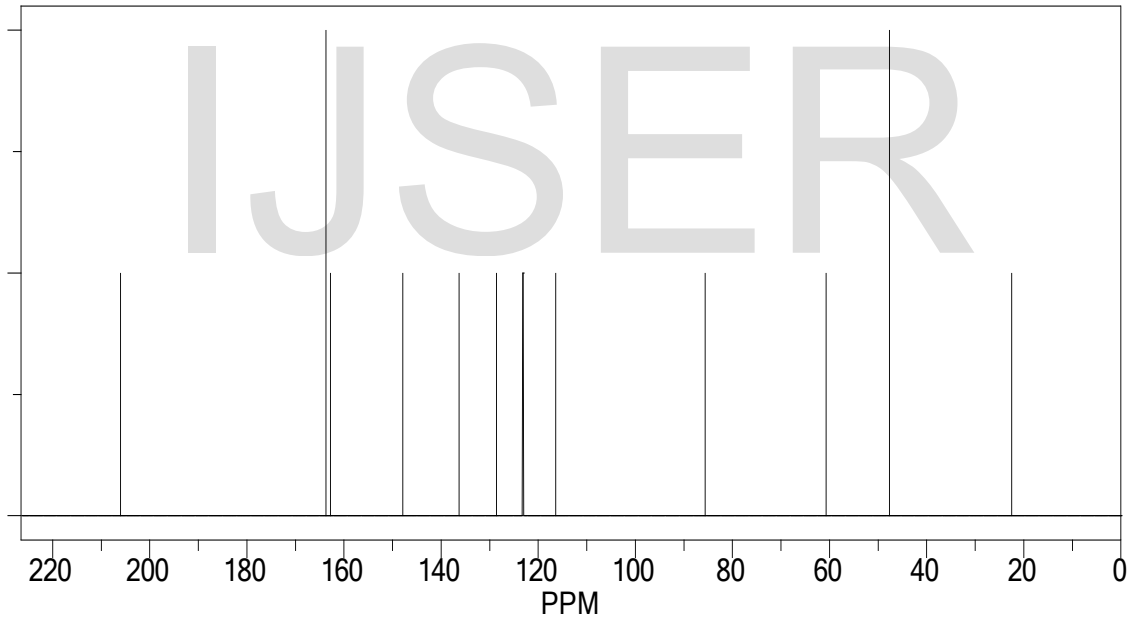
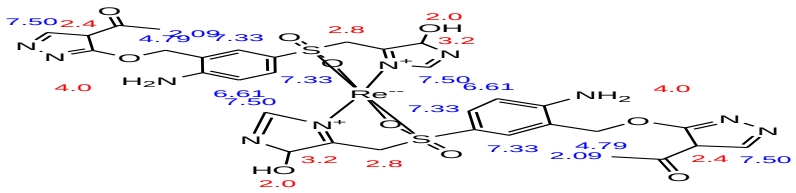
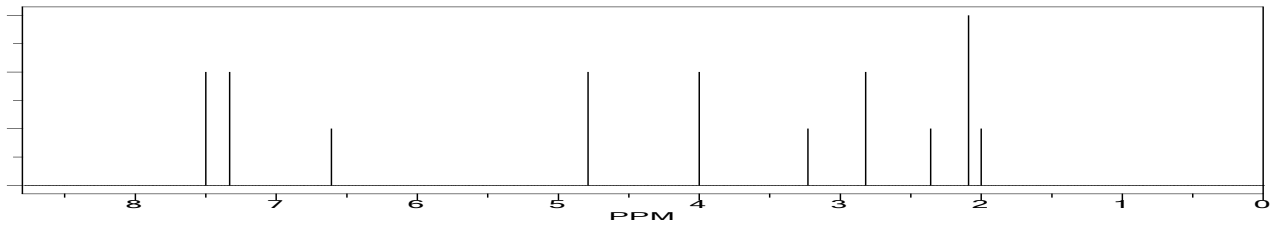


Figure 2.21: ^{13}C-NMR Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Cu (II) complex

