Synthesis, characterization and analytical study of new azo ligand driven from benzocaine and its metal complexes

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Abstract.

The synthesis and spectrum of of a new azo ligand derived from acetylacetone and benzocaine (Ethyl p-aminobenzoate)). Spectral investigations such as 1H NMR,FT.IR, 13C-NMR and Mass spectra were performed to investigate the azo dye ligand's structure. Several physiochemical approaches, FT-IR, electronic spectra, molar conductivity, atom absorption, and magnetic susceptibility were used to identify new complexes with CO(II), and Zn(II) ions Complexes that are all 1:2 [M:L] were formed using the procedures described, and an tetrahedral geometry with sp3 hybridization. At several pH ranges (2–12), the electronic spectra of these azo dyes have been examined in terms of their acid–base properties, which included determining their isosbestic points and protonation and ionization constants. In the other study, azodye were used as an inductor for acid-base titration.

Key word – azodyes, benzocaine, complexes, acid-base indicator and analytical study

Introduction

The most significant synthetic colorants, azo dyes are used extensively in the production of textiles, paper, and other materials. [1]. Due to its versatility in both colorant and non-colorant applications, such as textile dyeing, food coloring, printing, dye-sensitized solar cells, and optical storage systems, azo dyes have a wide variety of uses [2], azo dyes can be employed in pharmaceutical applications since they have demonstrated a high potential to be antimicrobial agents, including antibacterial, antifungal, and anticancer agents [3,4]. The potent bioactivities of azo dyes and their derivatives, including their antibacterial, antifungal, antiviral, anticonvulsant, antidiabetic, anti-inflammatory, antitubercular, anticancer DNA binding, analgesic characteristics, and chemo sensing activities, have attracted particular interest. [5-8].

Many acetylacetone Azo dyes were created [9-12] including luminol and procaine Were synthesized and reacted with Cu and Ni, forms of metals (II) complexes CuL2, and NiL2 complexes, [13]. Azo dyes have a wide range of applications in biological systems and as indicators in spectrophotometric titrations in analytical chemistry. [14,15]. As acid-base indicators, aromatic azo compounds in particular are utilized. Changes in the degree of electron delocalization cause differences in color. In the presence of more delocalization, the absorption maximum shifts to longer wave lengths, making the absorbed light redder, while in the absence of more delocalization, the absorption maximum shifts to shorter wave lengths, making the absorbed light bluer. [16]

The current study involves the synthesis of a new azodye produced from acetylacetone and benzocaine (Ethyl p-aminobenzoate) and characterized by FT-IR.,1H-NMR,13C-NMR, and Mass spectra .Spectrophotometric research on the dye have been conducted, covering acid-base properties at various pH values, the dye's ability to be used as an acid-base indicator, and its complex with Zn (II) and Co (II). , azodye was tested as an inductor for acid-base titration.

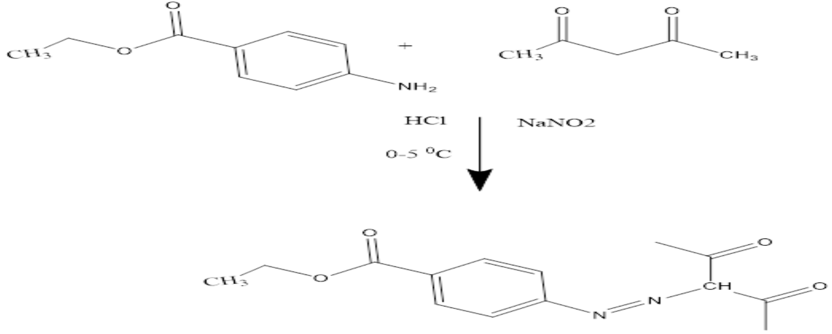
Experimental

Spectral solvents, double-distilled water, and only the purest compounds were employed.

