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Spectroscopic Studies of 1,4-bis(4-dimethylaminobenzyl)-2,3-diaza-1,3-butadiene as Colorimetric Reagent for Cu^{2+}

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Abstract: A chromogenic Schiff base ligand 1,4-bis(4-dimethylaminobenzyl)-2,3-diaza-1,3-butadiene (BDABD), has been synthesized and characterized by CHN elemental analysis, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. Experimental parameters that effect the ligand-metal ion complexation such as solvent, color stability, metal and ligand concentrations were investigated. Results show that BDABD is preferentially bind to Cu^{2+} in acetone. The addition of Cu^{2+} to the ligand in acetone gives rise to a large bathochromic shift, resulting in a change of color from yellow to orange. The reaction is instantaneous and the absorbance for more than 24 hr. From the linear regression analysis, Beer's law was obeyed over 1.0 - 8.0 × 10^{-6} M Cu^{2+}. The stoichiometric study shows that Cu^{2+} and BDABD combine in the mole ratio of 1:1 with the formation constant equals to 1.44 × 10^{7}. The average molar absorptivity and Sandell sensitivity were found to be 6.97 × 10^{4} L $mol^{-1}cm^{-1}$ and 0.0009 μg cm^{-2}, respectively.

Keywords: Hydrazone · Schiff base · Chromogenic · Copper · 1,4-bis(4-dimethylaminobenzyl)-2,3-diaza -1,3-butadiene

INTRODUCTION

Over the past few decades, the recognition and sensing of ionic species such as anions and cations have been key research areas of many scientific research groups. Research on colorimetric reagents is attractive as it can lead to inexpensive, simple and rapid determination [1]. Many organic reagents that form chelate complexes with metal ions have been reported [2-5]. The determination of metal ions is commonly done using atomic absorption spectrometry (AAS) [6] or inductively coupled plasma atomic emission spectrometry (ICP-AES) [7]. However, spectrophotometric methods are still popular due to their simplicity, sensitivity, rapidity and involves cheaper instrumentation.

Transition metal complexes of Schiff bases are among the most widely studied coordination compounds because they have a number of useful applications. Various studies have shown that the C=N group having a lone pair of electrons in either the π or sp^2 hybridized orbital on the trigonal nitrogen atom has considerable biological activity [8]. The electronic and structural properties of the Schiff bases also play an important role in catalytic activities [9]. Considering the important roles that transition-metal ions played in many environmental and biomedical researches, the development of hydrazone derivative ligands as artificial receptors for the selective sensing and recognition of biologically important copper ions has attracted attention of many authors [10-12].

In this work, we present a new colorimetric receptor that is able to provide visual detection of transition metal cations. The method is based on the reaction of 1,4-bis(4-dimethylaminobenzyl)-2,3-diaza-1,3-butadiene (BDABD) in organic medium with copper (II) ions to produce a highly colored chelate product, which can be directly measured using UV-Vis spectroscopy.

MATERIAL AND METHODS

Reagents and Chemicals: Hydrazine sulphate, 4-(dimethylamino)benzaldehyde (1) and hydrochloric acid (36%) were obtained from Merck (Darmstadt, Germany). All solvents (methanol (MeOH), ethanol (EtOH), acetone, acetonitrile (ACN), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), chloroform, dichloromethane (DCM) and 1,2-dichloroethane (DCE)) were of analytical grade and used without further purification.

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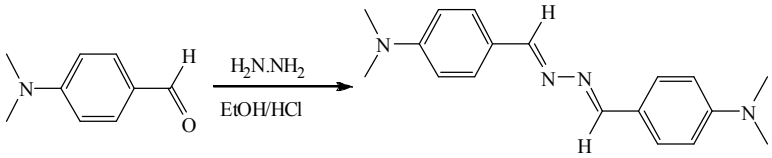

(1) **(BDABD)**

Scheme 1: The synthetic route for the preparation of 1,4-bis(4-dimethylaminobenzyl)-2,3-diaza-1,3-butadiene (BDABD).

