Synthesis, characterization, and spectroscopic properties of new azo dyes derived from Sulfamerazine based on β-diketones and azo-metal (II) complexes

Noor Al AlBaheley*, Asaad A. Ali and Tarek A. Fahad
Department of Chemistry, College of Education for Pure Science, Basrah University, Iraq.

corresponding author’s e-mail address: noor86hakim@gmail.com

Abstract. In the present study, two new azo dyes from 4-amino-N-(4-methyl-2-pyrimidinyl)(benzenesulfonamide) with acetylacetone (L1) and benzoyl acetone (L2) were synthesized. The characterization of dyes has been described by IR, CHN, 1H-NMR, and TGA. The reaction of these new dyes with acetate salts of copper(II) and nickel(II) in molar ratios of 1:2 was carried out to produce azo metal(II) complexes. The analytical data show that the metal to ligand ratio [M:L] in all complexes is (1:2). The spectral and analytical data revealed that this ligand behaves as a bidentate chelating. The thermal behavior of these compounds was investigated based on thermogravimetric (TGA) analyse. Thermal decomposition of these compounds is multi-stage processes.

1. Introduction

Heterocyclic azo-dyes play an essential role in the enhancement of coordination chemistry and their biological and analytical efficiencies [1]. Azo dye derivatives were applied to stabilize, the lower oxidation states of several transition metal ions [2, 3]. Additionally, sulfonamide and azo-dye derivatives were chelated with broad range of metals having antitubercular, antibacterial antimalarial and anticancer features [4-9]. Most azo dyes are synthesized by diazotization of an primary aromatic amine, followed by coupling with amino and hydroxyl [10]. Azo dyes are the most essential synthetic colorants which have been widely used in textile, printing, paper manufacturing [11]. Azo – β-diketone has a wide spectrum of abiological activity, which act as an antimicrobial component of hemoglobin, vitamin B12, and some drugs, against types of mouth bacteria [12]. Due to the –N=N– group and a β-diketone moiety in a single compound, their effectiveness of complex formation and increase the stability [13, 14]. Recently, metal complex azo dyes have also attracted increasing attention due to their interesting electronic and geometrical features in connected with their application for molecular memory storages, nonlinear optical elements, printing system [15, 16]. Transition metal complexes of azo compound have improved dyeing properties of textiles and fibers compared to free dyes. Fabrics dyed using metal complex dyes show good lightfastness [17]. They have various of applications like wood stains, leather finishing, stationery printing inks, inks coloring for metals, plastics [18]. Complexes of transition metals with azo ligands have interesting physical and chemical properties [19, 20]. The present study aimed chiefly to throw more light on the synthesis and characterization a novel two azo dyes from sulfamerazine with acetylacetone (L1) and benzoyl
acetone(L2). The coordination behavior of these azo compounds towards Cu and Ni ion is reported using different analytical tools.

2. Experimental.

All the chemicals used were of AR grade, melting points were uncorrected and determined on an electrothermal apparatus. The infrared spectra of the ligands and their metal complexes were run as KBr discs in in range(4000-400)cm$^{-1}$ on a shimadzu 8400 FTIR spectrophotometer. Element analysis C.H.N was performed by using a Euro EA elemental analyser. 1H NMR spectrum of ligand were determined in DMSO-$d_6$ as solvent using TMS [Si(CH$_3$)$_4$] as internal standard and chemical shifts are expressed as $\delta$ ppm on BRUKER-500 MHz spectrophotometer. Conductivity measurements of the chelate complexes were recorded at room temperature in DMSO (10$^{-3}$M) Jenway Pcm3 Conductivity meter. The metal contents of the complexes was measured by using phoenix-986 atomic absorption, thermal analysis(TG ) were carried out in a dynamic nitrogen atmosphere ( 50 ml/min ) with a heating rate of 10C/min using TGA Q500- V6.7

2.1. Synthesis of the azo-dyes(L1 andL2)

ligands L1 (4-amino-N-(4-methyl-2-pyrimidinyl)benzenesulfonamide , azo-2,4-pentadione) L2, 4-amino-N-(4-methyl-2-pyrimidinyl)benzenesulfonamide, azo-2,4-dibenzoylmethane) [21, 22] were prepared by dissolving 0.004 mole of 4-amino-N-(4-methyl-2-pyrimidinyl)benzenesulfonamide with 1.4 ml concentrated HCl and 20 ml distilled water then adding drop by drop with stirring solution of (0.304 g. sodium nitrite in 20 ml distilled water ) to form diazonium salt at -5°C. The alkaline solution of 0.004 mole of each (Acetyl acetone and benzoylaceton) in (1.2% w/v. NaOH) was added to the above diazonium salt. Then convert the prepared dye from sodium form into hydrogen form by adding dilute HCl ( to keep pH value between 6.5 – 7.5). The precipitate was filtered and washed with distilled water and ethanol to remove the excess of unreacted substances. Recrystallized from ethanol and dried in vacuumed oven at 50°C for 5 hours) scheme 1

