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Synthesis and Analytical Studies of 3-((4-acetyl-3-hydroxyphenyl)diazenyl)-4-amino-N-(pyrimidin-2-yl)benzene sulfonamide with some Metals

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ABSTRACT

Synthesis new organic azo dye as reagent 3-((4-acetyl-3-hydroxyphenyl) diazenyl)-4-amino-N-(pyrimidin-2-yl)benzene sulfonamide (SDA) and Analytical Study of Co(II), Ni(II) and Cu(II), metals complexes .The reagent and its complexes were characterized by elemental analysis, Uv-Vis, FT- IR and molar conductivity measurements. The data show that the complexes have the composition of $[MR]X_2$ type. The conductivity data for all complexes are consistent with those expected for an electrolyte. Octahedral environment is suggested for metal complexes.

Keywords: conductivity data, organic azo dye

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INTRODUCTION

Azo compounds constitute one of the largest classes of industrially synthesized organic compounds, for their widespread applications in many areas of dye-stuff industry, pharmacy and dosimetry due to the presence of azo (-N=N-) linkage 1-3. [1,2] It can simply be defined as any class of artificial dyes that contains the azo group (-N=N-). Describing a dye molecule as nucleophiles will be known as auxochromes, while the aromatic groups are called chromospheres. The dye molecule is often described as a chromogen.[3]Azo compounds are highly colored and have been used as dyes and pigments for a long time. A large number of (N,N′)-donor reagent azo compounds have been prepared in the last years.[4-7] These are the largest group of organic dyes[8,9]. A number of these azo dyes have been used as chelating reagents in addition of the uses as reagents in analytical chemistry[10-14]. The present study reports the preparation, spectral characterization and analytical study of new azo imidazole reagent (SDA) and metal complexes.

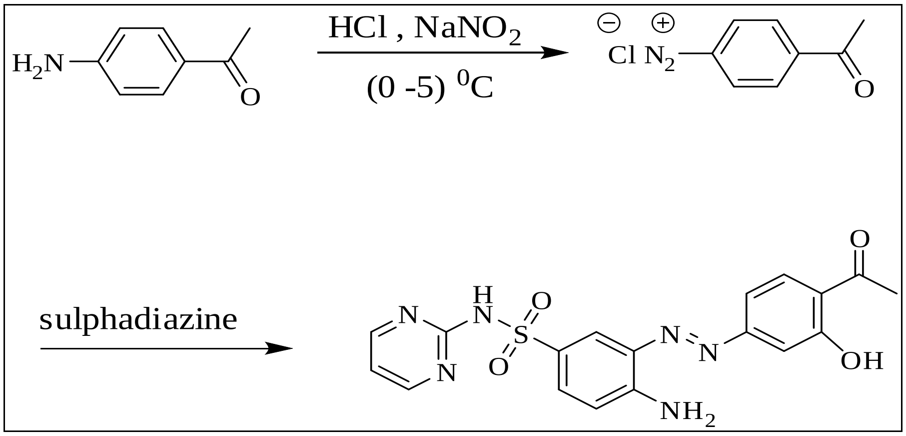
MATERIALS AND METHOD

Apparatus and materials

All reagents and solvents were obtained from Fluka, The Merck and BDH. The melting points were determined on a Electro thermal, melting point 9300. Elemental analyses were carried out by means of Micro analytical unit of 1108 C.H.N.S Elemental analyzer. FT-IR spectra were recorded using KBr discs in the range (4000-400) cm^{-1}on FT-IR teas scan Shimaduz model 8300 . while the UV-Vis. Spectra recorded in ethanol on Shimaduz model 1650PC. Molar conductance measurements were determine in DMF by using a Alpha Digital conductivity meter model 800. pH measurements were carried out using pH-meter Hanna. The metal contents of the complex was measured by using atomic absorption technique by Perkin-Elmer model 2280.

