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### Synthesis and Analytical Studies of 3-((4-acetyl-3-hydroxyphenyl) diazenyl)-4-amino-N-(5-methylisoxazol-3-yl)benzene sulfonamide. with some Metals

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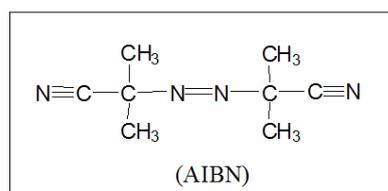
new azo compound ; analytical studies  
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#### ABSTRACT

Synthesis new organic azo dye as reagent 3-((4-acetyl-3-hydroxy phenyl) diazenyl)-4-amino-N-(5-methylisoxazol-3-yl)benzene sulfonamide (SDA) and Analytical Study of Co(II), Ni(II) and Cu(II), the preparation characterization and spectroscopy study of new azo reagent derived from imidazole and its complex with Cu(II) metal ion. The aryl azo reagent (SDA) behaves as a bidentate chelating agent and coordinating through the N<sub>2</sub> atom of imidazole and another nitrogen atom of azo group which is the farthest of imidazole ring to form five-member metallo ring. And oxygen atom for cobalt and nickel complexes. The coordination of the metal ion Cu(II) with reagent(SDA) are to give hexa coordinated show octahedral stereochemistry metals complexes. The reagent and its complexes were characterized by elemental analysis, UV-Vis, and molar conductivity measurements. The data show that the complexes have the composition of [MR]X<sub>2</sub> type. The conductivity data for all complexes are consistent with those expected for an electrolyte. Octahedral environment is suggested for metal complexes.

#### INTRODUCTION

Azo compounds are compounds bearing the functional group (R–N=N–R\*), in which R and R\* can be either alkyl or aryl (Rathod and Thaker,2013). Aryl azo compounds are more stable than alkyl azo compounds (R and R\* aliphatic) (Marmion,1999). One example is diethyldiazene(Et–N=N–Et). At elevated temperatures, the carbon - nitrogen (C–N) bonds in certain alkyl azo compounds cleave with loss of nitrogen gas to generate radicals like azo bisisobutyl nitrile (AIBN)( Bassam,2015)



Aryl azo compounds are stable and have a broad range of colors (Mathur, Ray and others,2005) including yellow, orange, red, brown, and blue. The colors differences are caused by different substituents on the aromatic rings which lead to differences in the extent of conjugation of the  $\Pi$ -system in the azo compound. In general, the less extensive the conjugated  $\Pi$ -system of a molecule, the shorter the wavelength of visible light it will absorb as shown below:

Colorless → yellow → orange → red → green → blue

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(Shortest wavelength) (Longest wavelength)

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 dissymmetry due to the presence of azo (-N=N-) linkage 1-3(Rathod and Thaker,2013).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(Bassam,2015) .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(Mathur, Ray and others,2005).These are the largest group of organic dyes(Enedoh,2015). A number of these azo dyes have been used as chelating reagents in addition of the uses as reagents in analytical chemistry(El-Shobaky and El-Bindary,2013).The present study reports the preparation, spectral characterization and analytical study of new azo reagent (SDA) and metal complexes. Synthesis of most azo dyes involves diazotization of a primary aromatic amines, followed by coupling with one or more nucleophiles. Amino and hydroxyl-groups that are commonly used coupling components (Dinda, Mustafa and others ,2013) .

Azo compounds are important structures in the medicinal and pharmaceutical fields. Furthermore, azo dye compounds also have a lot of applications in industry and photodynamic therapy as well as photosensitive species in photographic or electro photographic systems and they are dominant organic photoconductive materials (Hihara,Okada and others,2007)

### Experimental:

#### Apparatus and materials:

All reagents and solvents were obtained from Fluke, 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. while the UV-Vis. Spectra recorded in ethanol on Shimaduz model 1650PC. Molar conductance measurements were determined in DMF by using a Alpha Digital conductivity meter model 800. pH measurements were carried out using pH-meter Hanna. The metal content 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 (Skeltonm, Dubois and others,2007),(Steter,Pontólio and others,2008), (Ofomaja and Ho,2007) 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 °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 °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 Sulfamethoxazole (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 re crystallized twice from hot ethanol, and dried in a vacuum desiccator. And shown in the following scheme in figure (1).

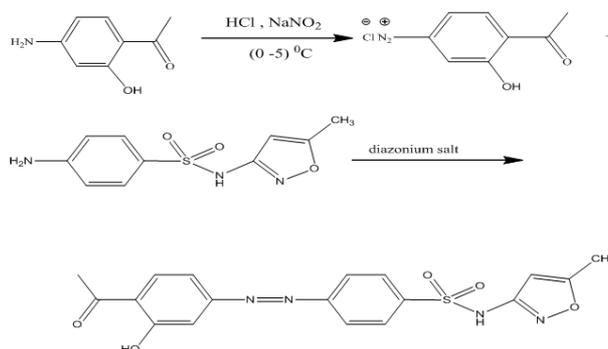


Fig. 1: scheme of the azo - coupling reaction.