The metal ions were perchlorate salts of Li^+, Na^+, Mg^{2+}, Ca^{2+}, Ag^+, Pb^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+}, purchased from Aldrich (Milwaukee, WI, U.S.A), were used as received.

Apparatus: ^{1}H NMR spectra were recorded using a Bruker 400 MHz spectrometer. ^{13}C NMR spectra was recorded on a Bruker 300 MHz spectrometer. The infrared (IR) spectra were recorded by using KBr on a Perkin Elmer 2000 FT-IR spectrometer. All absorption spectra were recorded using a JASCO V-530 spectrophotometer equipped with a quartz cell of 1.0 cm path length. Elemental analysis (C, H, N) were carried out on a Perkin Elmer Series II 2400. Melting point for BDABD was measured using Gallenkamp Variable Heater (Germany).

Synthesis of the Ligand (BDABD): The BDABD ligand was synthesized in two steps (Scheme 1) following the report by Wang *et al*. [13], with slight modification. Firstly, the hydrazine was freshly prepared [14] as follows: 1.38 g (0.01 mol) of finely powdered hydrazine sulphate was suspended in 50 mL of hot water in a 250 mL beaker. While stirring, 10.85 g (0.08 mol) of sodium acetate hydrate was added to this solution. The mixture was boiled and stirred until all the sodium acetate hydrate was dissolved. The mixture was cooled to about 70°C and 100 mL of absolute ethanol (EtOH) was added into it. The white precipitate was isolated by suction filtration, washed with fresh amount of hot EtOH. The filtrate was kept for the next stage of the preparation.

Secondly, while stirring the hydrazine solution, 3.01 g (0.02 mol) of 4-(dimethyl-amino) benzaldehyde (1) in ethanol was added dropwise. When the addition was completed, a yellow precipitate was formed after a few minutes. Addition of two drops of warm hydrochloric acid enhanced the formation of the compound. The yellow precipitate was filtered and recrystallized from THF. (Yield of 70 %), m.p. 252-253°C. ^{1}H NMR (400 MHz; $CDCl_3$), ä*H* (ppm): 8.06 (1H, s, CH), 7.72 (2H, d, Ph, *J*= 8.88), 6.74 (2H, d, Ph, *J*= 8.96), 3.06 (6H, S, CH_3). ^{13}C NMR ($CDCl_3$, 300 MHz.) ä (ppm): 161.16, 152.52, 130.26, 122.67, 112.15, 40.58. IR (KBr) ν_{max}1637 cm^{-1}(s, C=N), 1600 cm^{-1}(m, C=C), 1178 cm^{-1} (m, C-N), (813, 609) cm^{-1} (m, =C-H). Elemental analysis: Calc. for $C_{18}H_{22}N_4$: C, 73.44; H, 7.53; N, 19.03. found: C, 73.48; H, 8.03; N, 19.15.

Spectroscopic Measurements: Stock solution of BDABD (1.0×10^{-3} M) was prepared by dissolving 0.0145 g of the ligand in the appropriate organic solvent. Stock solutions of metal ions (2.5×10^{-3} M) were prepared by dissolving the appropriate amount of metal salts in the organic solvent. These solutions were immediately used for the spectroscopic measurements.

RESULTS AND DISCUSSION

Synthesis and Characterization of Bdabd: The BDABD (1,4-Bis(4-dimethylaminobenzyl)-2,3-diaza-1,3-butadiene) ligand was prepared by the Schiff-base condensation of two equivalents of 4-(dimethylamino)benzaldehye with one equivalent of hydrazine (Scheme 1). The structure of the ligand was established by spectral data (IR, ^{1}H NMR and ^{13}C NMR). The interaction of BDABD with different cations was investigated by naked eye and UV-Vis spectrometry.