Preparation of the reagent (SDA)

The reagent (SDA)was prepared according to the following general procedure (15,16)4-amino-2-Hydroxy acetophenon (0.01 mol) (1.511 g) was dissolved in (3 ml) concentrated hydrochloric acid and (15 ml) distilled water. The mixture was cooled at (0-5 ^{0}C) in ice-water bath. Then a solution of sodium nitrite (0.01 mol) dissolved in (5 ml) of distilled water was cooled at (0-5 ^{0}C). This solution was added a drop wise to the mixture with stirring at the same temperature. The resulting diazonium chloride solution was mixed with sulphadiazine (2.5 g, 0.01 mol) dissolved in (200 ml) alkaline ethanol cooled below 0°C. After leaving in the refrigerator for 24 hr, the mixture was acidified with dilute hydrochloric acid until pH = 5. The precipitate was filtered off, and recrystallized twice from hot ethanol, and dried in a vacuum desicator.



Preparation of metal complexes

The metal complexes were prepared by the mixing of 50 ml ethanolic solution of ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$) with the 50ml of ethanolic solution of reagent in (1:1) (metal : reagent) ratio. The resulting mixture was refluxed for 2h. Colored product appeared on standing and cooling the a above solution. The precipitated complexes were filtered, washed and recrystallized with ethanol several times and dried over anhydrous $CaCl_2$ in desiccators.

RESULTS AND DISSCUSION

The analytical data for the reagent and complexes together with some physical properties are summarized in Table 1. The analytical data of the complexes correspond well with the general formula $[MR]X_2$ where M= Co(II), Ni(II), and Cu(II), R=(SDA).

Table 1: Analytical data and physical properties of the reagent (SDA) and complexes.

No.	Compound color	m.P ^{o}C	Yield%	Molecular formula	Found (Calc.)%				
					C	H	N	S	M
1	R=(SDA) brwon	223-225	91	$C_{18}H_{16}N_6O_4S$	52.287 (52.42)	3.838 (3.91)	20.025 (20.38)	7.57 (7.77)	-
2	Co-SDA brwon–red	262-264	82	$C_{36}H_{32}N_{12}O_8S_2Cl_2Co$	45.101 (45.39)	3.091 (3.17)	17.469 (17.64)	6.523 (6.73)	5.97 (6.19)
3	Ni-SDA green	186-188	89	$C_{36}H_{32}N_{12}O_8SCl_2Ni$	45.211 (45.40)	3.03 (3.17)	17.512 (17.65)	6.52 (6.73)	6.021 (6.16)
4	Cu-SDA blue	203-205	75	$C_{36}H_{32}N_{12}O_8S_2Cl_2Cu$	44.873 (45.17)	2.98 (3.16)	17.441 (17.56)	6.49 (6.70)	6.28 (6.64)

Absorption spectra

The absorption spectra in aqueous ethanolic solution 50% (V/V) were studied for the prepared complexes showed a bath chromic shift ranging about (84-207)nm. The absorption spectra of reagent (SDA) and Co(II),Ni(II) and Cu(II) chelat complexes is shown in Figure (1-4).

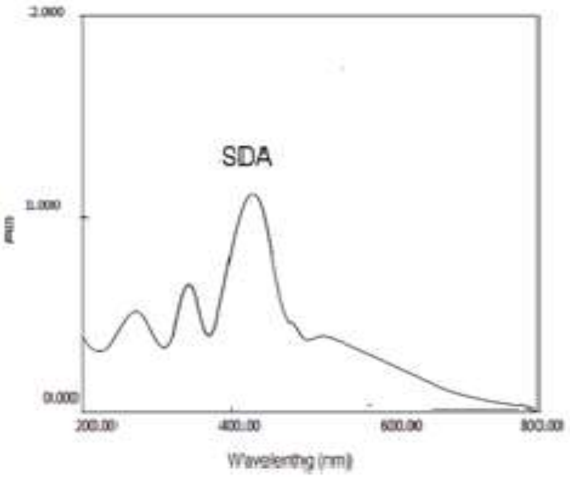


Figure 1: The absorbance spectra of free Reagent (R)

