International Scholars Journals

African Journal of Internal Medicine ISSN 2326-7283 Vol. 7 (7), pp. 001-009, July, 2019. Available online at www.internationalscholarsjournals.org © International Scholars Journals

Full Length Research Paper

Preparation and investigation of complexes (bisazo)-imidazole with Co(II) and Cu(II)

Hawraa Mehdi Farhan

Department of Chemistry, College of Science, University of Kufa, Iraq. E-mail: hawara.mh@yahoo.com.

Accepted 13 February, 2019

In this study, transition metal complexes of Co(II) and Cu(II) with a newbisazo dye (2-(4- methoxy-2-(4-methoxy phenyl)diazenyl)phenyl)diazenyl)-4,5-diphenylimidazole were synthesized and characterized by elemental analysis, electronic data, FT-IR, ^{1}H-NMR, ^{13}C-NMR, HMBC, HQSY and molar conductivity measurements. It has been found that the bisazo ligand behaves as tridentate (N,N',N") donor ligand forming chelates with (1:2) (metal: ligand) stoichiometry.

Key words: Tridentate, HMBC, HQSY, Transition,coloured complexes.

INTRODUCTION

Azo dyes are characterized by the presence of one or more azo group (-N=N-) in association with two or more aromatic or heterocyclic system (Olayinka et al., 2013; Zainab et al., 2013; Asniza et al., 2011; Gapala et al., 2011; Swati et al., 2011; Hanan, 2008). In recent years, many transition metal coloured complexes with azo dyes as ligand were prepared and widely studied in different application such as biological studies (Modhavadiya, 2011; Mamdouh et al., 2012), coordination polymers (Hemang et al., 2013; Hemang et al., 2013), textile industry (Hrdina et al., 2004; Emel and Hamit, 2002), solvent extraction (Shawket et al., 2011), and spectrophotometric determination (Banjit and Sudarsan, 2009; Girish and Raksha, 2011; Chauhan et al., 1980). Azo dyes usually react with metal ions as bidentate ligand (Amer et al., 2010) or as tridentate (Savic and Vasic, 2006) in the field of coordination chemistry. In this work, the synthesis and characterization of Co (II) and Cu(II) complexes with a new bisazo dye derived from 4,5-diphenyl imidazole by several techniques such as spectroscopic methods.

MATERIALS AND MEASUREMENTS

All chemicals used in the present investigation were obtained from commercial sources with expect of 4,5-diphenyl imidazole prepared following the procedure of Hofmann (1953).

Elemental analysis was carried out by Vario Elemental Apparatus Shimadzu. IR spectra were recorded on a Shimadzu 8000 FT-IR spectrophotometer in the (4000-400) cm^{-1} range using KBr discs. Electronic spectra were obtained on a Shimadzu 1700 UV-spectrometer using ethanol as solvent in the (1000-200) nm range. The NMR spectra (^{1}H-NMR and ^{13}C-NMR) were taken in BrukerBiospis 600 MHz Auance III and 400 MHz (Germany) using DMSO-d_6 as the solvent.

Synthesis of bisazo ligand [(2-(4- methoxy-2-(4-methoxy phenyl)diazenyl)phenyl)diazenyl)-4,5-diphenylimidazol

Bisazo dye was synthesized according to the following general procedure (Shibata et al., 1976)(Scheme1). There are two diazotization and two coupling reaction in the synthesis of bisazodye:

Step (1): Synthesisof 4-methoxy-2-(4-methoxy phenyl azo) aniline

p-methoxy aniline (1.23 gm , 0.01 mole) was dissolved in 30 ml of water and 2 ml concentrated hydrochloric acid.

This solution was diazotized below 5°C with 15 ml of aqueous solution (4.5 ml, 0.01 mole) of sodium nitrite. The resulting diazonium chloride solution was mixed with p- methoxy aniline (1.23 gm , 0.01 mole) dissolved in 30 ml alkaline ethanol and cooled below 5°C. The orange precipitate was filtered off, recrystallized from ethanol and dried. (m.p: 125° , Anal.Calc. for $C_{14}H_{15}N_3O_2$):C(65.35); H(5.88); N(16.33);O (12.44). Found: C(65.15); H (5.63); N(16.12); O(12.34%).

Step (2): Synthesis ofbisazo ligand [2-(4- methoxy-2-(4-methoxy phenyl)diazenyl)phenyl)diazenyl)-4,5-diphenylimidazole]

Monoazo dye (prepared in step (1)) (2.57 gm, 0.01 mole) was dissolved in 30 ml ethanol and 2 ml concentrated hydrochloric acid. This solution was diazotized below 5°C with 15 ml of aqueous solution (0.69 gm, 0.01 mole) of sodium nitrite. The resulting diazonium chloride solution was mixed with 4,5- diphenyl imidazole (2.2 gm ,0.01 mole) dissolved in 150 ml alkaline ethanol and cooled below 5°C. After leaving for 24 h, the mixture was acidified with (0.1 mole L^{-1}) hydrochloric acid until pH=6. The brown precipitate was filtered off, recrystallized from ethanol and dried. (m.p :145° , Anal.Calc. for $C_{29}H_{26}N_6O_2$:C(71.0);H(5.34) ,N(17.13) ,O(6.52). Found: C(71.4) ,H(5.14) , N(17.1) , O(6.54%) (Scheme 1).