Optimization of the Colorimetric Method

Effect of Solvent: BDABD is not soluble in water but readily soluble in most common organic solvents such as MeOH, EtOH, acetone, ACN, THF, DMSO, $CHCl_3$, DCM and DCE. Heating or stirring for a certain period (approximately 30 minutes) is required to dissolve the compound in the aprotic solvents such as acetone, THF, ACN and DMSO. Since BDABD is not soluble in water, its chromogenic complexation behavior was investigated by examining the UV-Vis absorption spectra of the free ligand and its complexes with metal ions in the above mentioned organic solvents.

ACN is widely used in metal-ligand complexation studies [2, 3, 5, 15]. Accordingly, the binding ability of BDABD for cations was investigated in CAN using UV-Vis absorption method. Fig. 1 shows the variation of absorption spectra of BDABD (1.0×10^{-5} M) in

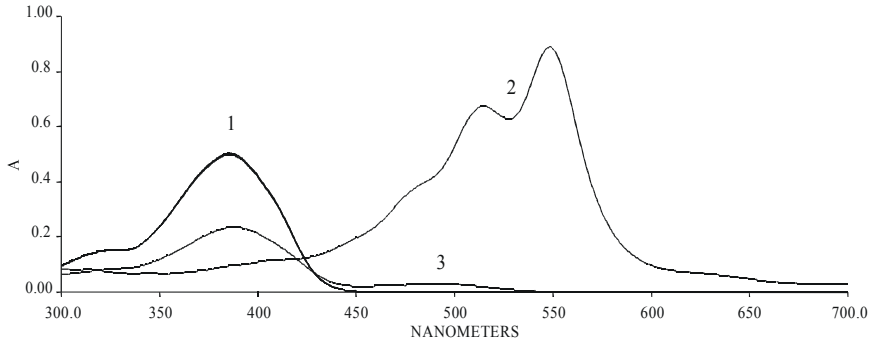

Fig. 1: Absorption spectra of BDABD (1.0×10^{-5} M) in ACN upon addition of transition metal cations (1.0×10^{-5} M). 1 = free ligand, Li^+, Na^+, Mg^{2+}, Ca^{2+}, Ag^+, Pb^{2+}, Ni^{2+}, Cd^{2+}; 2 = Cu^{2+}; 3 = Zn^{2+}

Fig. 2: Color changes of BDABD (1.0×10^{-5} M) in ACN upon addition of various metal ions. From left to right: addition of Li^+, Na^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Ag^+, Pb^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+}.

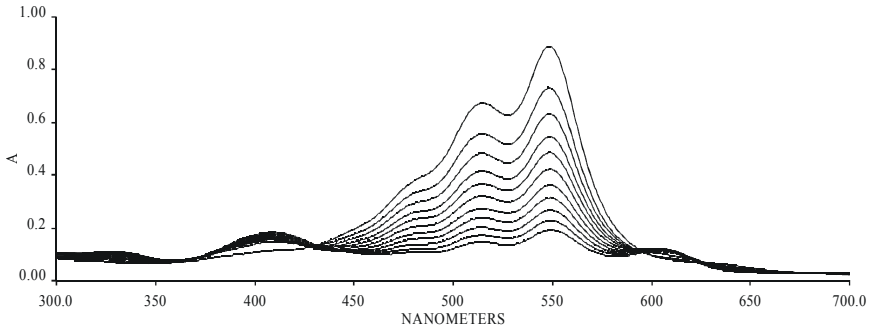

Fig. 3: Changes in the absorption spectra of BDABD-Cu^{2+} complex in ACN against stability time. The absorption spectra were taken at every 6 minutes. [BDABD] = 1.0×10^{-5} M. [Cu^{2+}] = 5.0×10^{-5} M.