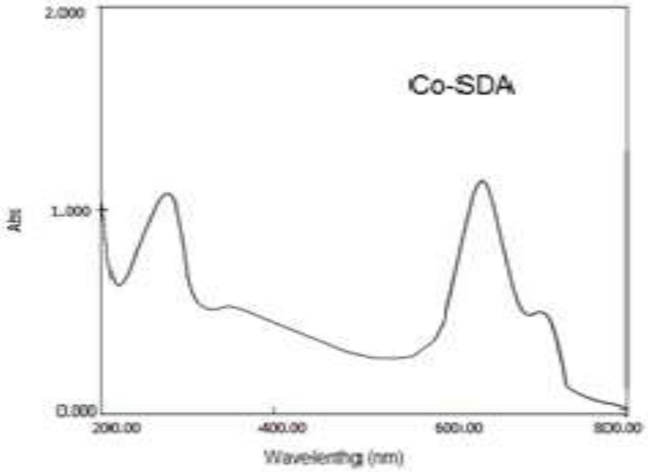


Figure 2: The absorbance spectra of Co(II) complex with(SDA)

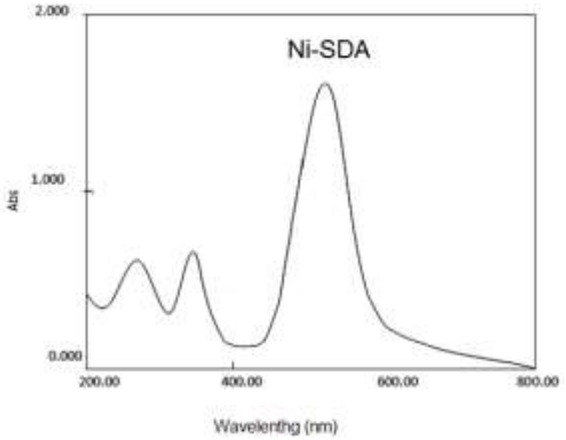


Figure 3: The absorbance spectra of Ni(II) complex with (SDA)

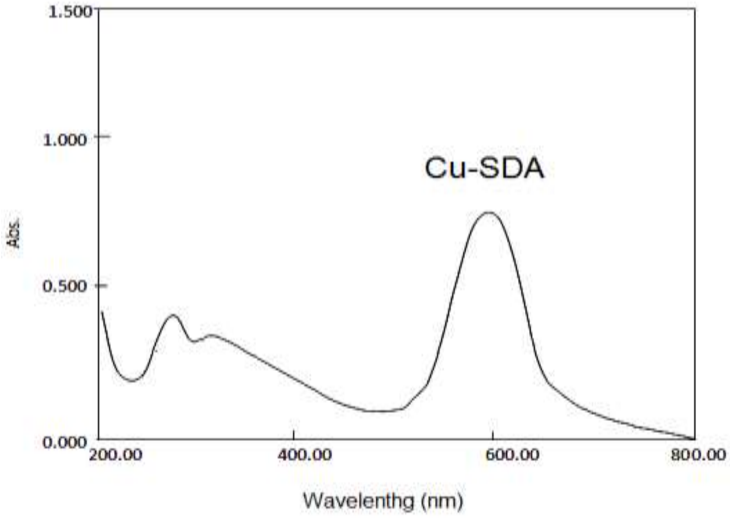


Figure (4:The absorbance spectra of Cu(II) complex with (SDA)

Effect of pH

The effect of acidity of the absorbance values of the complexes was studied in the 50%(v/v) ethanolic by changing the pH value of the solution and the results is shown in Fig (5-7), where demonstrated that the best absorbance of Co(II),Ni(II) and Cu(II) (SDA) system is in the range (6.5-8). The reagent formed a stable complexes with metal ions at same pH.

