RESEARCH ARTICLE

Spectrophotometric Determination of Cu(II) Using DMIPNI as a New Reagent Derived from 4,5-Diphenyl Imidazole

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Received: 25th February, 2022; Revised: 08th April, 2022; Accepted: 16th May, 2022; Available Online: 25th June, 2022

ABSTRACT

Copper (II) ion was determined spectrophotometrically by the reagent 1-(4-(((4,5-dimethyl-1H-imidazol-2-yl)diazenyl)methyl) phenyl)-N-(4-nitrobenzyl)ethan-1-imine (DMIPNI), prepared by condensing reaction between p-aminoacetophenone with p-nitroaniline, and the Schiff base results were undergone diazotization with 4,5-diphenyl imidazole. The reagent was used to determine Copper(II) ion in aqueous solution after optimizing the preparational conditions such as the pH of reaction solution, the best reagent concentration, and time reaction. The prepared complex was characterized by UV-visible, fourier-transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (H-NMR) spectroscopies, the stoichiometric composition of the complex was studied by mole ratio and continuous variation, which proves that the M:L ratio in the complex is equal to 1:2. The current study shows that the best pH and reagent concentration equal 9 and 3×10^{-5} molar, respectively. The stability time of Copper (II) complex after its preparation was still stable until to 120 minutes. Beer's law is obeyed in the concentration range (0.01–1.00) µg/mL of Cu(II), with a molar absorptivity 0.857 x 10^{6} L.mo1^{-1}.cm^{-1} and Sandell's sensitivity 7.418 x10^{-5} µg.cm^{-2} with an excellent linearity depicted by correlation coefficient value of 0.9995. Limit of detection (LoD) and Limit of quantification (LoQ) are 0.0105 and 0.035 µg/mL. Recovery and relative error values of precision and accuracy of method were found to be RSD% = 1.391, Re= 101.00% and Erel = 1.00%.

Keywords: P-aminoacetophenone schiff base, Schiff-Azo complex of copper(II) ion, Schiff base -Azo of imidazole.

International Journal of Drug Delivery Technology (2022); DOI: 10.25258/ijddt.12.2.10

How to cite this article: Nayif AA, Al-Da,amy MA, Kadhim SH. Spectrophotometric Determination of Cu(II) Using (DMIPNI) as a New Reagent Derived from 4,5-Diphenyl Imidazole. International Journal of Drug Delivery Technology. 2022;12(2):522-527.

Source of support: Nil.

Conflict of interest: None

INTRODUCTION

Copper (II) is a reddish–colored a heavy metal whose color and properties changes when it is combined with other elements forming different compounds.[1,2] It is the third most important element in the human body after iron and zinc.[3] It helps to absorb iron from the intestine and is important in forming hemoglobin and red blood cells in the Skeleton.[4] Copper enters in the composition of the skin and hair and accordingly it is responsible for coloring hair and skin and enters in the formation of joints and nerves are responsible for the sense of taste also involves the synthesis of many enzymes to maintain the activity and health of the heart.[5,6]

Its deficiency causes osteoporosis, leukopenia and anemia.[7] Increasing its concentration causes nausea, kidney failure, diabetes and cancer.[8,9] Many organic reagents have been synthesized and used as photometric reagents in analytical chemistry.[10] They have a good ability to coordinate with many metal ions.[11,12] These reagents have high selectivity, high molecular weight, strong colores and high solvation in organic solvents.[13,14] Schiff base ligand catch more attention due to their ability to bind with metal ion.