ChemNMR H-1 Estimation



Estimation Quality: blue = good, magenta = medium, red = rough



Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH3	2.09	0.86	methyl
		1.23	1 alpha -C(=O)C
CH	2.4	1.50	methine
		0.86	1 alpha -C=O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
CH	7.50	7.50	aldimine
CH2	4.79	1.37	methylene
		1.22	1 alpha -1:C*C*C*C*C*C*1
		2.20	1 alpha -O
CH	6.61	7.26	1-benzene
		-0.07	1 -C-O
		-0.80	1 -N
		0.22	1 -S(=O)-R
CH	7.33	7.26	1-benzene
		-0.07	1 -C-O
		-0.25	1 -N
		0.39	1 -S(=O)-R
CH	7.33	7.26	1-benzene
		-0.07	1 -C-O
		-0.25	1 -N
		0.39	1 -S(=O)-R
CH2	2.8	1.37	methylene
		1.45	1 alpha -S(=O)-1:C*C*C*C*C*C*1
		?	1 unknown alpha substituent(s)
			-> 1 increment(s) not found
CH	7.50	7.50	aldimine
CH	3.2	1.50	methine
		1.73	1 alpha -O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
OH	2.0	2.00	alcohol
NH2	4.0	4.00	aromatic C-NH
CH3	2.09	0.86	methyl
		1.23	1 alpha -C(=O)C
CH	2.4	1.50	methine
		0.86	1 alpha -C=O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
CH	7.50	7.50	aldimine
CH2	4.79	1.37	methylene
		1.22	1 alpha -1:C*C*C*C*C*C*1
		2.20	1 alpha -O
CH	6.61	7.26	1-benzene
		-0.07	1 -C-O
		-0.80	1 -N
		0.22	1 -S(=O)-R
CH	7.33	7.26	1-benzene
		-0.07	1 -C-O
		-0.25	1 -N
		0.39	1 -S(=O)-R
CH	7.33	7.26	1-benzene
		-0.07	1 -C-O
		-0.25	1 -N
		0.39	1 -S(=O)-R
CH2	2.8	1.37	methylene
		1.45	1 alpha -S(=O)-1:C*C*C*C*C*C*1
		?	1 unknown alpha substituent(s)
			-> 1 increment(s) not found
CH	7.50	7.50	aldimine
CH	3.2	1.50	methine
		1.73	1 alpha -O
		?	2 unknown alpha substituent(s)
			-> 2 increment(s) not found
OH	2.0	2.00	alcohol
NH2	4.0	4.00	aromatic C-NH

Figure 2.22: ^{1}H-NMR Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Re (II) complex