Synthesis of Co (II) and Cu (II) complexes

The complexes were synthesized by the addition of ethanolic solution of bisazo ligand to an aqueous solution of the metal chloride Co(II) and Cu(II) in 1:2(Metal:Ligand) molar ratios. After stirring for 15 min, the colored precipitates were filtered off, washed with 5 ml hot ethanol, recrystallized from ethanol and dried. [red brown precipitate of $[CoL_2]Cl_2.H_2O$ (m.p: >300°, Anal.Calc. for $C_{58}H_{54}N_{12}O_5Co$:C(65.84), H(5.14), N(15.89), O(7.56), Co(5.57); Found: C(65.67), H(5.11), N(15.78), O(7.46), Co(5.43%). -[red brown precipitate of $[CuL_2]Cl_2.H_2O$ (m.p: >300°, Anal.Calc. for $C_{58}H_{54}N_{12}O_5Cu$: C(65.55), H(5.12), N(15.82), O(7.53), Cu(5.98); Found: C(65.35), H(5.04), N(15.76), O(7.46), Cu(5.88%).

Standard metal solutions

Stock solution of 10^{-3}M Co(II) and Cu(II) were prepared by dissolving the appropriate weight of $CoCl_2.6H_2O$ and $CuCl_2$ in distilled water. A series of standard of Co(II) and Cu(II) solutions were prepared by several dilutions (10^{-3} – 10^{-5}) of the stock solution.

Standard ligand solutions

Ethanolic solution of the standard ligand 10^{-3} M was prepared. A series of standard of dye solutions were prepared by several dilutions (10^{-3} – 10^{-5}) of the stock solution.

Buffer solution

Buffer solutions in 5-10 range were prepared by standard method for the pH adjustment by dissolving 0.0077gm of ammonium acetate in 100 ml and adjusted by acetic acid and ammonia solution and measured by pH-meter.

RESULTS AND DISCUSSION

Spectroscopic characterization of bisazo ligand

Nuclear Magnetic Resonance Spectra: (^{1}H, ^{13}C, HMBC and HSQC spectra were acquired in DMSO-d6 solvent):

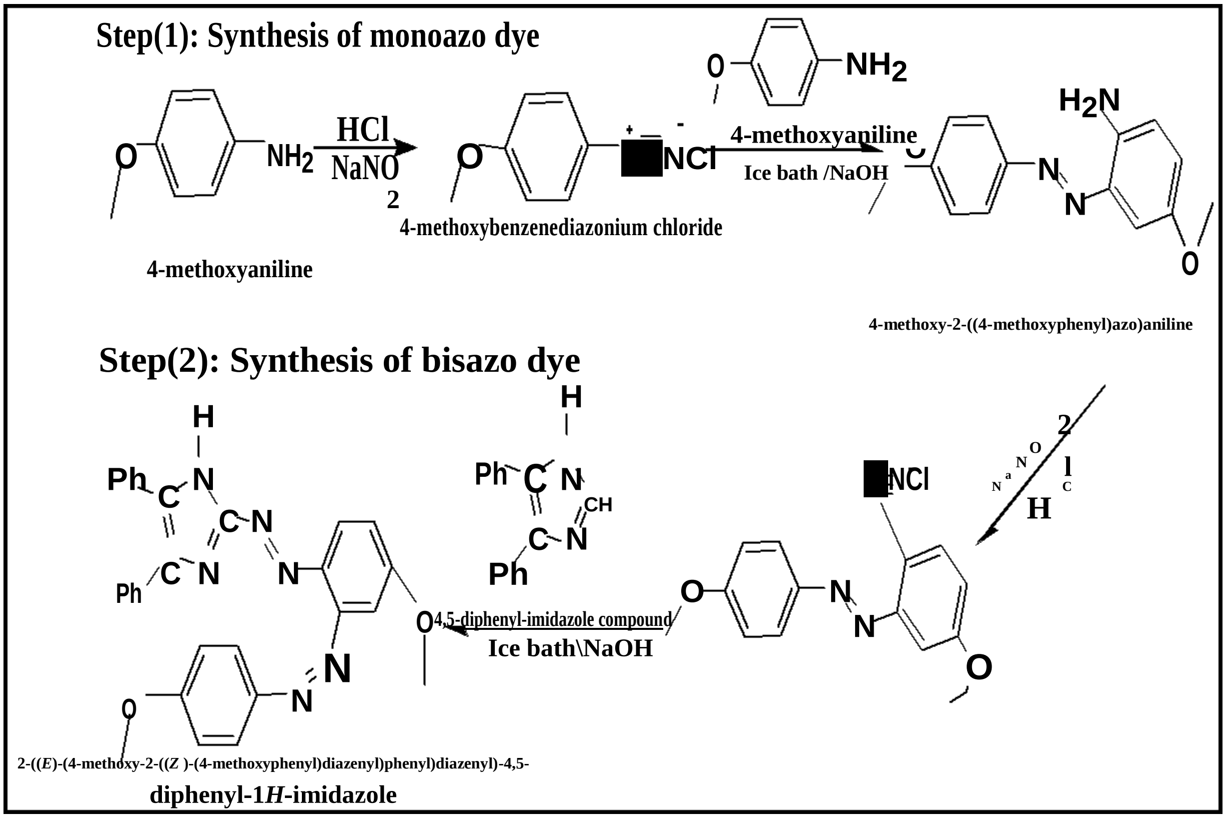
1. The ^{1}H-NMR spectra of bisazo ligand (400 MHz) shows characteristic signals due to the following protons (Silverstein et al., 2005):

-Methoxy protons: Bisazo ligand shows in the region 3.89 ppm, the hydrogens on the carbon next to oxygen are deshielded due to the electronegativity of the attached oxygen.
-Aromatic protons: The bisazo ligand exhibited multiple signals due to the aromatic hydrogen's of the phenyl and imidazole ring in the range of 7.16-7.93 ppm.