Azo dye also the most common organic reagents; the reason for their name is due to the presence of the bridging azo group (N=N) with hybridization Sp^3[15] and the azo compounds are characterized as spectral reagents with sensitivity, selectivity, high stability[16,17] such as methyl orange and methyl red dye, as well as in the manufacture of wool, silk and wood.[18] Many methods which is used for Cu (II) spectrophotometrically, such as using chromogenic reagent HPEDN at PH= 9, The linear range of the calibration graph is between 1.7 to 5.4 µg/mL, the molar absorption is 0.5038×10^{4} L.$mol^{-1}cm^{-1}$, sandell's sensitivity is found to be 0.0039 µg.cm^{-2}, with LoD and LoQ 0.2225 and 0.7406 µg.mL^{-1}, respectively. The value RSD% = 0.2746.[19] Also, it is determined by using reagent (MBBAI) at pH=5, with concentration ranging from (5–80) µg/mL of Copper(II), which obeyed Beer`s Law. Maximum absorption of the complex is 409 nm with molar absorptivity is $0.127x10^{4}$ L $mol^{-1}.cm^{-1}$.(LoQ)= 6.42 µg/mL, LoD = 1.924 µg/mL, Sandell's Sensitivity 0.040 µg/cm^{2} and RSD% = 0.230.[20]

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EXPERIMENTAL

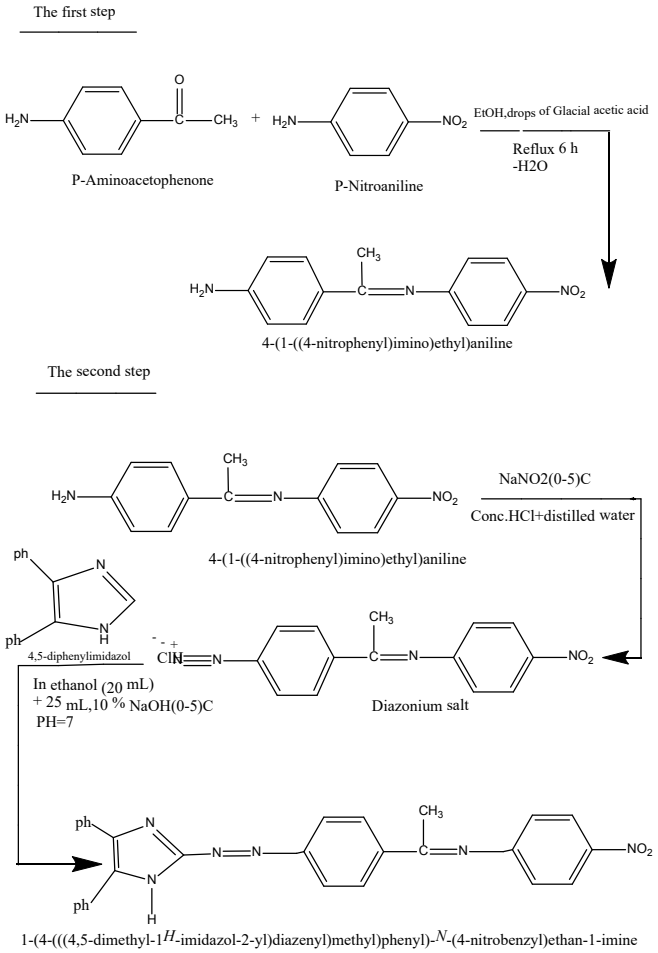
Materials and Procedures

Reagent and Solutions

All analytical reagents and solutions used in the preparation are of the highest purity possible.

Instrumentation

pH-meter, InoLab, WTW, 135i, Germany, Balance BL 2105, Sartorius, Germany. UV-6100 PC Double Beam Spectrophotometer, EMCLAB, Germany. Melting point, SMP30, Sturt, England. Conductivity meter, Digital, InoLab, Germany. FT-IR Spectrophotometer 8400S, Shimadzu, Japan. Mova 400MHZ,^{1}HNMR spectrophotometer.



Scheme 1: Pathway of synthesis of ligand

Synthesis of New Ligand

The ligand 1-(4-(((4,5-dimethyl-1H-imidazol-2-yl)diazenyl) methyl)phenyl)-N-(4-nitrobenzyl)ethan-1-imine was synthesized in two steps. The first step is to prepare the Schiff base derivative by reacting P-aminoacetophenone with P- nitroaniline refluxing of the mixture for 6 hours; then, the resultant solution is cooled to room temperature the 4-(1-((4-nitrophenyl)imino)ethyl)aniline yellow solid precipitant filtered and washed with ethanol and dried in oven at 60ºC.