ChemNMR C-13 Estimation

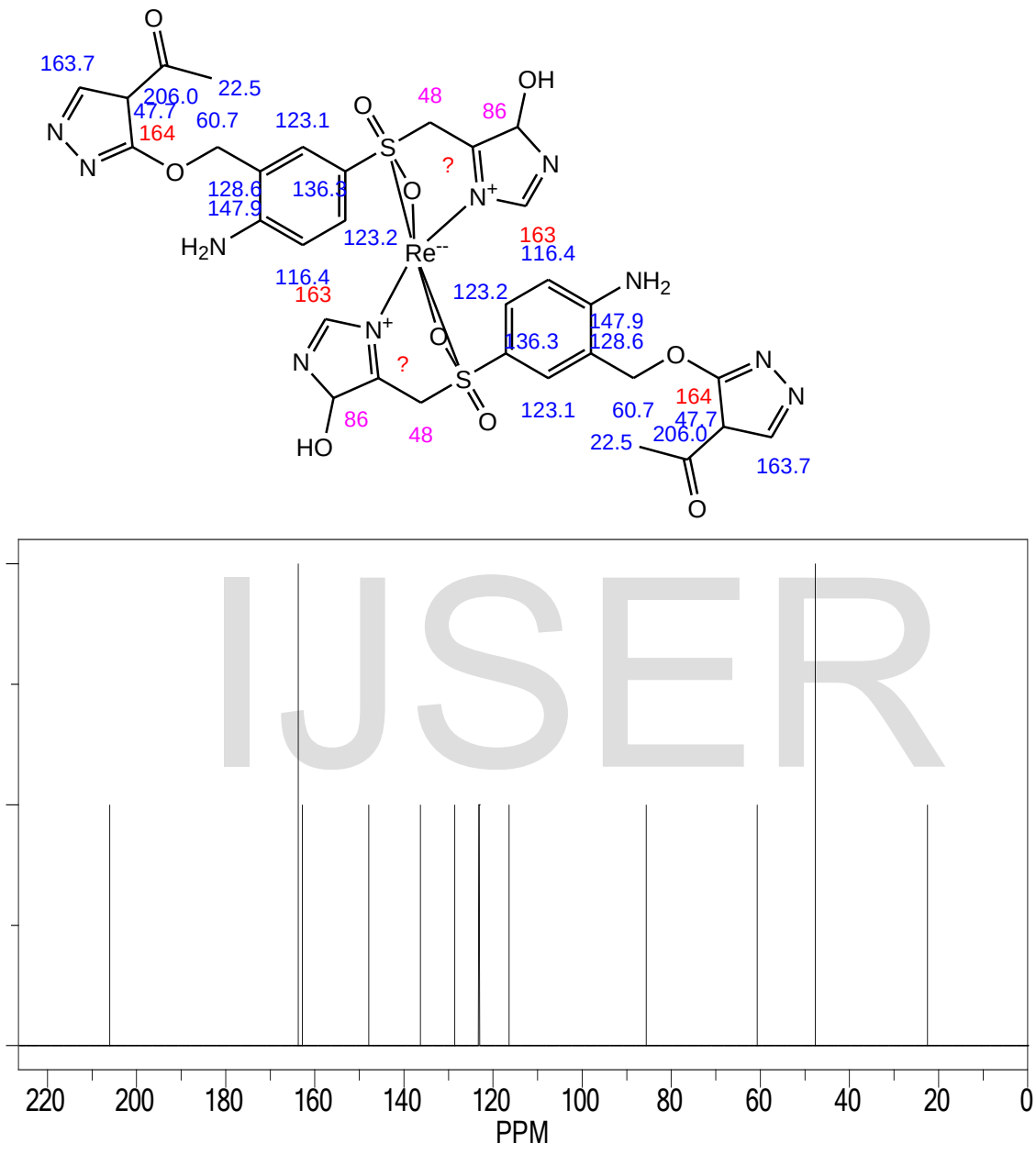


Figure 2.23: ^{13}C-NMR Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Re (II) complex