2. N-H imidazole: This hydrogen is deshielded due to the resonance that removes electron density from nitrogen and changes it hybridization, appears in the region of 13.24 ppm.
3. The ^{13}C-NMR Spectra of bisazo ligand shows absorption signals for Methoxy –O-CH_3 in the region of 56.6 ppm. The dye exhibit absorption signals due to the carbon atom of aromatic groups (C aromatic +C4+C5 imidazole) in the range of 115.31-129.32) ppm, (C2 imidazole appear in the region of 136.08 ppm, (C1a+1b) in the region of 139.69 ppm and the carbon attached oxygen (4'+4''(C-OMe)) appear in the region (162.61) ppm. ^{1}H, ^{13}C, HMBC and HSQC spectral data of the synthesized bisazo dye are shown in Figures 1 to 4.

Infrared spectra

The IR spectra data (KBr disk) of bisazo ligand and Co(II) and Cu(II) complexes are summarized in Table 1. The IR spectrum of the free bisazo ligand showed a medium and broad band around 3400 cm^{-1}, which can be attributed to (-N-H) stretching vibration of imidazole moiety (Koji and Solomon, 1977). The position of this band interacts with broad band at (3409-3186 cm^{-1} in the spectra of Co(II) and Cu(II) complexes due to the presence of water molecule (Khalid, 2007). The IR spectra of ligand appear band at (1604)cm^{-1} due to v(C=N) of the N imidazole nitrogen, which shifted to lower frequencies (1542-1545)cm^{-1} in the prepared complexes spectra due to the presence of diazo group with conjugated system and the linkage of metal ion with nitrogen imidazole ring (Abid Allah et al., 2008). The v(N=N) stretching vibration appears at 1490 cm^{-1} in the free ligand spectra, this band



Scheme(1): Sy

Scheme 1. Synthesis of the bisazo ligand.

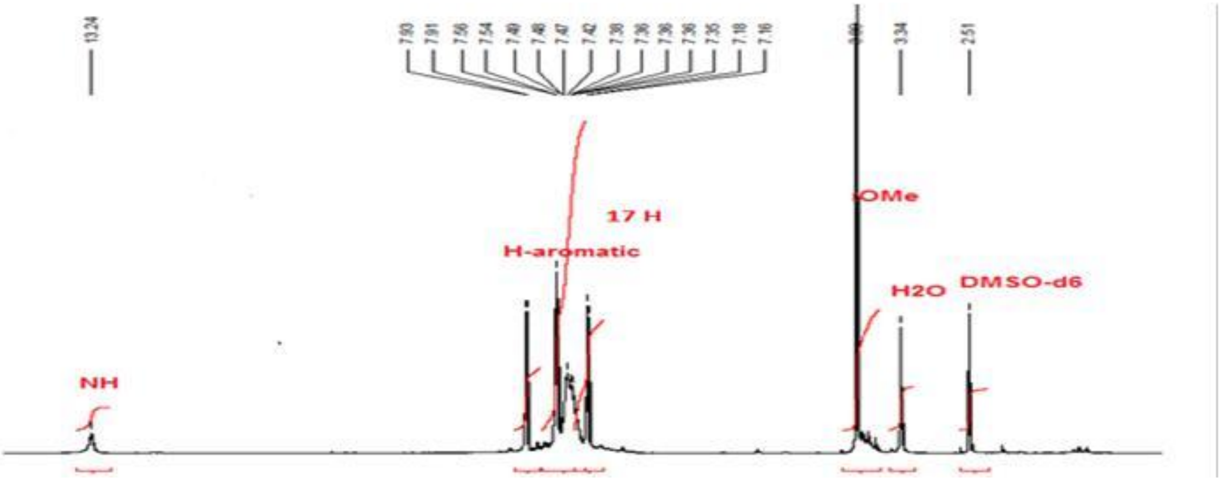


Figure 1. ^{1}H-NMR spectra of bisazo ligand in DMSO-d6 solvent.

shifted to relatively lower energy (1458-1465)cm^{-1} in the complexes spectra indicates the N=N group coordination (Mahmoud et al., 1986; Anitha et al., 2011). New weak bands in the region (462-563) cm^{-1} in the complexes spectra which were not present in the spectra of the ligand may be attributed to ν(M-N) (Biulent and Ramazan, 2008). The ν(O-CH$_3$) methoxy vibration appears at 1250 cm^{-1} and 1031 cm^{-1} due to C-O-C asymmetric and symmetric, respectively which were not change in the spectra of the complexes spectra (Silverstein et al., 2005).

The results presented above guide us to suggest that

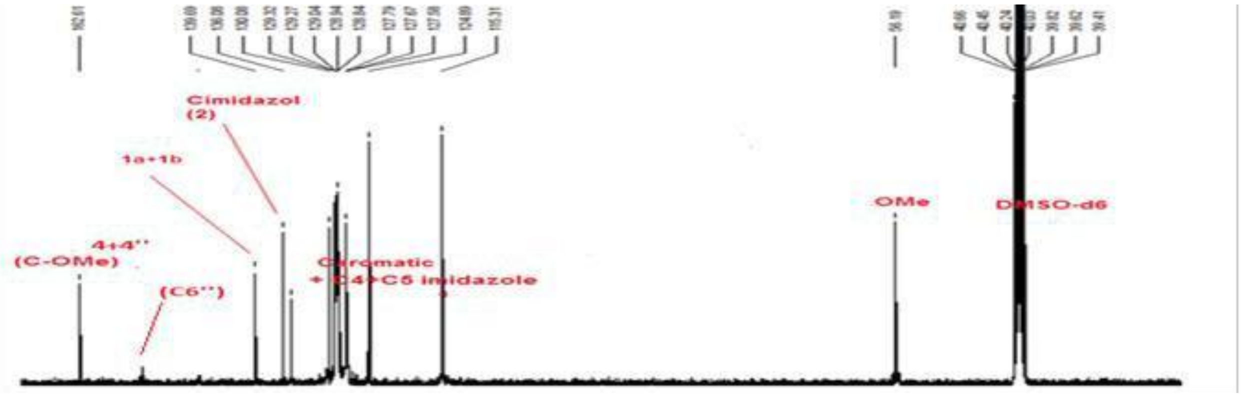


Figure 2. ^{13}C-NMR spectra of bisazo ligand in DMSO-d6 solvent).