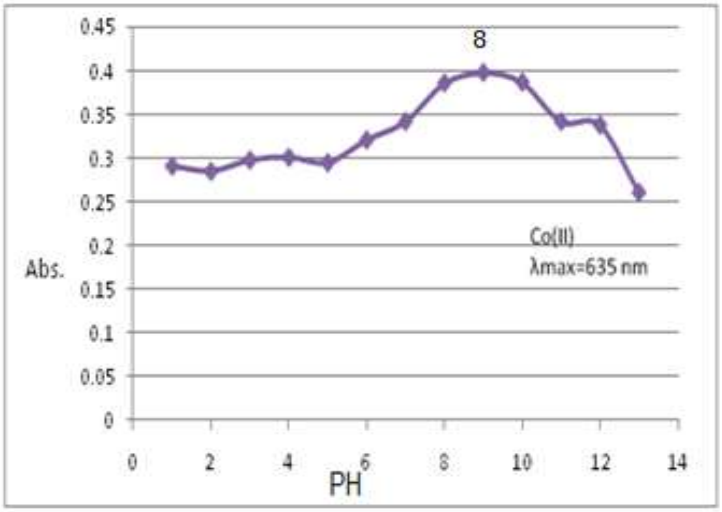


Figure 5: Effect of acidity on Co (II) complex absorbance

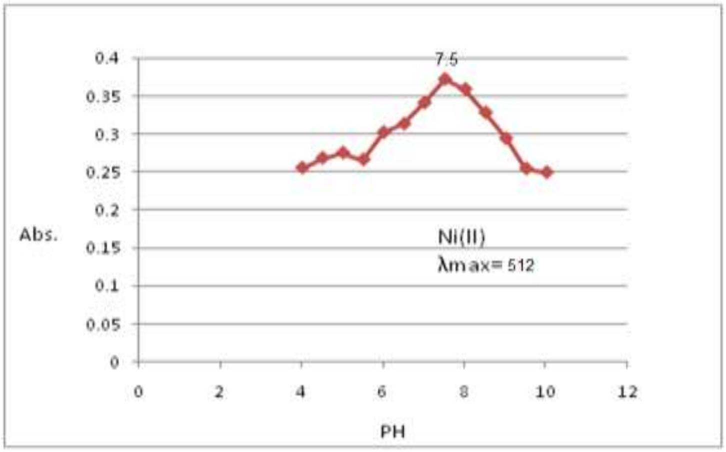


Figure 6: Effect of acidity on Ni(II) complex absorbance

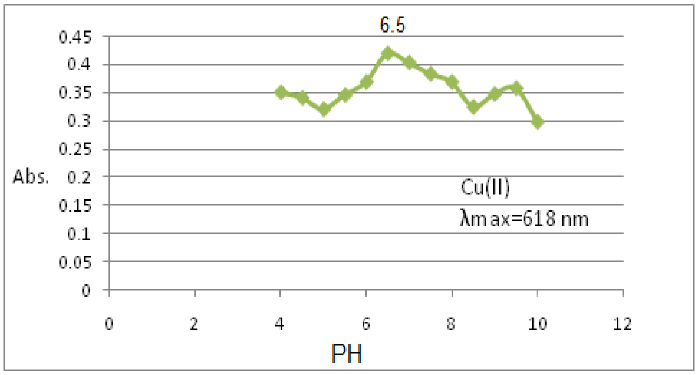


Figure 7: Effect of acidity on Cu (II) complex absorbance

Effect of Time

Also the reaction is complete in 5 min at room temperature and remains stable for about 180 min. This show the reagent (SDA) strong coordination with metal ions in this time. The result are shown in Figure 8.