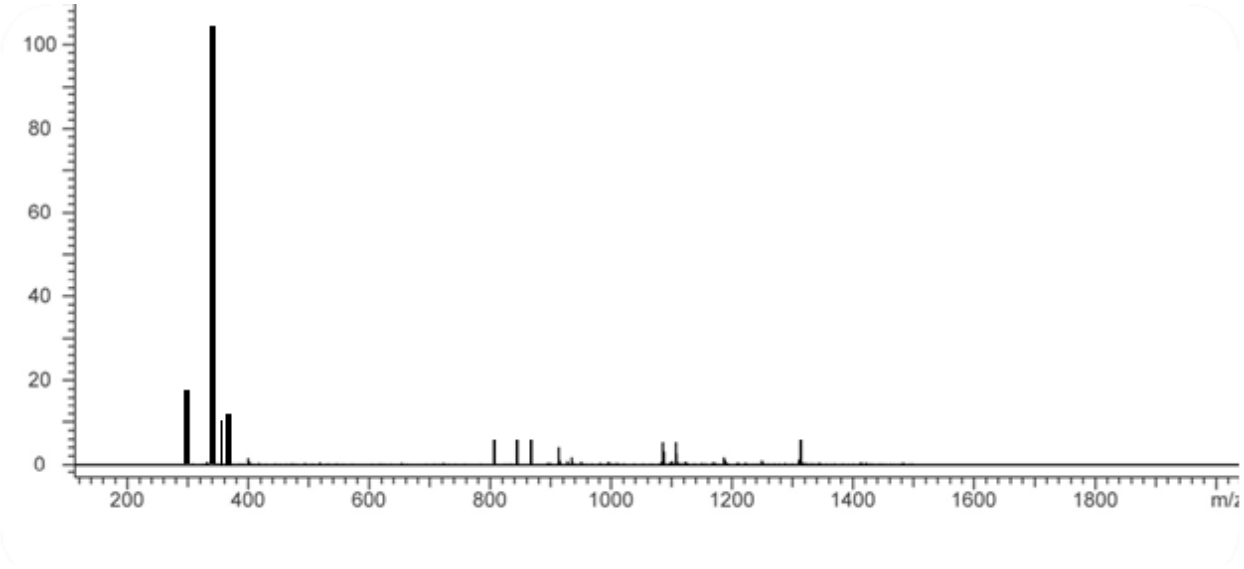


Figure 2.24: Mass Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone

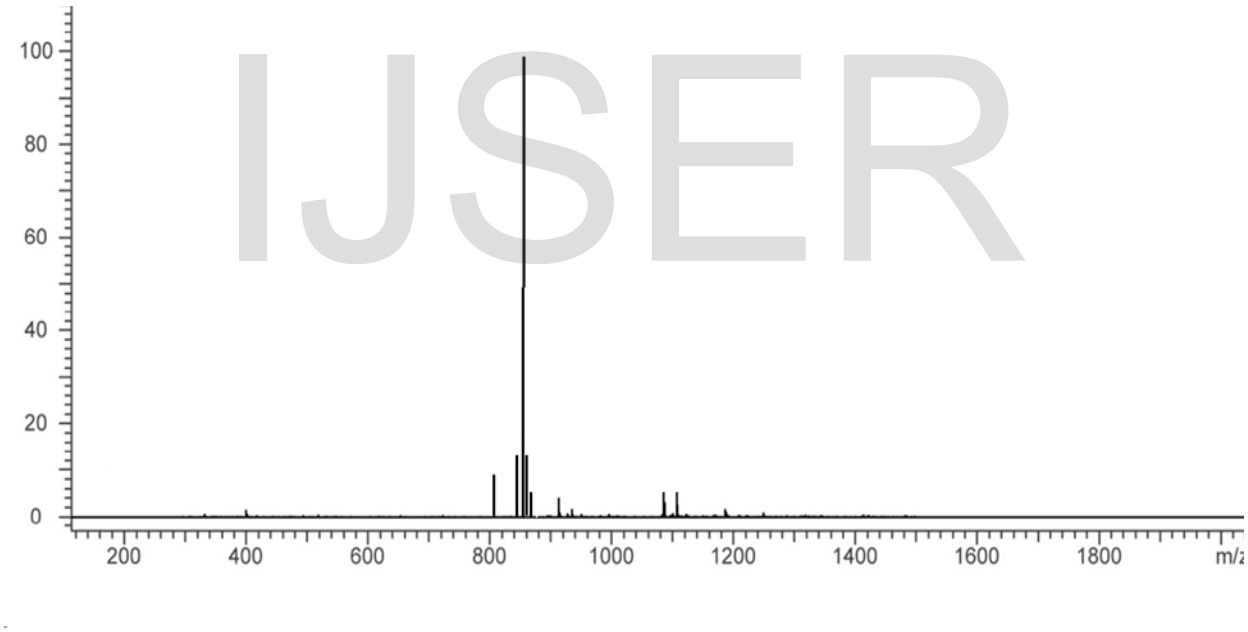


Figure 2.25: Mass Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Iron (III)