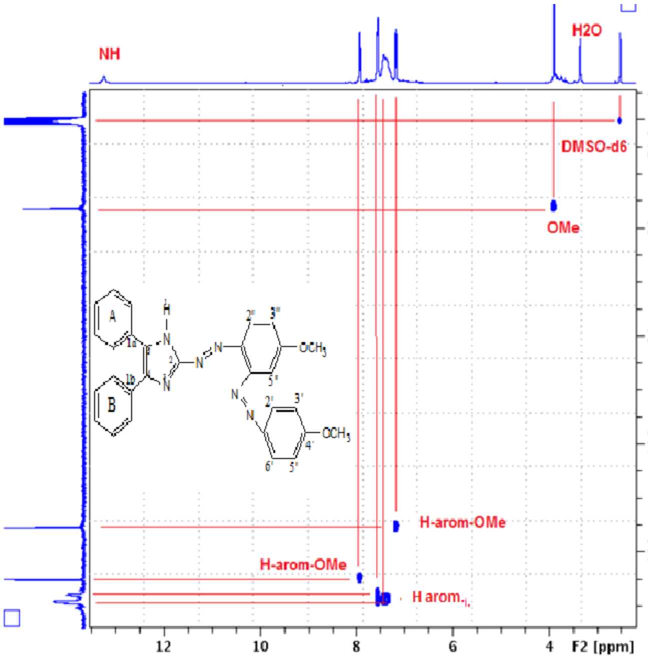


Figure 3. HMBC spectra of bisazo ligand.

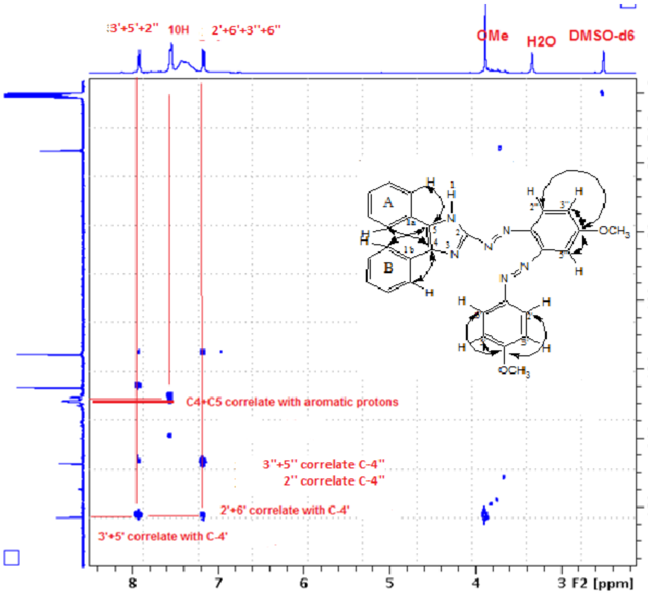


Figure 4. HSQC spectra of bisazo ligand.

the ligand behaves as tridentate chelating agent, coordinating with metal ions by a nitrogen of two azo group and nitrogen in imidazole ring to give six and five – membered chelate rings. The FT-IR spectra are shown in Figures 5 to 8.

Electronic spectra

The electronic spectra data of the bisazo ligand and its complexes are shown in Figures 9 to 11. The ligand is characterized by three bands in UV-Visible. These bands are appearing at the position 213 nm (46948 cm^{-1}) and 291 nm (34364 cm^{-1}), the first UV band can be attributed to a π-π* transition within heterocyclic imidazole, while the second UV band observed at longer wave length can be ascribed to the excitation of the π-electrons of the phenyl system (Figgis and Lewis, 1960). The characterization third visible band occurred at 413 nm (24213 cm^{-1}) and may be due to π-π* transition in the presence of conjugation in the ligand molecule (Modhavadiya, 2011). The position of ligand bands are shifted which may be due to chelation between metal ions and bisazo ligand that were assigned to d-d transition (weak in intensity) and ligand field.

Effect of pH and time

The effect of optimal pH values on the absorbance of metal complexes solution are shown in Figure 12 and Table 2. The ligand formed stable complexes with metal

Table 1. Characteristic IR frequencies (cm^{-1}) of the monoazo,bisazo dye and its metal complexes.