Using a silica gel-coated plate, TLC was used to track the reaction's progress, and spots were evident when exposed to UV lig. Shimadzu FT.IR-8400S infrared spectra (in KBr pellets) were recorded. A melting point apparatus was used to determine melting points. pH-meter (H. Jurgons Co. Bremen, L.Puls Munchen15) was used to measure the pH.

Preparation of azodye A [17]

The azodye reagent (A) was made by combining 0.02 mole of diazonium salt of Ethyl p-aminobenzoate with an alkaline solution of 0.02 mole of acetylacetone at 0o C, then converting the ligand from sodium salt into hydrogen form with a solution of diluteHCl. Recrystallization from aqueous methanol was employed for purifying the dye. Thin layer chromatography and melting point analysis were used to check the purity of the produced dye. Scheme -1 shows the proposed molecular structures of azo compound.



Scheme -1-the proposed structures of prepare azodye A

The preparation of azo complexes

The reaction was performed by dissolving (0.002mole) of the ligand (L) in 50ml Ethanol with (0.001 mole) of metal salts of $CoCl_2.6H_2O$, $Zncl_2$ at molar ratios of 1:2 [metal: Ligand]. This metal chlorides were dissolved in 50 ml of methanol and refluxed with stirring for 30 minutes. A colorful precipitate formed at room temperature, and the particles were filtered and washed multiple times with distilled water. The chelate complexes were recrystallized from ethanol, dried in an oven at 70°C for several hours before being dried in the air for a period of time. .

Solutions

1- 1 x 10-3M each of the azo dye L

2- pH(2-13) universal buffer solution [18]

3- Buffer solutions of pH 7 ($Na_2HPO_4.2H_2O$ + KH_2PO_4 , hexamine , KH_2PO_4+ NaOH , KH_2PO_4+ borax , $Na_2HPO_4.2H_2O$ + citric acid.)

Acid-base aspects during different pH values

Using universal buffer, For a total dye concentration of 8 x 10-5 M (for A1), a series of buffer solutions with varying pH values (2–12) were made.. The absorbance of these solutions was measured at (350 - 660 nm.) using the pH value as a blank solution. The constants were determined using the half height method.

Discussion

The new azo ligand and its complexes are soluble in DMF, DMSO, methanol, ethanol, and acetone and stable at room temperature air The metal complexes were found using analytical data [1:2]. metal: ligand, the Physical properties, conductivity and magnetic properties of ligand and its complexes are show in table-1

Table-1- : Physical properties, conductivity and magnetic properties of ligand and its complexes.

Chemical formula	**M.P C**	**Colour**	**Yelid %**	**M Found (cal.) %**	**conductivity Λ ohm-1 cm^2mol-1**	**μeff (B.M)**
A	**190**	**yellow**	**73**	**-**	**-**	**-**
Zn(A)2	**235**	**Brown**	**68**	**(10.90) 10.56**	**18**	**di**
Co(A)2	**240**	**Red-brown**	**75**	**10.03 (9.53)**	**17**	**4.2**

IR Spectra

The most important ligand and complexes-related IR absorption bands are shown in Table (2). The detected band in the 1425 cm-1 range is attributable to the ligand's v (N=N) group. These bands are moved to a higher area during complex formation, indicating that they are involved in coordination with the metal ions. The sharp band in the range 1604-1 is caused by v (C=C) (fig -1). The strong band was observed in the 1622 cm-1 range. The emergence of these bands suggests that -OH and N=N groups are involved in the formation of novel azo ligand complexes. Some bands in the 490-511 and 590-611 cm-1 ranges have been attributed to the (M-O) and (M-N) vibrations, which are absent in the free ligand.[19]

Table-2. The significant infrared peaks of A and its complexes

Comp.	**ν(N-H) cm-1**	**ν(N=N) cm-1**	**υ(C =C)cm-1**	**ν(C=O)**	**υ(M–O)**	**υ(M–N)**
A	**3423**	**1425.40**	**1604.7**	**1676.14**		
[Zn(A)2]	**3664**	**1427.32**	**1606**	**1674**	**511**	**611.43**
[Co(A)2]	**3419**	**1442.75**	**1602**	**1676.14**	**490**	**590**