Scheme 1. : Coupling reaction in the synthesis of azoligands (L1&L2)

2.2 Preparation of nickel and copper azo complexes [22]

In a round bottom flask equipped with a magnetical stirrer, a solution of Ni(CH$_3$COO)$_2$.4H$_2$O (1 mmol) or Cu(CH$_3$COO)$_2$.H$_2$O (1 mmol) in ethanol (10 mL) was added to the ligands (2 mmol) in 20 ml of the mixture of equal volumes of ethanol-chloroform (1:1). A distinct change in color was observed.
The mixture was refluxed for 3h. The colored precipitate was filtered off, washed several times with ethanol and then dried vacuum.

3. Results and Discussion

The new two azo ligands and their complexes are stable in air at room temperature and soluble in DMF, DMSO, methanol, ethanol, acetone, and water on the basis of analytical data the metal complexes are found [1:2] metal:ligand. Elemental analysis data and physical properties of are summarized in Table 1 complexes are in good agreement with a proposed molecular formula that ligand is behaving bidentate in prepared complexes.

| Compound | Molecular formula | Yield (%) | Color     | m.p °C | Elemental Analysis | Con. S cm² mol⁻¹ | %C | %H | %N |
|----------|------------------|-----------|-----------|--------|-------------------|------------------|----|----|----|
| L1       | C₁₀H₁₇N₂O₄S     | 83        | Red       | 290    | 51.19 (50.72)     | -                |    |    |    |
| L1       | C₁₀H₁₇N₂O₄S     | 83        | Red       | 290    | 4.56 (4.36)       | -                |    |    |    |
| Ni.L1    | C₃₂H₄₀N₁₀O₁₁S₂Ni | 73        | Dark brown| 276    | 18.65 (18.21)     | -                |    |    |    |
| Cu.L1    | C₃₂H₃₈N₁₀O₁₀S₂Cu | 77        | Light brown| >300   | 4.56 (4.36)       | -                |    |    |    |
| Ni.L1    | C₃₂H₄₀N₁₀O₁₁S₂Ni | 73        | Dark brown| 276    | 16.47 (16.39)     | -                |    |    |    |
| L2       | C₂₆H₃₁N₃O₄S     | 82        | Orange    | 284    | 6.58 (6.47)       | -                |    |    |    |
| L2Cu     | C₅₂H₴₈N₁₀O₁₀S₂Cu | 79        | Yellow    | >300   | 5.78 (5.68)       | -                |    |    |    |
| L2Ni     | C₅₂H₴₈N₁₀O₁₁S₂Ni | 75        | Green     | >300   | 5.18 (5.07)       | -                |    |    |    |

3.1. The infrared spectral

Table 2 contains information on azoligands and their metal chelat complexes. The free ligand's IR spectrum shows a medium band about 3400-3500cm⁻¹, which can be due to stretching vibrations (N-H), the (N-H) group's remaining unchange means that the ligand is not involved in metal ion coordination [23]. Due to the (C-N) in the azo ligands (a strong intensity band in the range of 1150-1380cm⁻¹ is observed). Strong intensity band in the range of 1150-1380cm⁻¹ due to (C-N) in the azoligands. This band was shifted to lower frequency in metal complexes, indicating the imine nitrogen atom coordination to metal ions [24]. The azo spectrum displays the azo (=N=N-) group at 1481 cm⁻¹, this group is changing to lower frequency at (1417-1516)cm⁻¹ suggests its participation in bonding with metal ions [25]. New bands at (580-592)cm⁻¹ which are not present in the free ligand are attributed to v(M-O) vibration. The appearance of weak intensity bands in spectra of metal complexes in the region of (430-480)cm⁻¹, assignable due to v(M-N) vibration. Also indicated the metal oxygen binding to formation the chelat complexes. IR spectra data lead to suggest that the azo behaves as bidentate chelating agent coordination through the nitrogen atom of azo group and oxygen atom of carbonyl group. It was also noticed in the spectra of the complexes, a new band corresponded to C-O vibration appears around 1260-1240 and strong bands assigned as v N=N appeared at low frequency. These spectral data show that in the complexes the azo ligand acts as azo-enol form coordinated through hydroxyl oxygen and azo group nitrogen to the center metal ions. Based on FT-IR spectral...
data, we can conclude that azo-dyes exist in keto-hydrazone or enol-azo forms during complexation and act as O,N-bidentate ligand [22].