No.	Compound	υ(O–H) H_2O	υ(NH_2) + υ(N-H) imidazole	υ(C=N)	υ(N=N)	υ (O-CH_3)	υ (M–N)
1	Monoazo dye	——	3200	1602	1506s	1250s	–
2	Bisazo dye (L)	——=—	3425m	1604s	1490s	1250s	–
3	$[CoL_2]Cl_2.H_2O$	3409br.	3186br	1542w	1465w	1257m	462m
4	$[Cu L_2]Cl_2 .H_2O$	3317br	3163br	1545w	1458w	1265m	563m

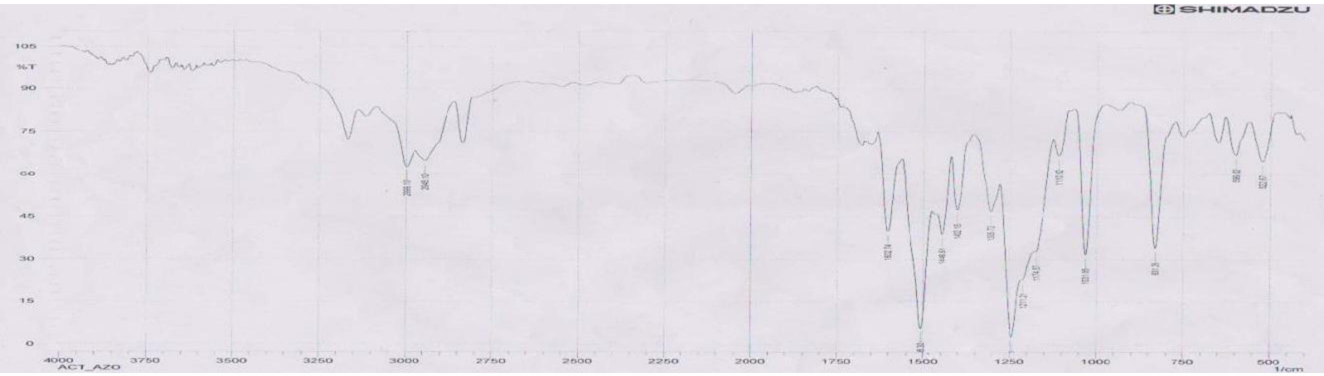


Figure 5. FT-IR spectra of the monoazo dye.

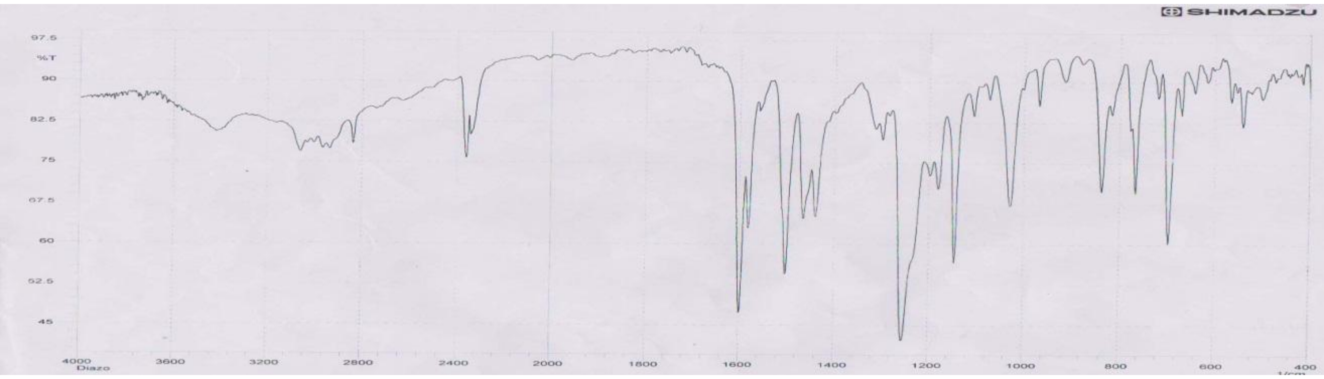


Figure 6. FT-IR spectra of bisazo ligand.

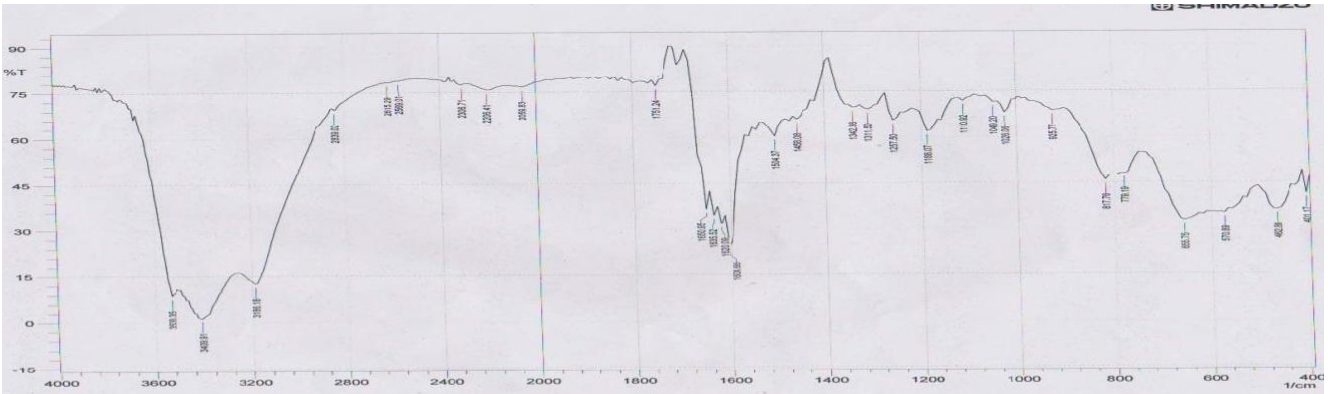


Figure 7. FT-IR spectra of the $[CoL_2]Cl_2.H_2O$ complex.