ACN upon addition of an equivalent amount of alkali (Li^+, Na^+), alkaline earths (Mg^{2+}, Ca^{2+}) and transition (Cu^{2+}, Ag^+, Pb^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+}) metal ions. No noticeable changes in the absorption spectra were observed when alkali and alkaline earths metal ions were used. On the other hand, addition of Cu^{2+} and Zn^{2+} showed significant differences from the other transition metal ions. It is interesting to note that the color of BDABD turned from slightly yellow to purple immediately after the addition of Cu^{2+}, which could be detected by the naked eye (Fig. 2) without resorting to any spectroscopic measurements. The original λ_{max} of the ligand (386 nm) disappeared completely and a new strong absorption band exhibiting two maxima at 515 and 548 nm was observed (Fig. 1). The addition of Zn^{2+} also induces a slight change in color (Fig. 2) with an absorption band at 489 nm.

However, it was observed that the stability of the BDABD-Cu^{2+} complex in ACN was affected by time. Therefore, the absorption of the complex was examined at different time (Fig. 3). From the plot of the absorbance

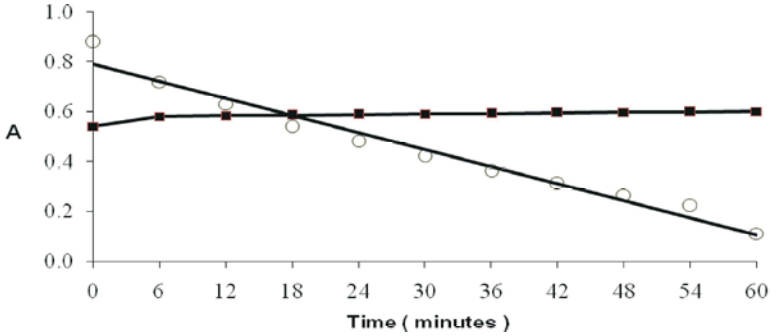

Fig. 4: Plot of absorbance of DABD-Cu^{2+} complex in, ™ ACN (548 nm) and ¾ acetone (487 nm). [Cu^{2+}] = 5.0×10^{-5} M. [BDABD] = 1.0×10^{-5} M.

Fig. 5: Color changes of BDABD (1.0×10^{-5} M) in acetone upon addition of Cu^{2+}ions.

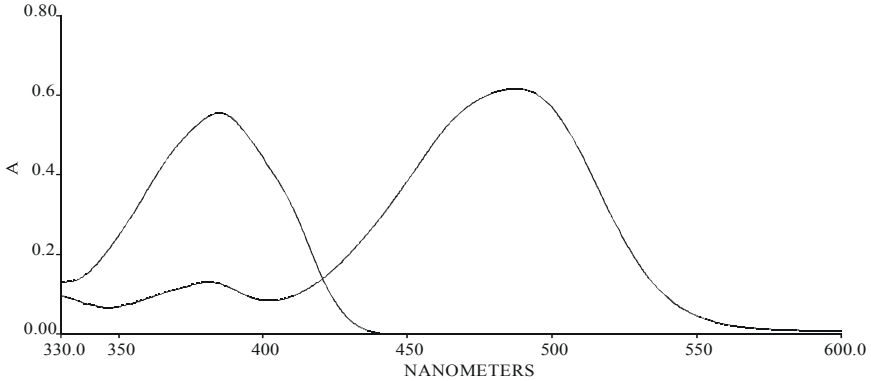

Fig. 6: Absorption spectra of BDABD (1.0×10^{-5} M) in acetone upon addition of Cu^{2+} (5.0×10^{-5} M). 1 = free ligand ; 2 = Cu^{2+}.

against time at 548 nm, a slope of -0.0114 was found (Fig. 4). This significant decrease in absorption indicates that the BDABD-Cu^{2+} complex in ACN is unstable. This may be due to the competition between the solvent nitrile group (-C=N) with the ligand for complexation with Cu^{2+} [16].