#### Preparation of metal complexes(Salwinska,2009):-

The metal complexes were prepared by the mixing of 50 ml ethanolic solution of (CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O and CuCl<sub>2</sub>.2H<sub>2</sub>O) 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 re crystallized with ethanol several times and dried over anhydrous  $\text{CaCl}_2$  in desiccators.

## RESULTS AND DISCUSSION

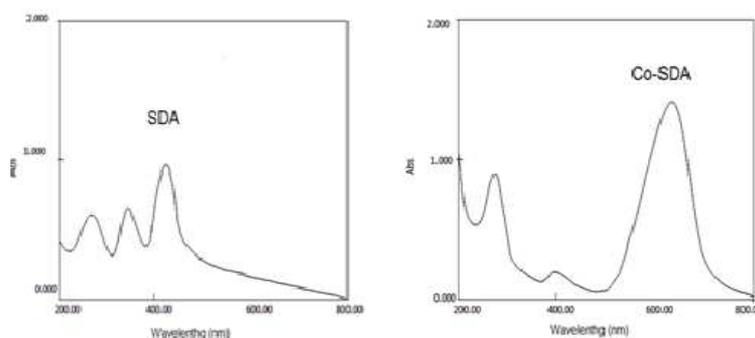
The analytical data for the reagent and complexes together with some physical properties are summarized in Table 1. The analytical data of the complexes correspond well with the general formula  $[\text{MR}]X_2$  where  $\text{M} = \text{Co(II)}$ ,  $\text{Ni(II)}$ , and  $\text{Cu(II)}$ ,  $\text{R}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

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

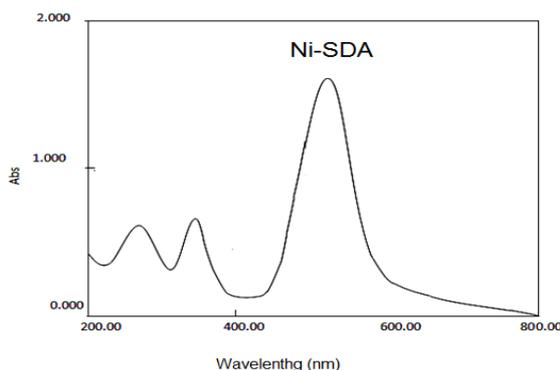
No.	Compound color	m.P °C	Yield%	Molecular formula	Found (Calc.)%				
					C	H	N	S	M
1	R=(SDA) brwon	250-255	91	$\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_5\text{S}$	52.287 (52.42)	3.838 (3.91)	20.025 (20.38)	7.57 (7.77)	-
2	Co-SDA brwon-red	272-264	82	$\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_5\text{S}$ $\text{Cl}_2\text{Co}$	45.101 (45.39)	3.091 (3.17)	17.469 (17.64)	6.523 (6.73)	5.97 (6.19)
3	Ni-SDA green	206-218	89	$\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_5\text{S}$ $\text{Cl}_2\text{Ni}$	45.211 (45.40)	3.03 (3.17)	17.512 (17.65)	6.52 (6.73)	6.021 (6.16)
4	Cu-SDA blue	223-211	75	$\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_5\text{S}$ $\text{Cl}_2\text{Cu}$	44.873 (45.17)	2.98 (3.16)	17.441 (17.56)	6.49 (6.70)	6.28 (6.64)

### Absorption spectra (Das and sinha, 1998):

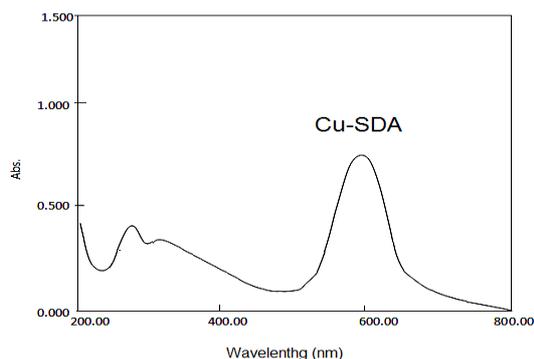
The absorption spectra in aqueous ethanolic solution 50% (V/V) were studied for the prepared complexes showed a bath chromic shift ranging about (84-207)nm. The absorption spectra of reagent (SDA) and  $\text{Co(II)}$ ,  $\text{Ni(II)}$  and  $\text{Cu(II)}$  chelat complexes is shown in Fig (1-4).



**Fig. 2:** The absorbance spectra of free Reagent (R). The absorbance spectra of  $\text{Co(II)}$  complex with (SDA)



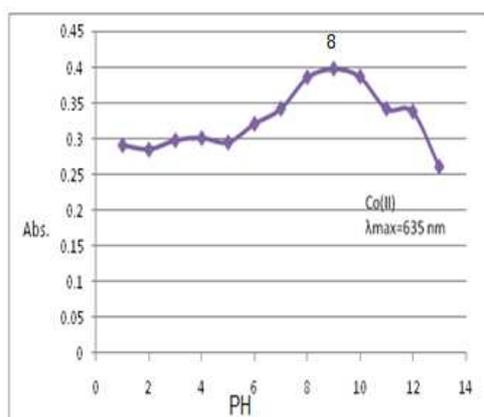
**Fig. 3:** The absorbance spectra of  $\text{Ni(II)}$  complex with (SDA).