The second step includes the preparation of diazonium salt by the reaction of 4-(1-((4-nitrophenyl) imino)ethyl)aniline with sodium nitrite in acidic media at (0–5)ºC, then added to solution of imidazole, which dissolved in 50 mL of alkaline solution of 10% NaOH at cooling to (0–5)ºC. The obtained precipitate is 76.33% of reddish brown crystals.

Synthesis of Copper(II) Solid Complex

The Copper(II) complex is prepared by molar ratio (1:2) (M:L) by dissolved (0.00l mole) of the metal chloride salts in 20 mL of buffer solution in optimal acidic function (pH=9) and (0.002 mole) in 40 mL of absolute ethanol of reagent is heated at 60–70ºC for an hour. The resultant mixture is cooled and allowed to crystallize. The precipitate is recrystallized with absolute ethanol and air dried. Table 1 displays the physical properties of the ligand and its complex.

RESULTS AND DISCUSSION

Spectra of Absorption

The maximum absorption peaks of the ligand was at (470 nm), The maximum absorption of Cu^{2+} complex was at 537 nm after the application optimal conditions, as shown in Table 2.

Optimization of Reaction Conditions

pH Effect

A series of Copper (II) ion solution (1×10^{-5}M) with ligand (1×10^{-5}M) were prepared at pH= (4-10) and measure the absorbance

Table 1: Physical properties of ligands and their complexes.

No.	*Molecular formula*	*Color*	*m.p (°C)*	*Yield (%)*	*Am Ohm^{-1}mol^{-1}cm^{2}* Ethanol	*Time reaction*
1	$C_{29}H_{22}N_6O_2$	Reddish brown	135–137	76.33	__	6h
2	$[Cu(C_{29}H_{22}N_6O_2)_2Cl_2]$	Black	320–322	70.57	2.6	1h

Table 2: The electronic transitions and magnetic sensitivity data for ligand and its complexes

Molecular formula of ligand and complex	*λ(nm)*	*Wave number (cm^{-1})*	*Transition type*	*μ eff (B.M)*	*Geometry*
$C_{29}H_{22}N_6O_2$	470	21276	n→π*	-------	-------
	301	33222	p→π*		
$[Cu(C_{29}H_{22}N_6O_2)_2Cl_2]$	537	18621	CT	2.25	Octahedral
	342	29239	p→π*		

for each solution at the maximum wavelength of Copper complex. The results showed that the best pH=9 in 25ºC,[21] as shown in Figure 1.

Effect of the Concentration of Ligand:

Serious of solutions were prepared by mixing of (1 x10 $^{-5}$M) of Cu(II) ion solution with different concentrations of ligand ranging from (0.5x10^{-5}–5 x10^{-5}M). The results show that the optimal concentration for ligand was (3 x10^{-5}M) as shown in Figure 2.

The Time Effect

It is noticed from Figure 3 that the absorbance of the complex remains almost constant for a period up to 120 min., indicating the change in color complex occurs immediately and that the complex has high stability.[22]

The Temperature Effect

The effect of temperature (10–65)ºC is studied under optimum conditions, the absorbance of the complex decreases with increasing temperature, as shown in Figure 4.

The Effect of Addition Sequences

The method summarized in Table 3 is used to investigate the effect of addition sequences under optimal circumstances Due to the maximum absorbance obtained, the first order addition was used based on the results shown.

Construction of Calibration Curve

A serious of different concentrations are prepare of metal ion with concentrations ranging from (0.01-2.00 µg/mL) and (3x10^{-5}M) from the ligand, where the results showed that the calibration curve follows the Lambert Beer's law for a range of concentrations (0.01–1.00 µg/mL). As shown in Table 4 and Figure 5, The method is extremely sensitive and can be used to estimate metal concentrations at very low concentrations.