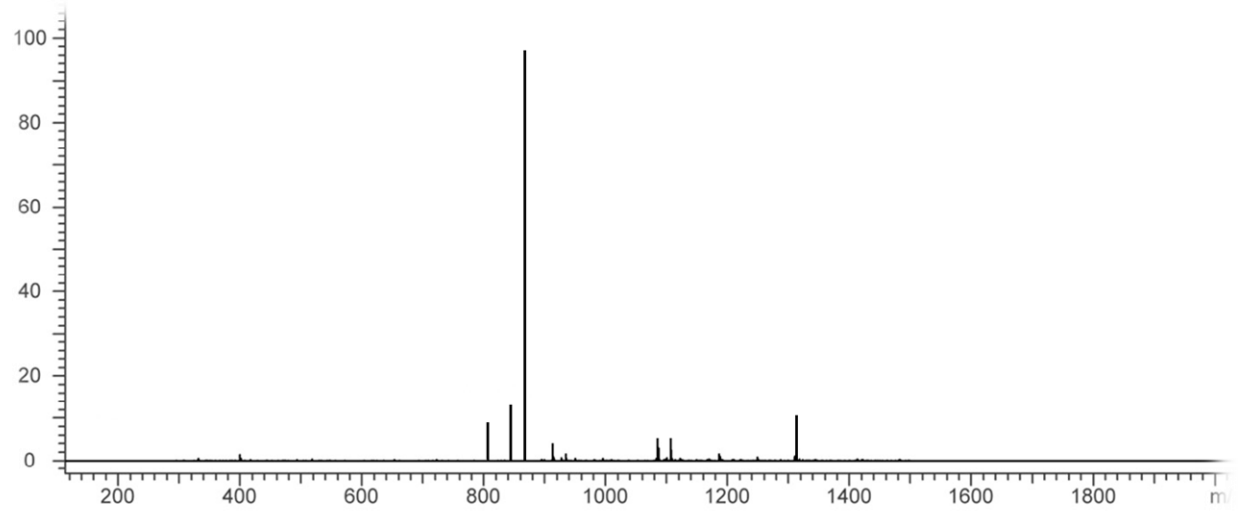


Figure 2.26: Mass Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Cooper (III)

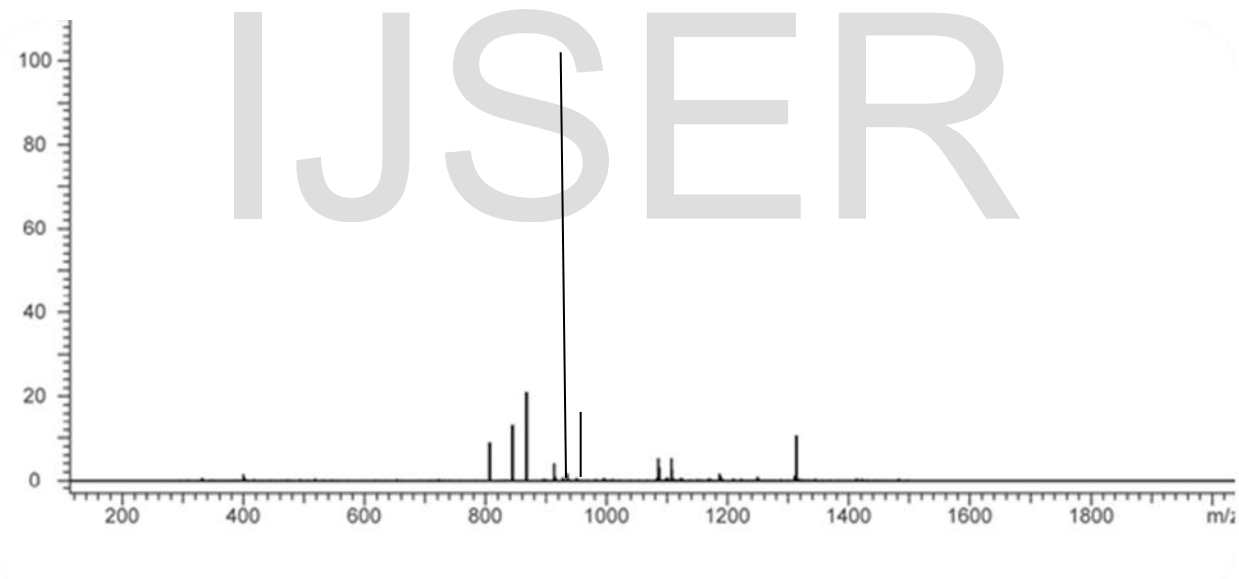


Figure 2.27: Mass Spectra of 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone Re (III)

Results and Discussion

The 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone ligand in this study synthesized using the reflux method. In this research, however,

the ligand was prepared at 140^0C temperature which afforded a higher yield of 12.2 gm. The ligand and metal (II) complexes of the ligand are new and it reported first time. The 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone ligand is soluble in hot ethanol and solvents such as DMF and DMSO.