Accordingly, complexation behavior of BDABD with Cu^{2+} was also investigated in acetone, methanol and THF. An orange color was observed when these solvents were used (Fig. 5). A new absorption band was observed at 487nm (Fig. 6). No significant difference was observed when DMSO was used as solvent. This is because DMSO is a strong solvating solvent and its donor number is relatively high to strongly compete with ligand for metal ions [17]. Among the solvents investigated (acetone, THF, MeOH, EtOH, DMSO), acetone exhibited the highest response towards BDABD-Cu^{2+} complexation (Table 1).

When acetone was used, the BDABD-Cu^{2+} complex absorption band at 487 nm increased markedly, as compared to the other solvents. Therefore, acetone was selected as the second choice for further investigation for the complexation of BDABD with Cu^{2+} ions. Similar to ACN, no remarkable changes in the absorption spectra were observed when other metal ions were used.

Table 1: Effect of solvent on the absorption of BDABD

Solvent	Relative polarity	Absorption maximum BDABD	BDABD-Cu^{2+}	λ_{max} (nm)
ACN	0.460	0.001	0.813	548
THF	0.207	0.005	0.052	487
DMSO	0.444	0.032	0.051	486
$CHCl_3$	0.259	0.014	---	486
DCM	0.309	0.011	----	486
EtOH	0.654	0.003	0.205	486
MeOH	0.762	0.001	0.111	487
Acetone	0.355	0.001	0.601	487

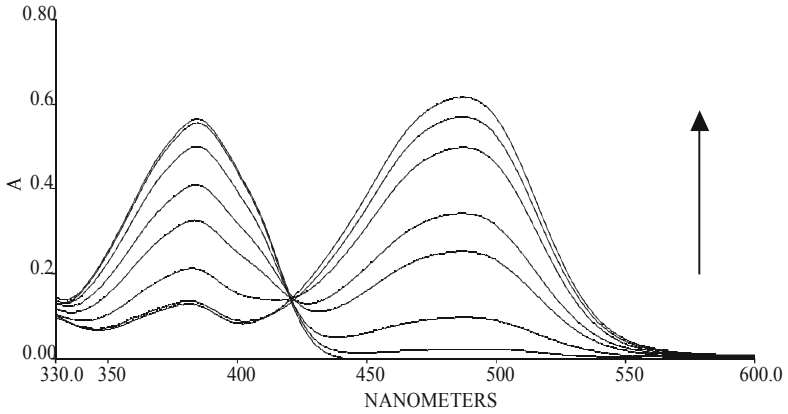

Fig. 7: Changes in absorption spectra as a function of [Cu^{2+}] in acetone against solvent blank. [Compound 1] = 1.0×10^{-5} M.

Stability of the BDABD-Cu^{2+} Complex: The stability of BDABD-Cu^{2+} complex in acetone was examined at room temperature. The absorbance of the complex was measured at 487 nm at every 3 minutes within 1 hour. The reaction between the ligand and Cu^{2+} took place immediately after the reagents were mixed together. Initially, the absorbance of the complex was found to increase within the first 10 minutes (Fig. 4). After that, the absorbance remains almost constant, indicating the high stability of the complex in acetone.

Effect of Cu^{2+} ion Concentration: At a constant ligand concentration (1.0×10^{-5} M), the absorption profile as a function of Cu^{2+} concentration was investigated. Fig. 7 shows the dependence of the absorbance on the Cu^{2+} concentration. With the addition of Cu^{2+} ions, the maximum absorption wavelength of the pure ligand at 385 nm decreased, accompanied with the increase of the wavelength at 487 nm. The clean isobestic point appeared at 421 nm revealed that the newly formed species (ABDAB-Cu^{2+}) are linearly related to the free BDABD [18]. This confirmed the formation of the ABDAB-Cu^{2+} complex [5].

Effect of BDABD Concentration: Optimum ligand concentration is required to give maximum sensitivity on the absorbance of BDABD-Cu^{2+} complex. Therefore, the effect of BDABD concentration on the absorbance of the complex with Cu^{2+} was also investigated. The color of the test solution deepened with the increase of ligand concentration. However, increase in ligand concentration ($> 4.0 \times 10^{-5}$ M) did not lead to any significant increase in the absorbance of BDABD-Cu^{2+} complex. By varying the concentration of the ligand, it was found that at least 4 fold molar excess of BDABD concentration is required to obtain the optimum color development when the Cu^{2+} concentration was 1.0×10^{-5} M. Excess of ligand concentration had no effect on the color intensity (Fig. 8).