1H NMR Spectra

The azo ligand and Zn (II) complex 1H NMR spectra in DMSO-d6 were obtained.Fig (1 and 2) show 1H NMR spectra of the azo ligand and Zn complex .
At 13.58 ppm, a singlet peak of the phenolic-OH group is observed [11]. The peaks range of (6.52-8.06(m,4H,Ar-H)) ppm is where the aromatic ring protons are found. In the azo ligand's spectral range, The -OCH3 protons are accountable for the singlet at 3.74 parts per million. [12]. a peak at 2.5 ppm related to the DMSO solvent and a strong peak at 3.3 ppm attributed to water that has dissolved in the solvent. The signal was given at (2.06 ppm)due to the (CH3) [20,21].

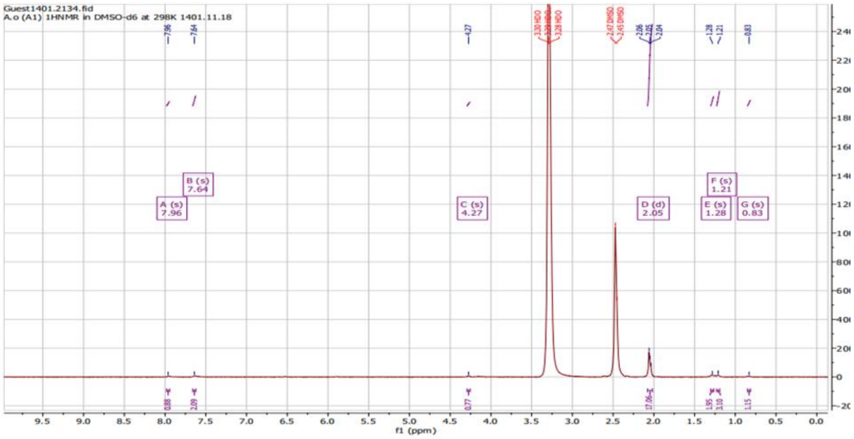


Fig 11H NMR spectrum of azo ligand .

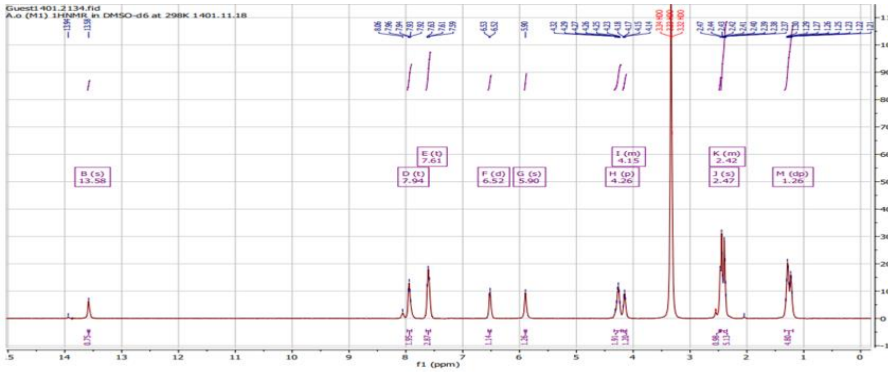


Fig 2. 1H NMR spectrum of Zn (II) complex .

Mass spectra

Figure 3-5shows mass spectra of the new azo ligand and its complex .The molecular ion at 276 and the base peak of the azo ligand at m/e+= 120 have a peak center at m/z = 341 due to the formula [Zn(A)]+, and table 4 displays the significant fragments of the ligand and its complex.[22]

Table 4-Slective mass fragments of compounds

Molcular Formula		m/z
A Ligand	$\{C_{14}H_{17}N_2O_4\}^+$	276
	$\{C_{12}H_{12}N\ O_3\}^+$	231
	$\{C_{10}H_{10}N_2O_2\}^+$	291
	$\{C_7H_4N\,O]+$	120
Zn complex	$[Zn(A)]^{+.}$	341
	$[Zn(C_{12}H_{14}N_2O_4)]+.$	301
	$[C_{14}H_{15}N_2O_2]]+.$	258
Co complex	$[Co(A)]+.$	335
	$[C_{14}H_{17}N_2O_4]$	276