The ligand yellow coloured and its metal (II) complexes are also coloured solids which are stable in air, the complexes were insoluble in common organic solvents such as methanol, dichloromethane, ethanol, and acetone but soluble in DMSO and DMF.

The melting points of the complexes were higher than that of the 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone ligand its Indicating that the complexes are more stable than the ligand. The chemical equations showing the preparation of its ligand and its metal (II) complexes scheme 2.1 and scheme 2.2.

Electronic Spectral Analysis

The electronic absorption was carried out by the instrument Shimadzu -1601 using alcohol as solvent The electronic spectral data of the 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone ligand and its metal complexes are given in the experimental part of unit. The 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone ligand showing three bands at λ max (nm) 223.4, 270.2 and 358 nm. These bands at 223.4 nm is due to the π–π∗ transition in benzene, the band appearing at 270.2 nm is assignable to n–π∗ transition of nonbonding electrons present on the –NH2, and the band at 358.1nm is due to n–π∗ transition of the phenolic group [46-47]. The UV-Vis spectra of the 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone metal complexes are presented in the similar absorption spectra as the ligand, but it have either a blue shift or red shift.

The bands of electronic spectrum for the Fe (III) complex goes to shorter wavelength and gave three bands similar to ligand at λmax (nm) 221.4, 251.8, and 342.1. The band at 221.4nm and 251.8nm was due to intra-ligand transition, and the band at 342.1nm was as a result of d-d low-spin transition which revealed that the complex have octahedral geometry around Fe (III) ion 48-49. In case of Re (II) complex, three bands were determined at λmax (nm) 243.1, 267.1 and 345.5. This was a shift towards longer wavelength with respect to the spectrum of the 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone ligand. (e band at 267.1 nm. It due to intra-ligand transition, and the band at 345.5nm was as a result of d-d transition for the range for octahedral configuration as reported in many octahedral Re (II) complexes[50-52]. The electronic spectrum of Cu (II) complex showed three bands at λmax (nm) 245.2, 315.1 and 422.9nm. The band at 245.2nm founds probably due to intra-ligand transition, while the band at 422.9 nm was due to charge transfer, the observed band at 422.9nm found as a result of d-d transition which favors the tetrahedral environment in Cu (II) complexes, the copper (II) complex spectrum[52-56] also the absence band below 10,000 cm−1 which is possibility of a tetrahedral environment in Cu(II) complexes[57-59]. It can also count that a shift in the spectral bands of the complexes with respect to the spectrum of the 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone is shifted towards bathochromic shift.

FT-IR Spectral Analysis of complex

Infrared spectra of the ligand and its complexes were carried out by using KBr pellets in the range of 4000-400 cm-1on with the Bucker model of IR instrument, the binding mode of the 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone ligand and metal ion combination in complexes was determined by comparing the FT-IR spectrum of the free ligand with the spectra of the metal complexes.

The stretching frequency for the ligand and the metal complexes were analyzed and we get the frequency for Fe (III) complex at IR (KBr, disc cm−1) 3429.0 υ (O-H), 1601. 1215.7 υ(C-O), 701.0 υ (H2O), 532.6 υ(Fe-N), 491.1 υ(Fe-O), similarly for Cu(II) and Re(II) complex we found the frequencies at %. FT-IR (KBr, disc cm−1) 3420.7 υ(O-H), 1595., 1214.8 υ(C-O), 697.9 υ(H2O), 527.4 υ(Cu-N), 489.2 υ(Cu-O)and for Re(II) we get FT-IR (KBr, disc cm−1) 3455.6 υ(O-H), 1599.7, 1213.9 υ(C-O), 695.8 υ(H2O), 536.1 υ(Re-N), 490.8 υ(Re-O) in which stretching 1601 cm-1,1595 cm-1 and 1599.7 cm-1 occurs for metal-NH2 bonding in complexes, respectively. This indicated coordination of ligand through the nitrogen[60]. Moreover, the appearance of weak bands in the region 532.6 υ(Fe-N), 491.1 υ(Fe-O) υ(H2O), 527.4 υ(Cu-N), 489.2 υ(Cu-O) 695.8 υ(H2O), 536.1 υ(Re-N), 490.8 υ(Re-O) found for υ(M-N) and υ(M-O), respectively 61 further confirmed complexation [61-62]. This showed that the ligand coordinated to the metal through the "N" and "O" atoms.