Effect of Copper Salt: The effect of the anion on the complexation was carried out by using different copper salts, namely, $Cu(NO_3)_2$ and $CuCl_2$. When both $Cu(NO_3)_2$ and $CuCl_2$ solution was added to the ligand (separately), the color of the solution turned into orange immediately, but the color was less intense compared with $Cu(ClO_4)_2$ solution. This may be due to the better solubility of $Cu(ClO_4)_2$ in the organic solvent [19].

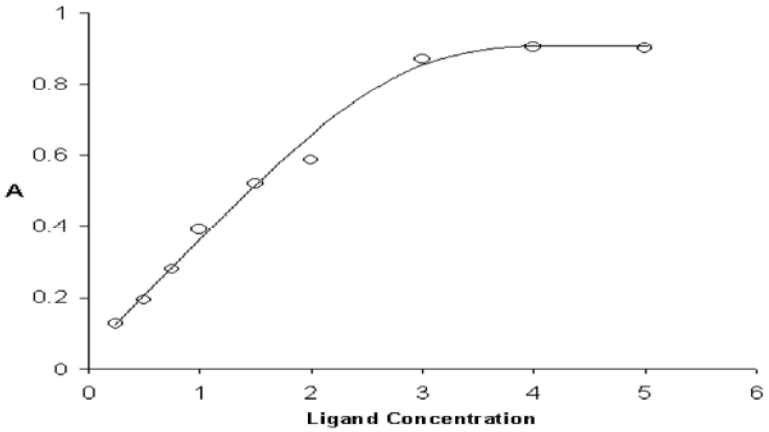

Fig. 8: Changes in absorption spectra as a function of BDABD concentration in acetone against solvent blank. $[Cu^{2+}] = 1.0 \times 10^{-5}$ M.

Table 2: Interference of metal ions in Cu^{2+} detection in acetone (ratio 1:1)

No.	Interferent	Absorbance (at 487 nm)[a]	Relative Error (%)[b]
1	Li^{+}	0.894	1.97
2	Na^{+}	0.907	0.55
3	Ca^{2+}	0.902	1.10
4	Mg^{2+}	0.889	2.52
5	Cd^{2+}	0.884	3.07
6	Ni^{2+}	0.881	3.40
7	Zn^{2+}	0.890	2.41
8	Pb^{2+}	0.899	1.43

[a] The absorbance of Cu: 0.912, Cu [1.0×10^{-5} M].

[b] $\{(\Delta A/A_0) \times 100\}$ [22, ΔA: is the difference between the absorbance before and after exposure to interferent cations.

Interference from Other Metal Ions: The interference of foreign metal ions on the detection of Cu^{2+} was investigated. Cu^{2+} (1.0×10^{-5} M) was added to the solution of BDABD (5.0×10^{-5} M) in the presence of 1 equivalent of other metal ions (Li^{+}, Na^{+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}). The absorbance of the mixture solutions were measured at the optimum condition for Cu^{2+}. No significant differences in the absorbance of the BDABD-Cu^{2+} complex (relative error < 5%) was observed (Table 2). This indicates that the studied metal ions (1.0×10^{-5} M) do not show significant interference on the Cu^{2+} assay. This is in contrast to the work of Aksuner *et al*. [22], where Ni^{2+} and Co^{2+} significantly interfered on the Cu^{2+} assay.