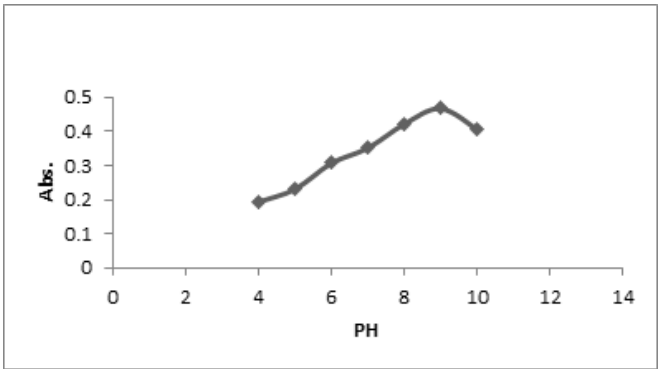


Figure 1: Effect of pH of solution on complex formation

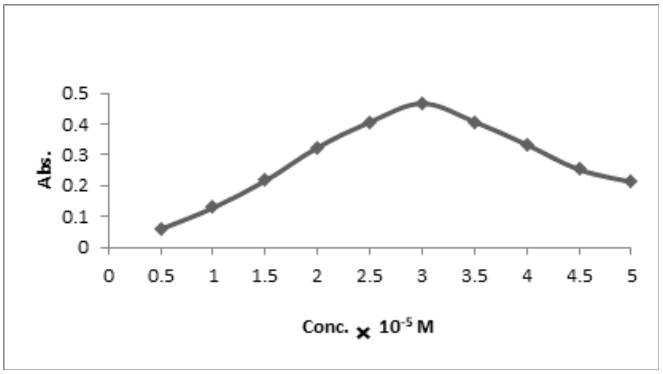


Figure 2: The influence of ligand concentration

Stoichiometry and Formation Constant Determination

To investigate the composition of the complex formed, the mole ratio method and Job's method were used. Their methods revealed that the metal ion to reagent molecule ratio (M:L) was significant (1:2).

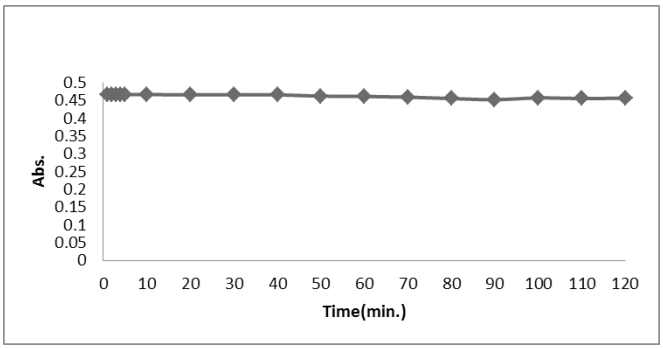


Figure 3: Time's effect on the stability of the Copper(II) complex

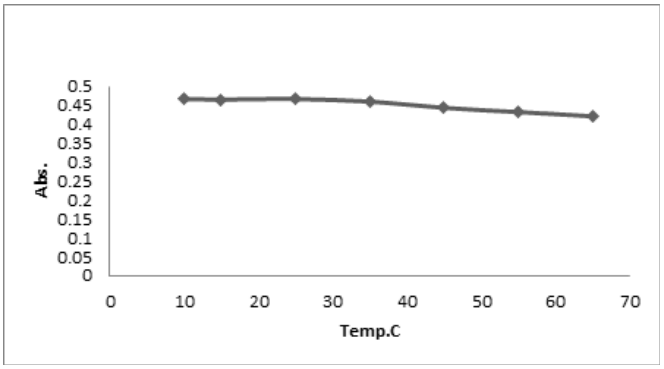


Figure 4: Effect of temperature on the complex's stability

Table 3: Effect of Sequence of addition on the formation of Cu^{2+}complex with ligand at pH= 9