### TABLE 2. Shows IR spectra of L1 and L2 and their complexes

| Symb. Of Comp. | vN-H | vC=Oz | vC=CAr | v N=N | v C-N | u(M-O) | u(M-N) |
|----------------|------|-------|--------|-------|-------|--------|--------|
| L1            | 3400w, 3500w | 1539.20s | 1508.33s | 1483.90m | 1157.29s | -     | -     |
| L1Cu          | 3452.58m | 1589.34s | 1506.41w | 1435.04s | 1280.73 m | 580.57m | 478.35w |
| L1Ni          | 3427.51m | 1585.39 m | 1508.33m | 1417.68s | 1274.95 m | 592/15m | 450w   |
| L2            | 3400-35000w | 1666.50s | 1597.06s | 1516.05s | 1153.43s | -     | -     |
| L2Cu          | 3400-35000w | 1597.06s | 1517.98s | 1446.61m | 1327.03 m | 588.29m | 340w   |
| L2Ni          | 3441.0m | 1593.20 m | 1516.05s | 1411.89s | 1382.95 m | 586.36m | 430w   |

### 3.2-The ¹H-NMR spectra

The 1HNMR spectrum of the ligand shown in Figure (1-2) exhibits a variety of signals between (δ=6.688-8.3) ppm, which correspond to aromatic protons, a peak at 2.5 ppm attributed to the DMSO solvent, and some spectra revealed a sharp peak at 3.4 ppm attributed to dissolved water in DMSO, (CH3) was assigned to the signal at (δ=2.320) ppm [2, 26]. The absence of the amino group (-NH2) characteristic of the starting material (hydrazide) indicates that it was not involved in the condensation process that resulted in the formation of the ligand [27]. Table3

### TABLE3.¹H-NMR- Spectra of L1 and L2 compounds.

| No. | Chemical shif ( ppm ) |
|-----|-----------------------|
| L1  | 2.5(s,6H,DMSO), 3.3(s, H,HOD) ,2.39(s,6H,CH3) 7.9-8.3(m,6H,Ar-H) , 13.75(s, H,NH) |
| L2  | 2.5(s,6H,DMSO),3.3(s, H,HOD), 2.3 (s,3H,CH3) 6.8-8.4(m,16H,Ar-H) ,11.7(s, H,NH) |
3.3. **Molar conductance data**

The molar conductance of the solid complexes ($\Lambda_m$, $\text{cm}^2 \text{mol}^{-1}$) was calculated. The DMSO solubility of the above complexes made calculations of the molar conductivity ($\Lambda_m$) of $10^{-3}\text{M}$ solution at 25 °C possible. The data in Table 1 in supplementary data show that the molar conductance are of relatively low values for Cu(II) and Ni(II), indicating the non-electrolytic nature of these complexes. Therefore, the molar conductance data confirm the results of the elemental analyses and IR spectral data [28, 29].

3.4. **Structural interpretation**

The prepared metal complexes are colored, air-stable and insoluble in water, ethanol, and non-polar solvents. They demonstrated a good solubility character in polar solvents, DMF and DMSO. All prepared metal complexes showed a non-electrolyte nature. The proposed configuration structures (Fig. 1-3) goes inconsistent with the elemental, thermal and spectral analyses (Tables 1-3).

From all of the above observations, the structure of all complexes for four ligands may be interpreted with a similar distribution of like coordinating sites fig(3), which coordinated to Cu(II) and Ni(II) [30].
3.5. Thermal properties

The Cu(II) and Ni(II) complexes are stable at room temperature and can be stored for several months without any changes. The obtained compounds were studied by thermogravimetric analysis (TG) from ambient temperature to 800 °C under N₂ atmospheres. Typical TG curve is presented in Fig.(4,5). The data from TGA indicate the decomposition of the complexes proceeds in three or four steps. Crystal water molecules were lost between 25 and 160 °C and coordinated water between 160 and 250 °C. The second step loss of organic moiety the third and fourth step included loss of metal oxide and some organic species table (4) [31].