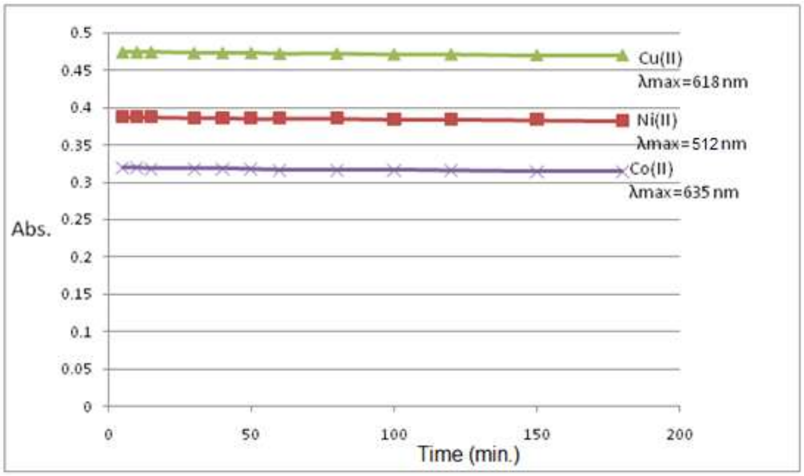


Figure 8: Effect of time on the absorbance of Co (II), Ni (II) and Cu (II) metal complexes at room temp.

Metal :Reagent ratio

The (metal: reagent) ratios of complexes were determined by molar ratio method at fixed concentration and pH at wavelengths of maximum absorption. The results are given in Table 2, the reagent was found to form (2: 1) chelates with all metal ions.

Calculation of the metal complexes stability constant

Stability constants are obtained spectrophotometrically by measuring the absorbance of solutions of ligand and metal mixture at fixed wavelength λmax and pH values. The degree of formation of the complexes is obtained according to the relationship[20], $\beta = (1 - \alpha) / (4\alpha 3c2)$, and $\alpha = (Am - As)/Am$, where As and Am are the absorbance's of the partially and fully formed complex respectively at optimum concentration. The calculated β and Log β values for the prepared complexes are recorded in Table (2).

Table 2: Metal: reagent stability constant value (β), molar conductivity, optimal concentration and wave length

No.	Metal ions color	PH	wave length (λ_{max})nm	molar conc. x 10^{-5} M	B $L^2.mol^{-2}$	log β	Molar conduc. $S.mol^{-1}.cm^2$
1	Co-SDA brwon–red	8	635	1	$683*10^{10}$		66.23
2	Ni-SDA green	7.5	512	3.4	$639*10^{10}$		63.91
3	Cu-SDA blue	6.5	618	5	$983*10^{11}$		69.21

Infrared spectra

In order to clarify the mode of bonding and the effect of the metal ion on the reagent, the FT- IR spectra of the free reagent and the metal complexes were studied and assigned based on carful comparison of their spectra with that of the free reagent. Relevant FT- IR bands for the reagent and metal complexes are presented in Table 3.The bands in the region 3457 cm^{-1} due to stretching mode of ν (OH) and ν (NH_2) groups of the reagent undergo some change in the spectra of the complexes Strong bands at region between1725-1720 cm^{-1} due to ν (C=O) group and 1600-1598 cm^{-1} due to ν (C=N) group of pyrimidine ring which is remains in the same region in free reagent and in complexation. The ν(N═N) stretching vibration appears at 1490 cm^{-1} in the free reagent spectra. This band appearing at 1470 – 1420 cm^{-1} with different in shape and reduced in intensity in the spectra of complexes. Both band shifted and reduced intensity due to complex formation. The spectrum of free reagent show two absorption bands at 1330 and 1170 cm^{-1} due to symmetrical and asymmetrical vibration of ν(O═S═O) group. These bands are stable in position and intensity in both reagent and its metal complexes. New weak bands in the region 465 - 420 cm^{-1} were observed in the spectra of metal complexes. These bands were not present in the spectrum of legend, and they due to ν(M─N).