Sequence of addition number	*Sequence of addition*	*Abs.*
1	M+L+PH	0.4663
2	L+M+PH	0.4322
3	M+PH+L	0.4015
4	L+PH+M	0.355

Table 4: The calibration curve of metal complexes

λ_{max} (nm)	537
Equation of Regression	y = 0.5381x+0.1274
Slope	0.5381
Correlation coefficient (R)	0.9995
Beer's Law limit (µg/mL)	0.01-1.00
Molar Absorptivity (L. mol^{-1}. cm^{-1})	0.857×10^{6}
Sandell's Sensitivity (µg. cm^{-2})	7.418×10^{-5}
Detection Limit (µg/mL)	0.0105
Limit of Quantification (µg/mL)	0.035

Mole Ratio Method

As shown in Figure 6, this was accomplished by combining a known concentration of Cu(II) ion (0.635 g/mL) with increasing concentrations of ligand.

Continuous Variation Method (Job Method)

Solution of different volume and equal concentration of Cu(II) ion with the ligand were mixed, as shown in Figure 7.

Study the Stability for the Complex

The mole ratio method was used to calculate the complex's stability constant based on the complex's equilibrium reaction. Table 5 shows the results of the calculations.

$$M^{+n} + nL^{-} \leftrightarrow MLn$$

K stability constant = $[ML^{+n}]/[M^{+n}][L^{-}]^{n}$

α = Am-As/Am Where **Am** is the greatest absorption and **As** is Absorption at the stoichiometry.

Thermodynamic Function of the Complex

Table 6 and Figure 8 show the results of calculating the thermodynamic functions ΔH, ΔG, and ΔS.

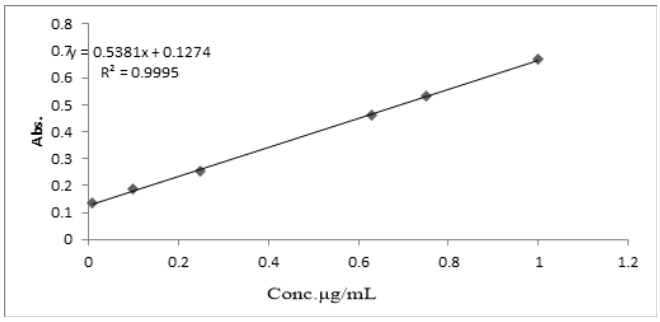


Figure 5: Calibration curve of Copper(II) complex

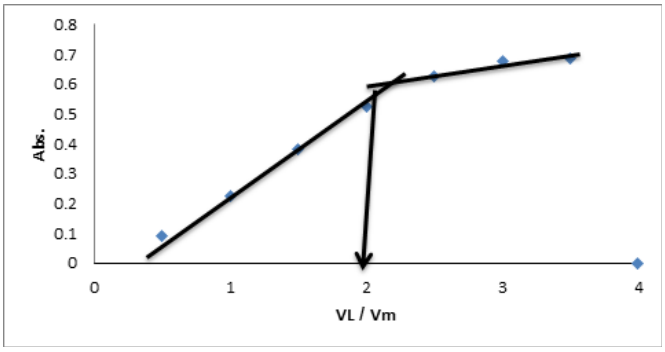


Figure 6: Mole ratio method curve of Cu(II) complex.

According to the negative sign of free energy, the negative value of enthalpy explains why the reaction is exothermic and spontaneous, as it is known that entropy is a measure of randomness in theory entropy is positive because high values of entropy lead to pushing the reaction toward the right, i.e., toward the products and the formation of the complex.[23]

Precision and Accuracy

The analytical method's precision is determined by calculating the standard deviation (S.D.) and relative standard deviation (%R.S.D.) of the complex and optimal conditions. The analytical method's accuracy is calculated using the percentage relative error and the recovery percentage of previously prepared complexes, as shown in Table 7. The results show that the ligand-based method for estimating metals is highly accurate.

$$\%Ereal = d/\mu \times 100$$

μ= Analytical value

d= Theoretical value - Analytical value.