The FT-IR spectra of the complexes also showed strong bands in the 3420.3–3455.6 cm−1 regions, suggested that the presence of coordinated/lattice water in complexes. This is also confirmed by the non-ligand band in the 695.8–701 cm−1 regions[63-64].

Elemental Analysis

The micro-analysis of data revealed that all the metal-ligand complexes are mononuclear where two moles of the ligand were coordinated to the central metal atom. Therefore, it suggested that the metal to ligand ratio in the complex was 1: 2 and the general formula for the complexes as $[M(L)_2(H2O)_2]$ where M=Fe (III), Cu (II), and Re (II) [65]. The theoretical (calculated) values were found to be in good agreement with the experimental values.

NMR Spectra Analysis.

The 1H and 13C NMR spectra of the 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone ligand and its Fe (III), Cu (II) and Re (II) complexes were recorded in DMSO. The 1H NMR spectrum of the 1-{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone showed a singlet peak at δ 7.50 ppm corresponding to proton 64-65, it indicate that the -{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone are formed during the reaction. Observation of a peak at δ 162.82 ppm in the 13C NMR spectrum was further proof that the ligand was successfully synthesized[66].

The 1 -{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone shifted up-field in the ^{1}H NMR spectra of the Cu (II) and Re (II) complexes (δ 7.50 ppm). The up field shifting of amino proton in Cu (II) and Re (II) complexes was showing the discharge of electronic cloud towards the Cu (II) and Re(II) ions which is the indication of coordination through the amine nitrogen to the metallic ion[67]. This is confirmation of de-protonation of the group and coordination of the negatively charged oxygen species to the metal cations. This observation also given proof of metal complexes and explains the non-electrolytic

behavior of the complexes. The ^{13}C NMR peaks for the carbon atom and imidazole group carbons are coordinate to organic ligand were we observed shift at δ 165 ppm and 162 ppm, in the spectra of the Cu (II) complex, a 2 ppm up field shift from free organic ligand, due to coordination bonding [68-69].
The data of ^{1}H NMR and ^{13}C NMR; spectroscopy confirmation the monobasic dentate nature of the organic ligand, it already observed by the FT-IR spectral studies.

Mass Spectrum analysis

The mass spectrum of the organic ligand showing a molecular ion peak at m/z 391 (M+2) which is consistent with the molecular weight of the ligand 389.3, and the m/z for Fe(III), Cu(II) and for Re(II) complexes obtained at 838.3, 846.58 and 968.3 respectively which is the confirmation of complex synthesis[70].

Conclusion

In this study, the synthesis of a new macro-cyclic derivative of pyrazol and imidazol is count as the 1 -{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone where, the spectroscopic analysis of data were investigated ligand complexes with Cu(II) in DMSO and ethyl alcohol.
The Electrochemical, IR, NMR, and MS analysis have been confirmed the unexpected and possibilities of metal complex formation by a new organic ligand that is 1 -{3-[2-Amino-5-(5-hydroxy-5H-imidazol-4-ylmethanesulfonyl)-benzyloxy]-4H-pyrazol-4-yl}-ethanone. The metal ligand ratio in complex is found stable 1:2 in the solvent. Furthermore, complex is attracted to nitrogen atoms and oxygen atoms. The NMR ^{1}H and ^{13}C is also revealed that the complex have tetrahedral structure and it also containing the biological activity.
Mass spectra analysis confirmed the existence of complexes with ions in same oxidation state but Only in the case of ions reduction from copper (II) to copper (I) ion has been observed during experimental conditions and the obtained complex is only formed by endo-cyclic nitrogen atom from complex. The mass analyses results show that the complexes are formed stable under the conditions of applied voltage and do not undergo fragmentation with metal ion detachment. And the mass spectrum occurs for Fe(III), Cu(II) and Re(II) complexes at 838.3, 846.58 and 968.3 respectively which is the confirmation of complex synthesis.

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