Table 3: Characteristic IR absorption bands of the reagent (SDA) and its complexes in cm^{-1} units (KBr disk)

No.	Compound	ν (OH) ν (NH_2)	ν (C=O)	ν (C=N)	ν (N=N)	ν (SO_2)	ν (M-N)
1	R=(SDA)	3457	1720	1598	1490	1330 1181	-
2	Co-SDA	3400	1715	1600	1470	1325 1170	465
3	Ni-SDA	3430	1725	1600	1474	1340 1180	450
4	Cu-SDA	3425	1730	1600	1460	1343 1190	421

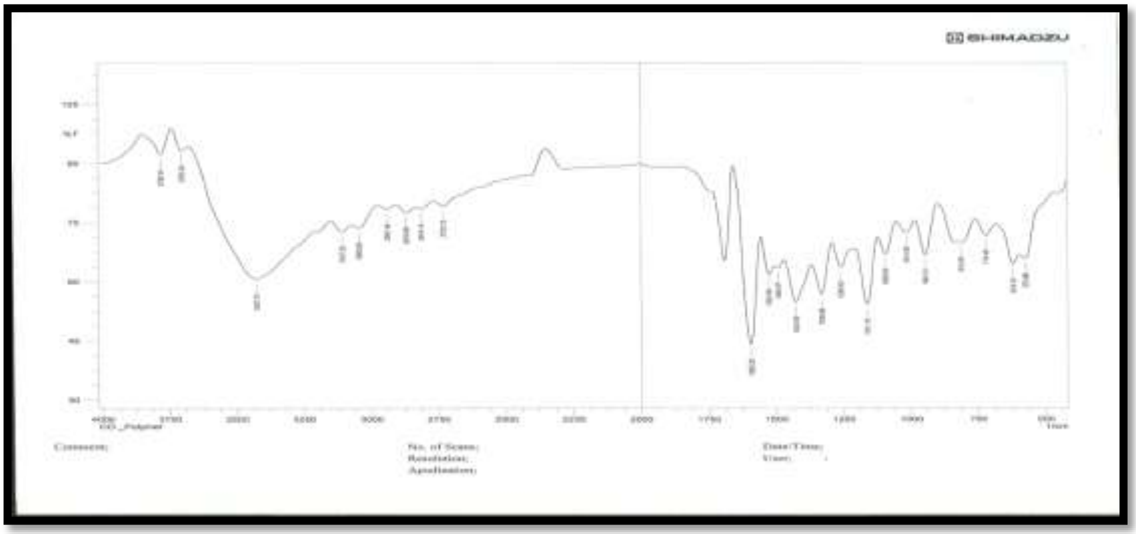


Figure 9: FT-IR Spectrum of (SDA) reagent

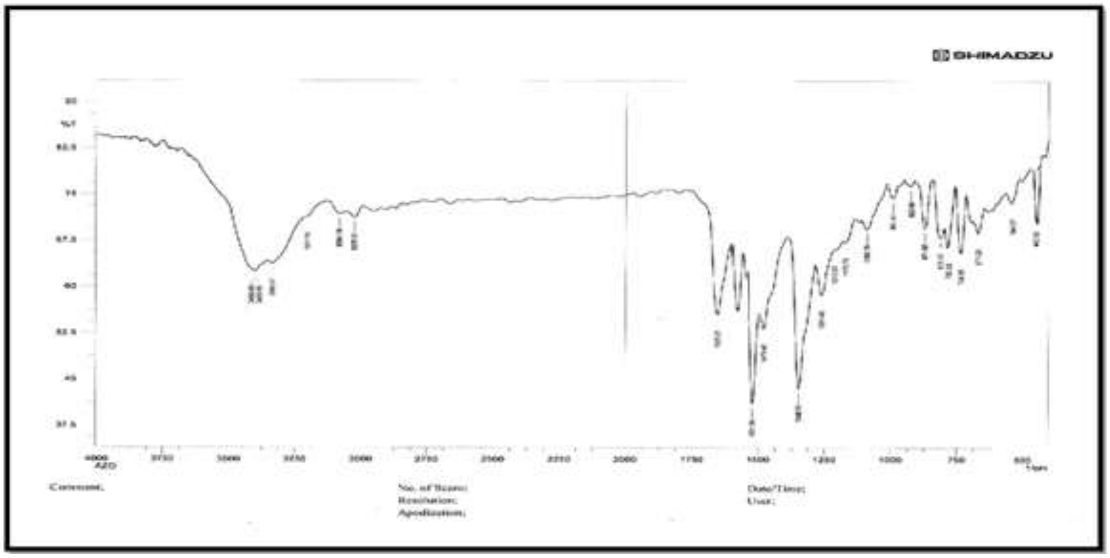


Figure 10: FT-IR Spectrum of Co(II) complex with (SDA) reagent