The Study of Ligand and Complex FTIR Spectra

The FT-IR study and the absorption frequencies for the reagent and complex were described in Figures 9 and 10, and Table 8.

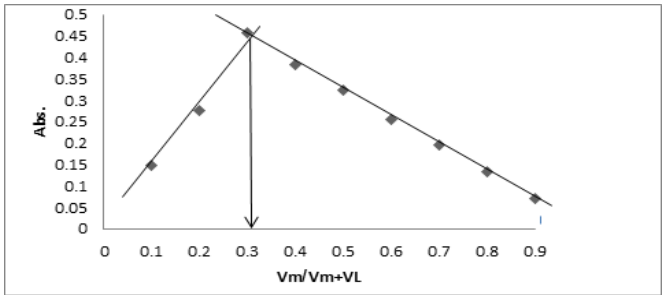


Figure 7: Continuous variation method curve of Cu(II) complex

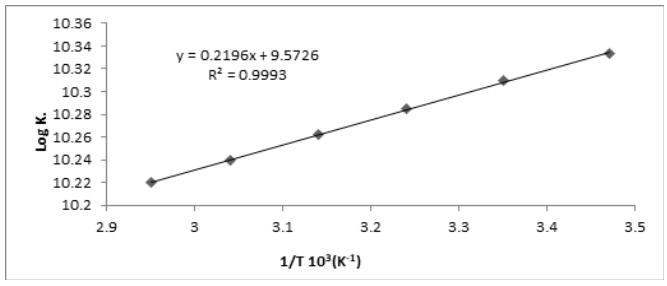


Figure 8: Log K. and 1/T of Cu (II) Complex Relationship

Table 5: The value of the stability constant for the Cu(II) complex.

Complex	*Am*	*As*	*α*	*Kinst.*	*Kst.*	*Log Kst*
[$Cu(C_{29}H_{22}N_6O_2)_2Cl_2$**]**	0.6865	0.5261	0.2336	6.6×10^{-11}	15.086×10^{10}	11.178

Table 6: The effect of temperature on thermodynamic function for Cu(II) complex.

T(K)	*1/T (K^{-1})*	*Log. K*	*ΔG (K.J/mol)*	*ΔH (K.J/mole)*	*ΔS (K.J/mole.K)*
288	3.47	10.333	- 56.983	-0.0042	0.1978
298	3.35	10.306	-58.806		0.1973
308	3.24	10.288	-60.673		0.197
318	3.14	10.26	-62.44		0.1963
328	3.04	10.247	-64.357		0.1961
338	2.95	10.22	-66.147		0.1956

Table 7: Results of Precision and accuracy

Ion complex	*Ion Conc.(M)*	*S.D*	*%R.S.D*	*d*	*% Ereal.*	*%Re*
	1.57×10^{-6}	0.0005	0.268	0.001	1.00	101
Cu(II)	1.00×10^{-5}	0.0026	0.568	-0.01	-1.58	98.42
	1.57×10^{-5}	0.0012	0.1797	0.005	0.5	100.5

Table.8: Ligand and Complex Absorption Frequencies in FT-IR.

Compound	*vC=N*	*vN=N*	*vN=H*	*Ph.imid.*	*vM-N*
Ligand	1666	1413	3736	769	--------
Cu(II) Complex	1672	1462	3740	769	449