| Complex | Steps | TG range °C | Mass loss found % | Mass loss calc. % | Assignment (Removal of molecule) |
|---------|-------|-------------|-------------------|------------------|----------------------------------|
| L1 Cu   | 1     | 50-180      | 5.37              | 5.72             | (C₂H₆)                           |
|         | 2     | 200-300     | 10.88             | 10.55            | C₆H₄N₂                          |
|         | 3     | 300-450     | 19.62             | 19.53            | C₃H₅SO₂N                       |
|         | 4     | 500-825     | 45.33             | 43.92            | C₁₁H₁₄SO₂N                      |
| L1Ni    | 1     | 87-150      | 5.95              | 5.93             | 2H₂O-CH₃                        |
|         | 2     | 200-450     | 39.97             | 40.68            | C₁₁N₅SO₂H₈                      |
| L2 Cu   | 1     | 50-475      | 48.99             | 46.78            | C₂₃H₁₈S₂O₂N₆                   |
|         | 2     | 550-1000    | 33.80             | 32.18            | C₁₃H₆O                          |
| L2 Ni   | 1     | 50-190      | 3.32              | 3.22             | 2H₂O                            |
|         | 2     | 200-325     | 24.21             | 23.36            | C₁₁H₁₀SO₄N₃                    |
|         | 3     | 350-500     | 28.54             | 28.89            | C₁₀H₂SO₄N₃                     |
|         | 4     | 500-1000    | 30.21             | 30.56            | C₁₃H₆O                          |
3.6. Solvent effect on electronic spectra of ligands

Fig. (6) shows the spectrum of azo dye L1 (of concentration $2 \times 10^{-4}$ M) at different solvents of different polarities (Acetone, chloroform, ether, DMF, DMSO, ethyl acetate, water, ethanol, and methanol). It was found the azo dye L1 having two bands in all solvents, the first in the UV region about 330 nm while the second intense band at 440 nm. The Fig. also shows the solvent ether gives the highest absorbance value. The Fig. shows no red shift or blue shift. That can be cleared in Fig. 7 by plotting of $(D-1)/(D+1)$ (Table 5) against the $\lambda_{\text{max}}$ of azo dye L1 gives more or less high linear relation with solvents of moderate polarities. This denotes that the dielectric constant of the medium is the main factor governing the band shift in such solvents.

![Electronic spectra of azo dye L1 at different solvents](image)

**FIGURE 6:** Electronic spectra of azo dye L1 at different solvents

![Therelation between $\lambda_{\text{max}}$ and $(D-1)/(D+1)$ for azo dye L1](image)

**FIGURE 7:** The relation between $\lambda_{\text{max}}$ and $(D-1)/(D+1)$ for azo dye L1 ($2 \times 10^{-4}$ M)

Fig. (8) shows the spectrum of azo dye L2 (of concentration $0.6 \times 10^{-4}$ M) at different solvents of different polarities (Acetone, chloroform, ether, DMF, DMSO, ethyl acetate, water, benzene, ethanol, and methanol). It was found that L1 having $\lambda_{\text{max}}$ at 375 nm with respect to benzene, chloroform and water, with slight blue shift to other solvents at 365 nm. The Fig. also shows the ethyl acetate gives the highest absorbance value. It was found also the solvent DMF gives two bands, the first intense band at 365 nm and the second with weak broad band at 470 nm [32].
TABLE 5. The values of dielectric function $(D-1)/(D+1)$ of solvents

| Symbol | Solvent     | $D$  | $(D-1)/(D+1)$ |
|--------|-------------|------|--------------|
| 1      | Acetone     | 20.60| 0.907        |
| 2      | Benzene     | 2.30 | 0.394        |
| 3      | Chloroform  | 4.80 | 0.655        |
| 4      | DMF         | 36.71| 0.923        |
| 5      | DMSO        | 47.00| 0.958        |
| 6      | Ethanol     | 24.30| 0.921        |
| 7      | Ether       | 4.33 | 0.625        |
| 8      | Ethyl acetate| 6.02| 0.715        |
| 9      | Methanol    | 32.70| 0.941        |
| 10     | Water       | 78.40| 0.975        |

By plotting of $(D-1)/(D+1)$ against the $\lambda_{365}$ of azo dye L2 (Fig.9) gives more or less high linear relation with solvents of moderate polarities for the same reason of L1. Table (6) shows the values of $\lambda_{\text{max}}$ and $\varepsilon_{\text{max}}$ azo dyes L1 and L2 at different solvents.