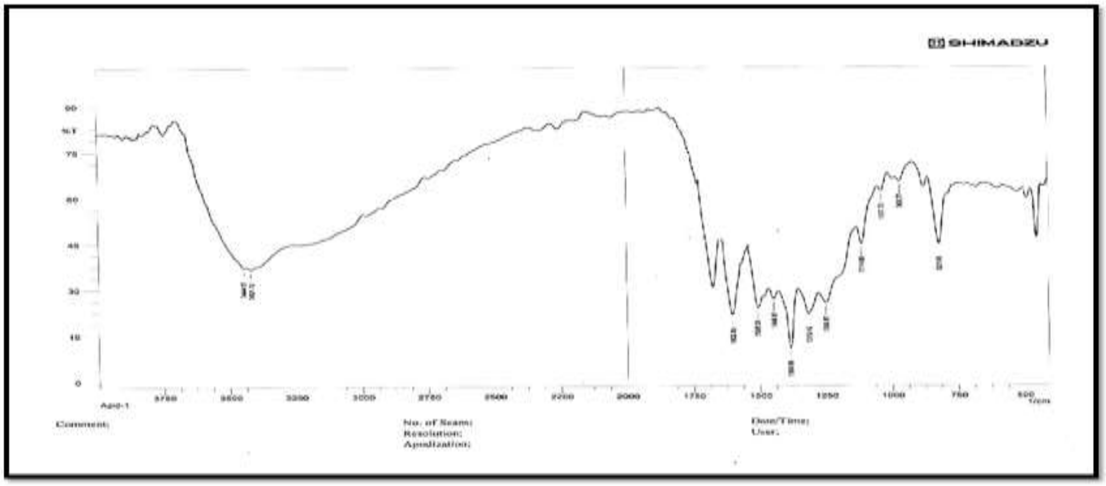


Figure 11: FT-IR Spectrum of Ni(II) complex with (SDA) reagent

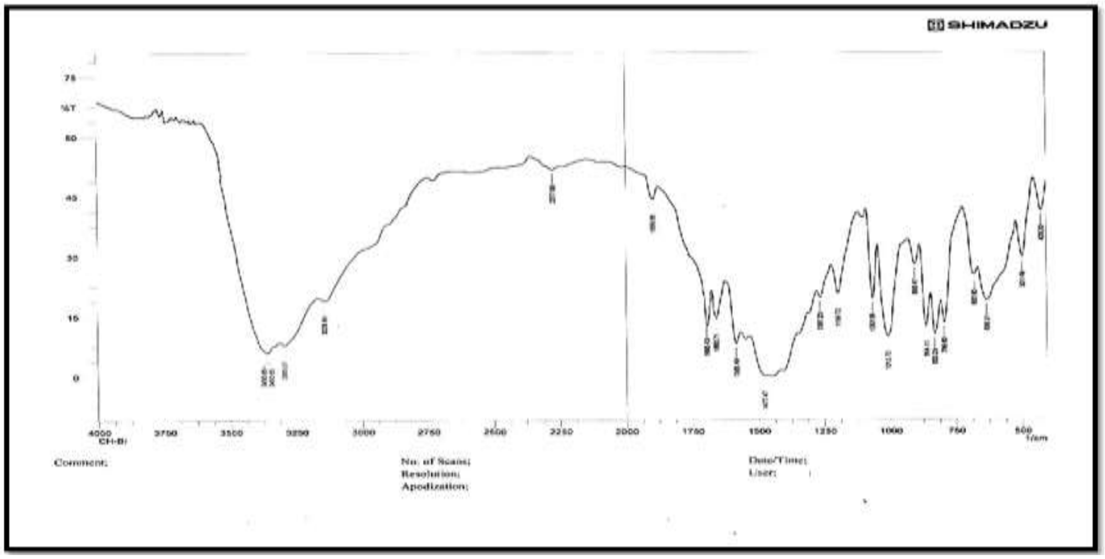
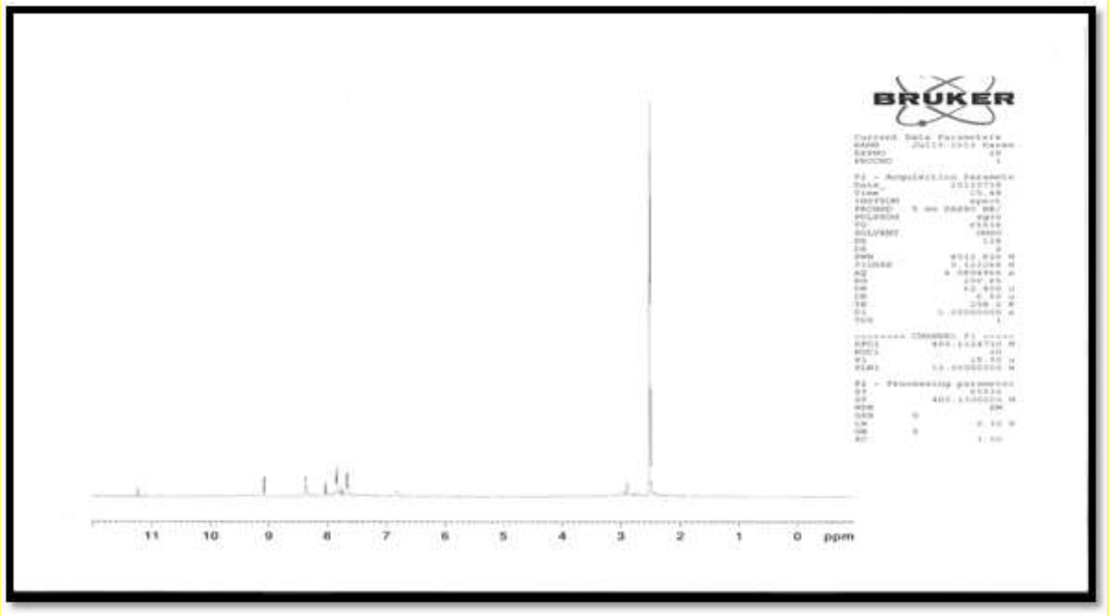


Figure 12: FT-IR Spectrum of Cu(II) complex with (SDA) reagent

((1H), (-NH)$_{\text{sulfonamide}}$ 11.3), ((1H) (OH) $_{\text{phenol}}$ 9.1) , ((10H) (Ar-H)) 6.8-8.5), ((2H) (CO-CH-CH-CO) 2.8).



CONCLUSION

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In this present study we report the preparation characterization and spectroscopy study of new azo reagent derived from imidazole and its complex with Cu(II) metal ion. The isolated complex was characterized by available techniques. The aryl azo reagent (PADDPI) behaves as a bidentate chelating agent and coordinating through the N_3 atom of imidazole and another nitrogen atom of azo group which is the farthest of imidazole ring to form five-memberd metalo ring. The coordination of the metal ion Cu(II) with reagent(PADDPI) are to give hexa coordinated show octahedral stereochemistry.

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