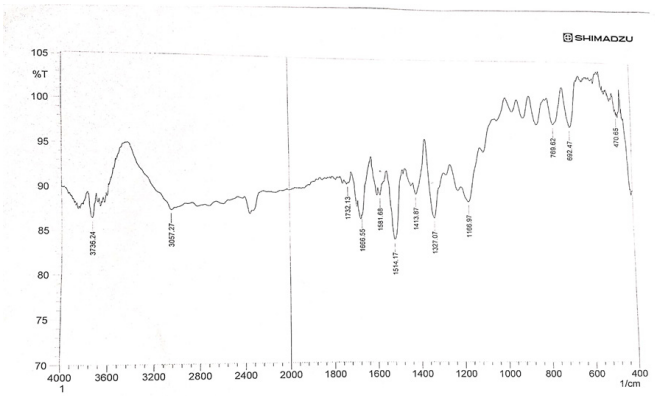


Figure 9: Ligand FT-IR spectrum

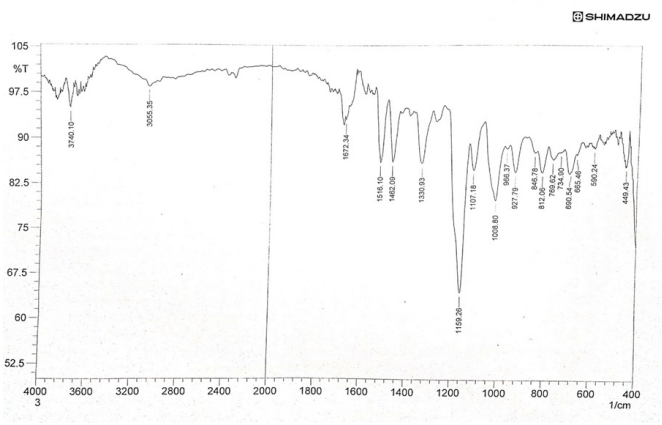


Figure 10: Cu(II) complex FT-IR spectrum

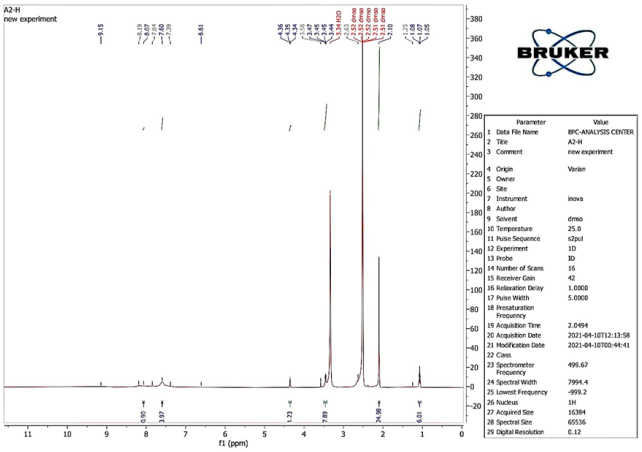


Figure 11: 1H NMR Spectra of Cu(II) complex

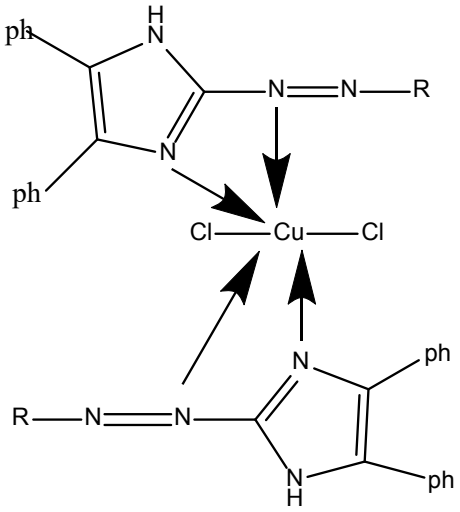


Figure 12: The suggested structures of Cu(II) Comple

Magnetic Resonance Spectrometer

^{1}H NMR Spectra of Cu(II) Complex

The single band at (9.15 ppm) corresponds to one proton of an amine group (NH) in an imidazole cyclic, (2.63 ppm) due to the protons of (CH3), the bands (6.61 – 8.2) ppm belongs to (H-Ar), while the band at (2.5 ppm) related to (DMSO) and (3.34 ppm) belong to moisture. as in Figure 11

The Complex's Suggested Figure

Figure 12 depicts a complex structure based on FT-IR spectra and stoichiometry calculated using the Job and Mole ratio methods.

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