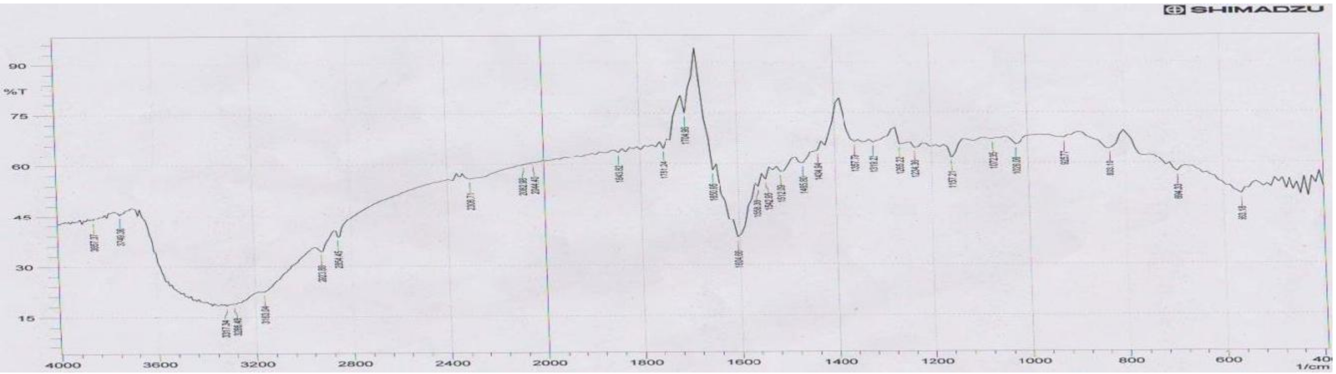


Figure 8. FT-IR spectra of the $[CuL_2]\ Cl_2.H_2O$ complex.

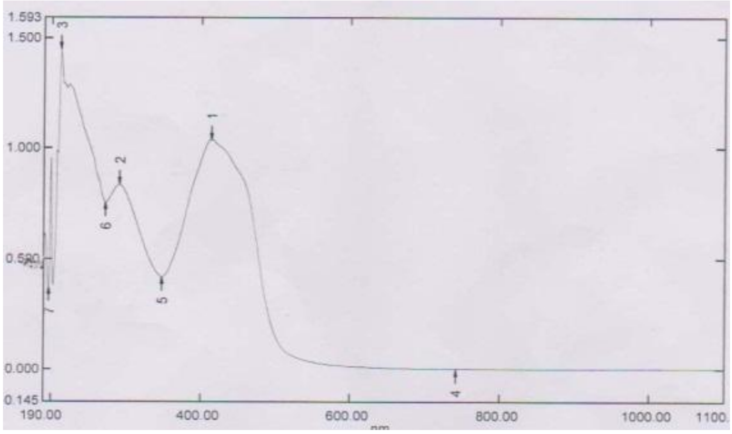


Figure 9. Electronic spectra of bisazo ligand.

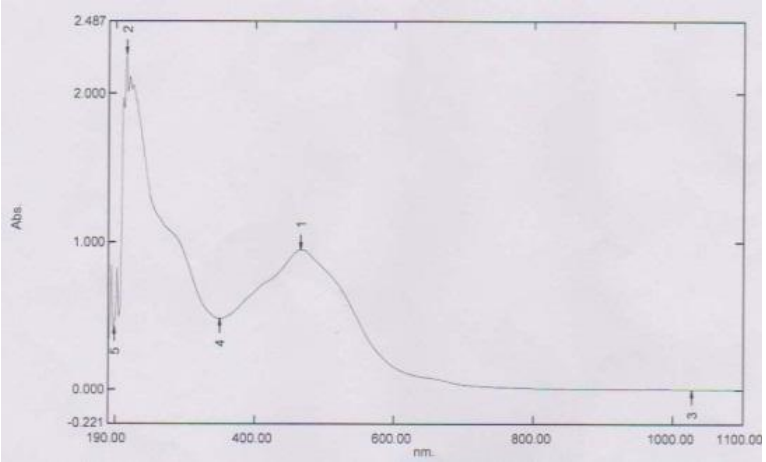


Figure 10. Electronic spectra of Co(II)-complex.

ions [Co(II) and Cu(II)] at pH (7-9)]. The reaction was completed at room temperature and remains stable for long time, this gave the ligand strong coordination with Co(II) and Cu(II) complexes . The results are shown in

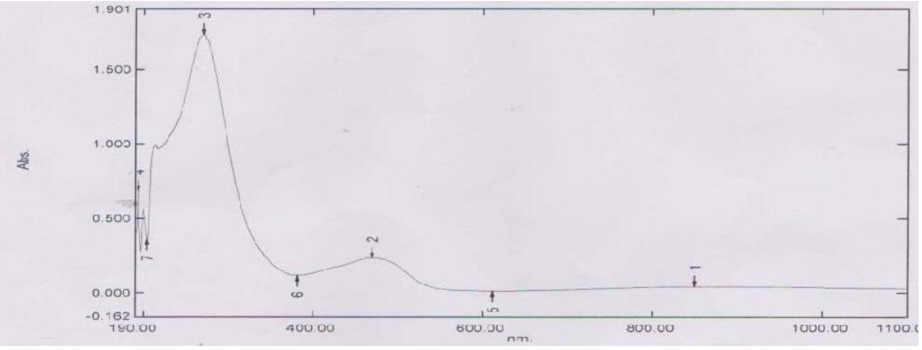


Figure 11. Electronic spectra of Cu(II)-complex.