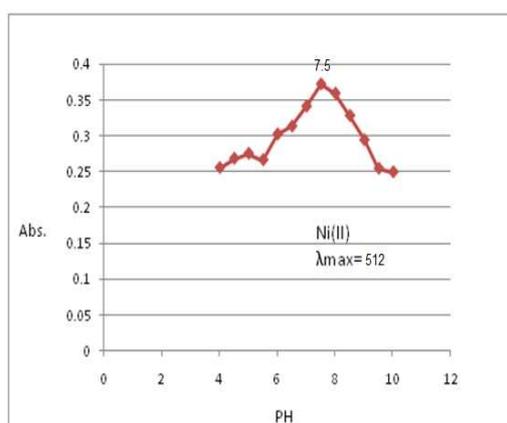
**Fig. 4:** The absorbance spectra of Cu(II) complex with (SDA).

**Effect of pH (Ray, Banerjee and others, 2003):**

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 stable complexes with metal ions at same pH.



**Fig. 5:** Effect of acidity on Co(II) complex absorbance .



**Fig. 6:** Effect of acidity on Ni(II) complex absorbance.

**Effect of Time (Salwinska, 2009):-**

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

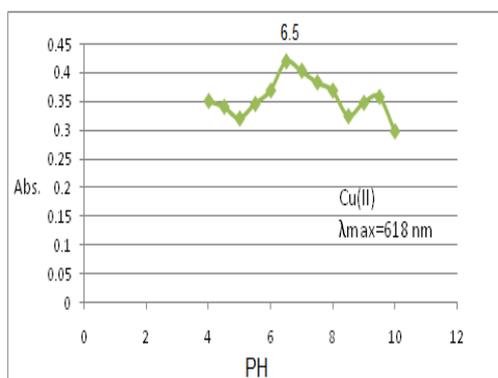


Fig. 7: Effect of acidity on Cu(II) complex absorbance.

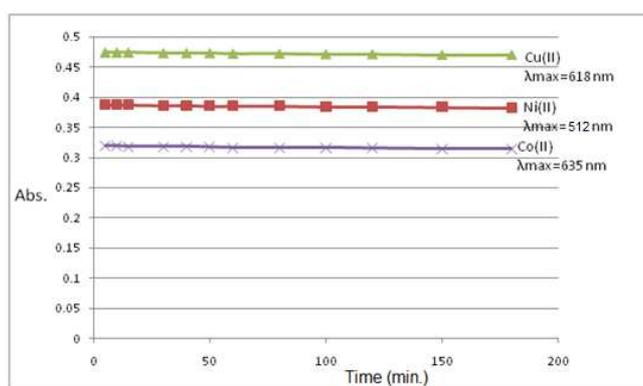


Fig. 8: Effect of time on the absorbance of Co(II), Ni(II) and Cu(II) metal complexes at room temp.

**Metal: Reagent ratio (Shibata, Furukawa and others, 2006):-**

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 (Gung and Taylor, 2004)

Stability constants are obtained spectrophotometrically by measuring the absorbance of solutions of ligand and metal mixture at fixed wavelength  $\lambda_{max}$  and pH values. The degree of formation of the complexes is obtained according to the relationship,  $\beta = (1 - \alpha) / (4\alpha^3c^2)$ , and  $\alpha = (A_m - A_s) / A_m$ , where  $A_s$  and  $A_m$  are the absorbance's of the partially and fully formed complex respectively at optimum concentration. The calculated  $\beta$  and Log  $\beta$  values for the prepared complexes are recorded in Table (2).

**Table 2:** Metal :reagent stability constant value ( $\beta$ ), molar conductivity, optimal concentration and wave length.

No.	Metal ions color	pH	wave length ( $\lambda_{max}$ ) nm	molar conc. $\times 10^{-5}$ M	$\beta$ $L^2 \cdot mol^{-2}$	log $\beta$	Molar conduc. $S \cdot mol^{-1} \cdot cm^2$
1	Co-SDA brwon-red	8	625	1	$6.83 \times 10^{10}$	10.83	66.23
2	Ni-SDA green	7.5	510	3.4	$6.39 \times 10^{10}$	10.80	63.91
3	Cu-SDA blue	6.5	608	5	$9.83 \times 10^{11}$	11.99	69.21

**Conclusions:**

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 (SDA) behaves as a bidentate chelating agent and coordinating through the  $N_2$  atom of imidazole and another nitrogen atom of azo group which is the farthest of imidazole ring to form five-member metallo ring. And oxygen atom for cobalt and nickel complexes. The coordination of the metal ion Cu(II) with reagent(SDA) are to give hexa coordinated show octahedral stereochemistry.

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