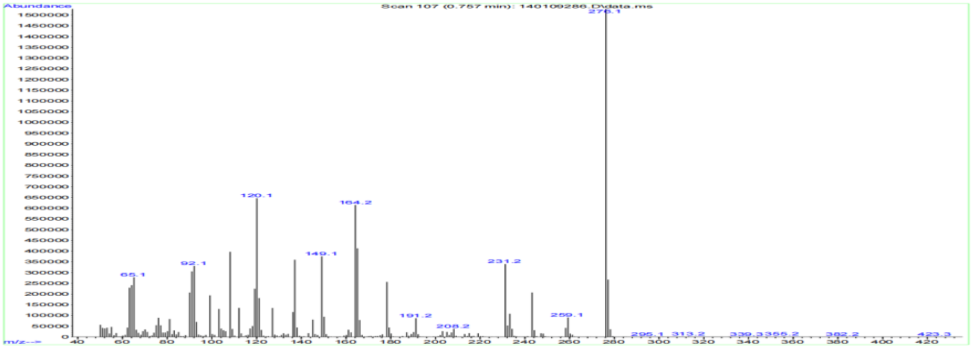


Fig3 .Mass spectra of azo ligand

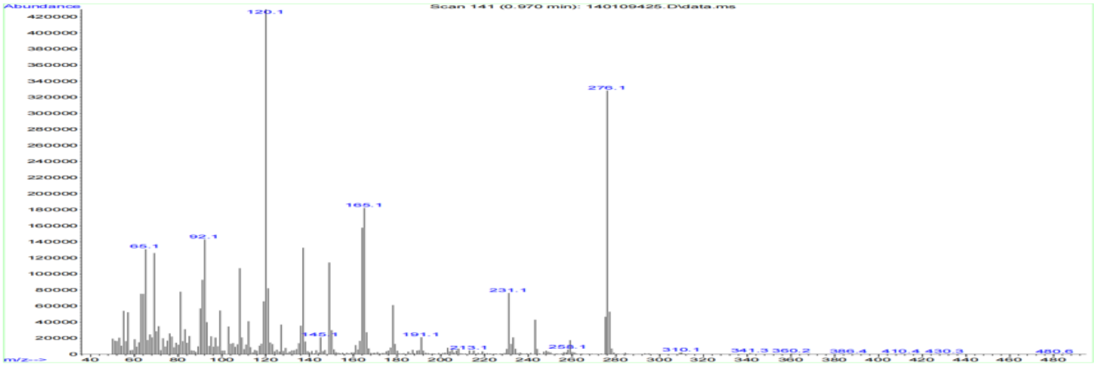


Fig 4. Mass spectra of Zn complex

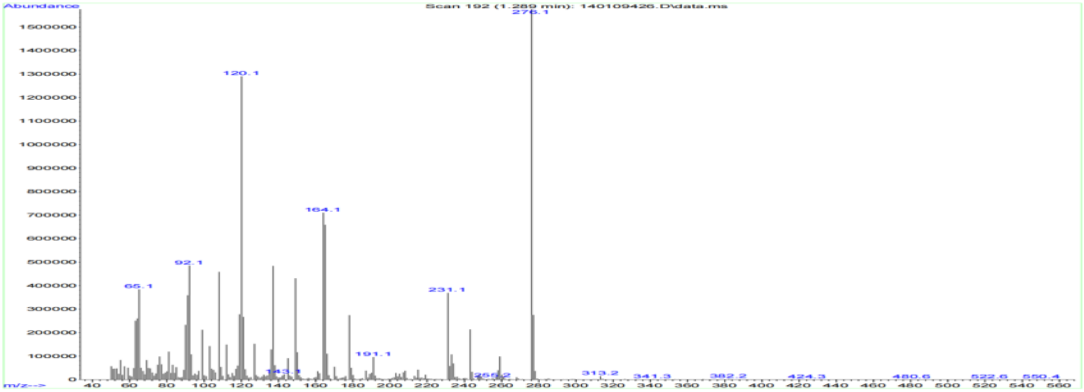


Fig 5. Mass spectra of Co complex

Structural interpretation

In order to further identify prepared complexes with regard to their ionic character, it was crucial to evaluate the molar conductivity of complex solutions using DMF as the solvent. The results show molar conductivity, proving that these compounds are not electrolytic. (table -1) [23]

Cobalt complex magnetic moment was discovered on 4.2 B.M., who was very near the tetrahedral environment.[24]

Acid-Base properties

The absorption spectra of 10-3 M dye solutions varying in pH values (2- 12) were represented graphically (Fig. 6). Three bands made up the spectra, the first of which was at 340 nm and was caused by dye protonation to be in the pH range of (3–8).The second and third bands (360 and 390 nm), which are of considerable intensity (8–12), are present in the pH range.The spectrum also showed an isobestic point at 400 nm (a wavelength with constant absorbance regardless of changes in the medium's pH value) at pH 3.The wavelength, 360nm, is used to calculate the protonation and ionization constants of azo dye. is used as the ideal wavelength to plot a pH curve as an x-axis with appropriate absorbance (Figure