Validity of Beer's Law: Under the optimum conditions, linear regression analysis of absorbance of the BDABD-Cu^{2+} complex versus Cu^{2+} concentration was carried out. The graph shows a good linear fit, with a linear regression equation A= 0.0697C-0.0174, where A is the absorbance and C the molarity of Cu^{2+} ($M \times 10^{-5}$). Linear plot was obtained over at least 1.0 - 8.0 $\times 10^{-6}$ M Cu^{2+}. The high value of the correlation coefficient ($r^2 = 0.9972$) and the closeness of the intercept to zero (-0.0174) indicates that the graph is linear and obeys Beer's Law. Molar absorptivity ($\acute{a}$) and Sandell sensitivity calculated from Beer's Law data was found equal to 6.97×10^4 L $mol^{-1}cm^{-1}$ and 0.0009 µg cm^{-2}, respectively. The sensitivity is comparable to other chromogenic reagents where molar absorptivity is always found to be higher than 1.00×10^4 L $mol^{-1}cm^{-1}$ [2, 20, 21].

Job's Plot: Investigations on the stoichiometry between the BDABD ligand and Cu^{2+} were carried out by the continuous variations method [23,24]. The related data for Job's method is shown in Fig. 9. The Job's plot analysis shows that the maximum absorbance reached in Cu^{2+} molar formation equal to 0.5, suggesting that the stoichiometry of the complex formed between BDABD and Cu^{2+} in acetone is 1:1. Based on this result, the probable structure of the complex is deduced as in figure 10.

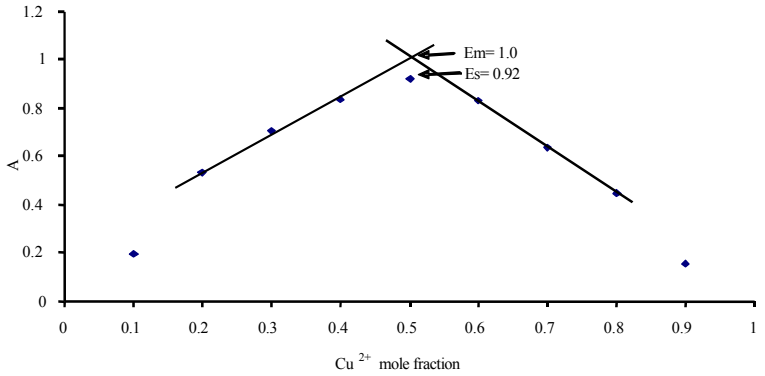

Fig. 9: Job continuous variation plots for BDABD with Cu^{2+} at 487 nm; the concentration of ligand and Cu^{2+} is 3.0×10^{-5} M.

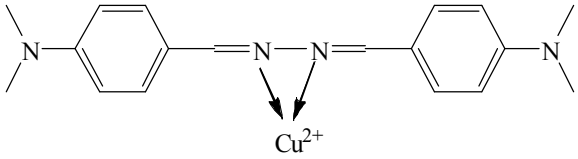

Fig. 10: DBADB-Cu^{2+} complex.

The selectivity of DBADB towards Cu^{2+} seems to be due to the selective complexation of Cu^{2+} ion with the nitrogen of imine group. Similar to that observed for the complexation of Cu^{2+} with 2-acetyl-2-thiazoline hydrazone [25]. The stability constant (K_s) of the complex is calculated using the following equation [26] and found equal to 1.44×10^{7}.

$$K_s = \frac{1-\alpha}{\alpha^2 C}$$

Where α = (Em-Es/Em). The values of Em, Es and C are calculated from the graph as 1.0, 0.92 and 1×10^{-5} M, respectively.

CONCLUSION

A new ligand, BDABD was synthesized and its chromogenic complexation behaviour with metal ions was studied. BDABD was formed to complex preferentially with Cu^{2+} in acetone at room temperature. An obvious color change from slightly yellow to orange can be observed by the naked eyes. Linear regression analysis shows that Beer's law is obeyed over the range of 1.0×10^{-6} M - 8.0×10^{-6} M Cu^{2+}. The reagent could find useful application for on site testing of water samples for Cu^{2+}.

ACKNOWLEDGEMENTS

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