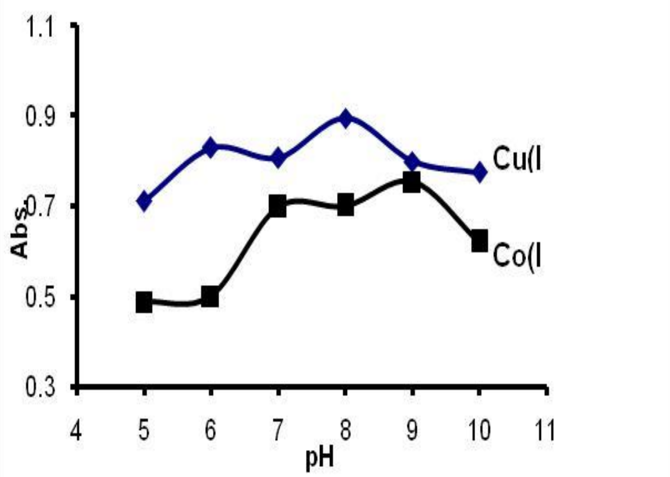


Figure 12. Effect of time on the absorbance of Co(II) and Cu(II) complexes.

Table 2. Optimum condition, conductivity and stability constant (B) values of Co (II) and Cu (II) complexes.

Compound	Berr's law validity ×10^{-5} M	pH	λ_{max}	Metal :Ligand	B	logB	Conductivity (S.mol^{-1}.cm^{2})
$[CoL_2]Cl_2.H_2O$	1-10	9	466	1:2	1.7 ×10^{12}	12.23	143.7
$[CuL_2]Cl_2.H_2O$	1-9	8	469	1:2	1.8 ×10^{13}	13.25	135.9

Figure 13.

Metal : Ligand ratio

The metal-ligand ratios of complexes were determined by molar ratio method at fixed concentration of metal ion and increasing concentration of ligand at optimum pH and λ_{max}. The mole ratio of complexes (Metal:Ligand) was (1:2) for the Co(II) and Cu(II) ions. These results are in agreement with values reported for some aryl azo imidazole complexes (Abid Allah et al., 2013; Fatema et al., 2009). The results are given in Table 2 and Figure 14.

Calculation of stability constant of the metal complexes:

Stability constant (B) values are obtained spectrophotometrically by measuring the absorbance of solutions of ligand and metal mixture at optimum condition (Skoog, 1988). The calculated B and log B values for the Co(II) and Cu(II) complexes are given in Table 2.

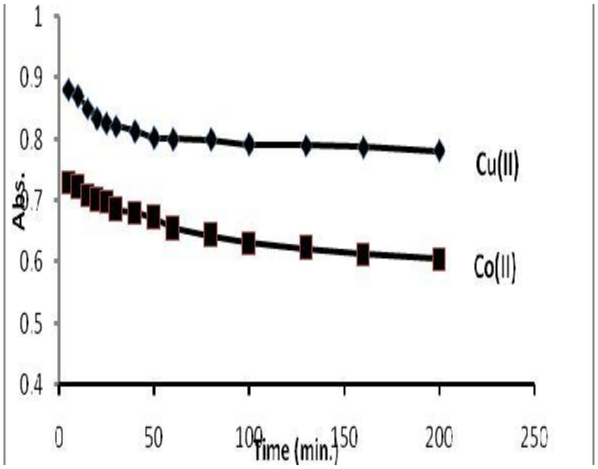


Figure 13. Effect of pH on the absorbance of Co(II) and Cu(II) complexes.

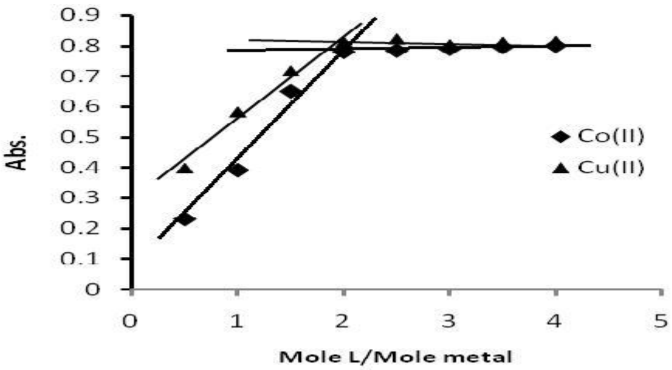


Figure 14. Mole ratio method (M:L) of Co(II) and Cu(II) chelates at optimum and concentration.

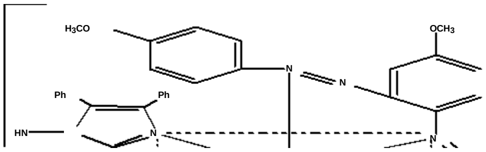


Figure 15. The suggest structural formula of Co(II) and Cu(II) chelate complexes.

Conductivity measurement

The data obtained from measurement of molar conductance of the complexes in DMF (10^{-3}) at room temperature are shown in Table 2. The high value of molar conductivity for Co(II) and Cu(II) complexes indicates 1:2 electrolyte and suggest that Cl^- anion is present outside the coordination spheres (Table 2) (Hasan, 2011). According to these results, the structure of these complexes may be proposed as shown in Figure 15:

REFERENCES

Abid Allah MA, Hussain JM, Afaak JK (2008). Preparation, identification and analytical studies of the ligand 2-[p-(2'-pyrimidyl sulphamyl)phenylazo]-4,5-diphenyl imidazole (PSPAI) and some of its metal complexes". The Islamic University (Series of Natural Studies and Engineering), 16(1): 85-94.

Abid Allah MA, Tahir AT, Raheem TM (2013). "Preparation and identification of some chelate complexes with new heterocyclic azo ligand"; Al-Mustansiriyah J.S Q; 2(24): 167-176.

Amer JJ, Khalida FS, Ahmed LH (2010). "Synthesis and spectroscopic studies of new heterocyclic azo dye and their complexes with selected metal ion". Al-Mustansiriya J. Sci., 21(6): 251-257.