5).The ionization of dyes in acidic and basic media is the process that creates the three isobestic points. The pk values of ionization and protonation, as well as the pka values of ionization and the pkp protonation constant, were determined from the absorbance vs pH and the from half height method(fig-8)and table (5) [17,25].

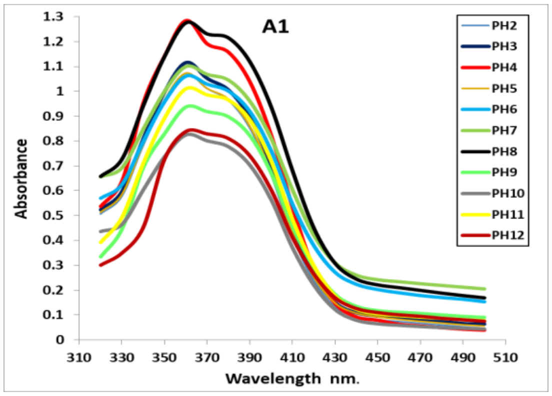


Fig-6. Absorption spectraof azodys A at different pH

Table-5-The protonation and ionization constants of azodys A

A at λ360 nm	A min	AL	A1/2	pKp	Amin	AL	A1/2	pKa1	Amin	AL	A1/2	pKa2
	1.07	1.29	1.18	3.41	1.05	1.29	1.17	7.42	0.83	1.01	0.92	10.52

P = protonation, a=ionization
Pkp = protonation constant for of azodys
pKa1 = ionization constant of azodys
pKa2= the second ionization constant

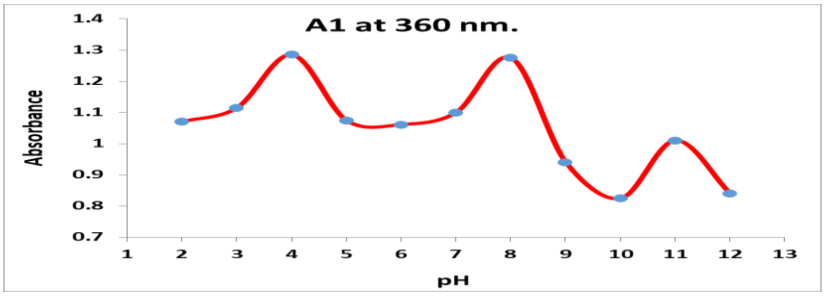


Fig 8 -The absorbance-pH curve of A

Beers Law

We investigated the linearity and sensitivity of Beer's law for azo dyes A at pH 7.. The maximum wavelength's molar absorptivity coefficient (max), Sandell sensitivity (S), specific absorptivity (a), and correlation coefficient (R2) were determined from the calibration curve. [24]. In addition, the Detection Limit (DL) and Standard Deviation (S.D.) were calculated.