Anitha KR, Venugopala R, Vittala Rao KS (2011). "Synthesis and antimicrobial Evalution of metal (II) complexes of a novel bisazo dye 2,2'[benzene -1,3-diyl di(E)diazene 2,1-diyl]bis(4-chloroaniline)". J. Chem. Pharm. Res., 3(3): 511-519.

Asniza M, Issam AM, Abdul Khalil HPS (2011). "Synthesis and characterization of a new heterocyclic azo pigment ". Sain Malaysiana, 40(7): 765-770.

Banjit B, Sudarsan B (2009). "Spectrophotometric determination of zinc in blood serum of diabetic patients using bis-[2,6-(2-hydroxy-4-sulpho-1'-napthyl azo)]pyridine disodium salt". Archiv. Appl. Sci. Res., 1(1): 74-83.

Biulent K, Ramazan G (2008). "Synthesis of new azo dyes and copper(II) complexes derived from barbituric acid and 4-amino benzoyl hydrazone". Turk. J. Chem., 32: 9-17.

Chauhan OS, Varma YS, Ishwar S, Garg BS, Singh RP (1980). "Spectrophotometric determination of Cadmium(II) and mercury (II) with water soluble pyridnalazo dyes". Proc. Indian Nath. Sci. Acad., 46(4): 369-373.

Emel Y, Hamit B (2002). "Synthesis of novel acidic mono azo and an investigation of their use in the textile industry". Turk. J. Chem., 26: 897-903.

Fatema JA (2009). "Preparation and spectral study of some transition metal complexes with new azo ligands"; Ms.D. Thesis, University of Kufa.

Figgis BN, Lewis (1960). "Modern coordination chemistry";Intersciencce,New York(1960).

Gapala KS, Nevaditha NT, Myhili CV (2011). "Antibacterial activity of azo compounds Synthesized from the natural renewable source, cardanol". J. Chem.

Pharm. Res., 3(4): 490-497.

Girish BV, Raksha VZ (2011). "Synthesis and analytical studies of some azo dyes as ligands and their metal chelates". Int. J. Chem. Sci., 9(1): 87-94.

Hanan HO (2008). "Algeldecolorization and degradation of mono azo and diazo dyes " Pakistan J. Biol. Sci., 11(10): 1310-1316.

Hasan SM (2011). "Preparation and characterization of 4-[6-(purinyl)azo]-1-naphthol and some transition". Iraqi Nat. Chem., 43: 347-360.

Hemang MS, Yogesh KS, Ashish RS (2013). "Synthesis ,characterization and antimicrobial studies of coordination polymers". Res. J. Chem. Sci., 3(1): 48-56.

Hemang MS, Yogesh KS, Ashish RS, Dilipsinh SR, Amish IS, Purvesh JS (2013). "Azo group containing bis ligand and its coordination polymers". Chem. Sci. Trans., 2(1): 301-307.

Hofmann K (1953). "Imidazole and its derivatives". Inter-Science, New York.

Hrdina R, Lustinec D, Stolin P, Burgert L, Lunak Jr S, Holcapek M (2004). "Iron complexes of reactive azo dyes". Adv. Colour Sci. Technol., 7(1): 6-17.

Khalid GA (2007). "Synthesis and spectrophotometric study of cobalt ,Nickel and copper ion complexes with some new azo dyes containing 4,5-diphenyl imidazole". Nat. J. Chem., 28: 585-602.

Koji N, Solomon PH (1977). "Infrared absorption spectroscopy practical"; 2nd Ed., Sanfrancisco: Holden-Day.

Mahmoud MR, Hammam AM, El-Gyar SA, Ibrahim SA (1986). "Coordination compounds of heterocyclic azo derivative ". Monatshefte Fur Chemie, 117: 313-325.

Mamdouh SM, Swasan SH, Alaa EA, Nessma MN (2012). " Synthesis and spectroscopic characterization of gallic acid and some of its azo complexes " ; J. Mol. Struct., 1014: 17-25.

Modhavadiya VA (2011). "Synthesis ,characterization and antimicrobial activity of metal complexes containing azo dye ligand of sulfa drugs". Asian J. Bio-Chem. Pharm. Res., 1(1).

Olayinka OA, Oluwabunmi EA, Alice OA, Abiola E, Winifred UA (2013). "Synthesis and Spectroscopic Study ofNaphtholic and Phenolic Azo Dyes". Phys. Rev. Res. Int., 3(1): 28-41.

Savic J, Vasic V (2006). "Complex formation between pd(II) and immobilized imidazole azochromotropic acid". Acta Chim. Solv., 153: 3642.

Shawket KJ, Zainab AM, Rafa MD (2011). "Solvent extraction of Co(II) from aqueous solutions by new ligand 2-[(4-chloro-2- methoxy phenyl)azo]-4,5-diphenyl imidazole". J. Thi-Qar. Univ., 7(1): 50-60.

Shibata S, Furukawa M, Nakashima R (1976). "Syntheses of azo dyes containing 4,5-diphenylimidazole and their evaluation as analytical reagents". Anal. Chim. Acta, 81: 131-141.

Silverstein RM, Webster FX, Kiemle DJ (2005). "Spectrometric identification of organic comounds", 7th Ed., Wiley,New York.

Skoog DA (1988). "Fundamental of analytical chemistry" 5th Ed. New York.

Swati, Ginni, Romila K, Sharma IK, Verma PS (2011). "Synthesis ,characterization and antimicrobial screening of some azo compounds ". Int. J. Appl. Biol. Pharm. Technol., 2(2): 332-338.

Zainab AA, Balgis WK, Amer JJ (2013). "Synthesis, characterization of new azo compounds and studies effect on the Ach enzyme (*In vitro*)". Int. J. Eng. Sci. Res. Technol., 2(2): 326-334.