Table (8) shows that good results for sensitivity, accuracy, and linearity were obtained.

Table 8-application of Beer's law

Dye	Limite of beer law ppm	DL x10-5 µg.ml	S.D	A ml.g-1.cm2	S	ε L.mol^{-1}.cm^{-1} x10^{4}	R^2
A	13.32	2.32	0.0071	0.0637	0.0157	0.4396	0.9793

Azodye (A) as titration indicator.[26]

Since azo dyes have different and unique colors in acidic or basic solutions, the ability of the produced azo compounds to function as acid-base indicator was examined. Azo dyes displayed reversible and abrupt color changes when transitioning from an acidic condition to a basic condition or vice versa. Azo dyes had a stable color in acid and base solutions. Using hydrochloric acid solution, titration was carried out against a NaOH solution. We added (0.5-3.0 ml) of solution (A) to the 8 mL of HCI solution. After that, the solution was titrated with a standard 0.1054N NaOH solution until the color changed. Tables-(9),fig (9&10) comprise titrations data of acid-base reactions that are used to assess the indicator property of azo dye and color change of the indicator with altering PH, the phenolphthalein indicators used as comparison indicators underwent the same processing.

Fig 9. Color change of solution of azodys A at various buffer solution with pH 2–12

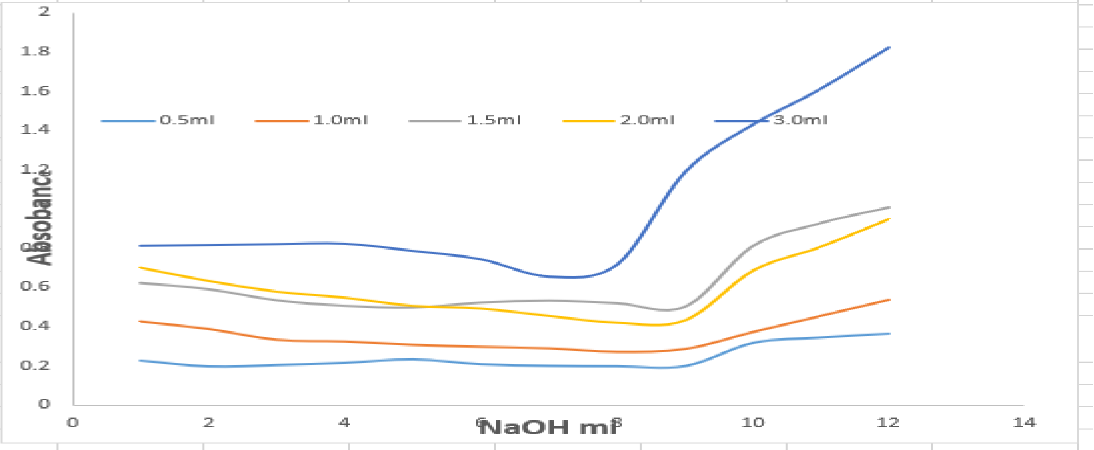


Fig-10. Spectophotmetric titration curves of NaOH with HCl solution using azodye A as titration indicator

Table -9. Results of NaOH titration with HCl solution using azodye A as titration indicator

dye	acid	ml. NaOH at E.P.	Standard concn. of NaOH N	concn. of NaOH N found	RE %	V. of dye	Jump
A1	8ml 0.111N HCl X NaOH	8.50	0.1054	0.1044	-0.94	0.5	Weak
		8.20	0.1054	0.1082	2.65	1.0	Medium
		8.70	0.1054	0.1020	-3.2	1.5	Strong
		8.25	0.1054	0.1076	2.08	2.0	Strong
		8.55	0.1054	0.1038	-1.5	3.0	strong

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