![Figure 8 Electronic spectra of azo dye L2 at different solvents](image-url)
4. Conclusion

In this paper, we reported the preparation, spectral identification, analytical data, and coordination chemistry of azo dye ligand derived from obtained from the coupling reaction of sulfamerazine with acetylacetone (L1) and benzoyl acetone (L2) and its metal complexes with Ni(II) and Cu(II). The azo ligands (L1 and L2) behaves as a bidentate chelating agent coordination through the N and O atom. All complex characterized solid metal complexes not effect by air, light, and moisture, suggesting high stability plus high degrees of melting points that gives another evidence of the stability of prepared metal complexes.

![Figure 9: The relation between $\lambda_{365}$ and $(D-1)/(D+1)$ for azo dye L2 (0.6 x10$^{-4}$ M)](image)

**TABLE 6. The values of $\lambda_{max}$ and $\epsilon_{max}$ azo dyes L1 and L2 at different solvents**

| Azo dye | Solvent      | $\lambda_{max}$ (nm.) | $\epsilon_{max} \times 10^4$ mole$^{-1}$.cm$^{-1}$ | Max (nm.$\lambda$) | $\epsilon_{max} \times 10^4$ mole$^{-1}$.cm$^{-1}$ |
|---------|--------------|------------------------|-----------------------------------------------|-------------------|-----------------------------------------------|
| L1      | Acetone      | 330                    | 0.284                                         | 440               | 0.297                                         |
|         | Benzene      |                        |                                               |                   |                                               |
|         | Turbid solution (error measurements due to scattering light) | |                                               |                   |                                               |
|         | Chloroform   |                        |                                               |                   |                                               |
|         | DMF          |                        |                                               |                   |                                               |
|         | DMSO         |                        |                                               |                   |                                               |
|         | Ethanol      | 330                    | 0.204                                         | 440               | 0.207                                         |
|         | Ether        | 330                    | 0.325                                         | 440               | 0.326                                         |
|         | Ethyl acetate | 340                   | 0.229                                         | 440               | 0.249                                         |
|         | Methanol     |                        |                                               |                   |                                               |
|         | Water        |                        |                                               |                   |                                               |
| L2      | Acetone      | 360                    | 1.040                                         |                   |                                               |
|         | Benzene      | 370                    | 1.173                                         |                   |                                               |
|         | Chloroform   | 370                    | 1.230                                         |                   |                                               |
|         | DMF          | 360                    | 1.100                                         | 470               | 0.217.                                        |
|         | DMSO         | 360                    | 1.233                                         |                   |                                               |
|         | Ethanol      | 360                    | 0.992                                         |                   |                                               |
|         | Ether        | 360                    | 0.892                                         |                   |                                               |
|         | Ethyl acetate | 360                  | 1.445                                         |                   |                                               |
|         | Methanol     | 360                    | 1.313                                         |                   |                                               |
|         | Acetone      |                        |                                               | 440               | 0.256                                         |
REFERENCES

[1] Gaffer H E, Fouda M M G and Khalifa M E 2016 Synthesis of Some Novel 2-Amino-5-arylazothiazole Disperse Dyes for Dyeing Polyester Fabrics and Their Antimicrobial Activity *Molecules (Basel, Switzerland)* **21** 122

[2] Kilincarslan R, Erdem E and Kocaokutgen H 2007 Synthesis and spectral characterization of some new azo dyes and their metal complexes *Transition Metal Chemistry* **32** 102-6

[3] Misra T K, Santra P K and Sinha C 1999 Use of steric crowding to synthesise ruthenium(II) N(1)-alkyl-2-(arylazo)imidazole isomers. Spectral characterization and redox studies *Transition Metal Chemistry* **24** 672-7

[4] Idemudia O G, Sadimenko A P, Afolayan A J and Hosten E C 2015 Synthesis and Characterization of Bioactive Aclypyrazolone Sulfanilamides and Their Transition Metal Complexes: Single Crystal Structure of 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one Sulfanilamide *Bioinorg Chem Appl* **2015** 717089

[5] Saad F A and Khedr A M 2017 Greener solid state synthesis of nano-sized mono and homo bi-nuclear Ni(II), Co(II), Mn(II), Hg(II), Cd(II) and Zn(II) complexes with new sulfa ligand as a potential antitumour and antimicrobial agents *Journal of Molecular Liquids* **231** 572-9

[6] K A A and S. K R 2017 Metal complexes of Proline-Azo Dyes, Synthesis, Characterization, Dying Performance and Antibacterial Activity Studies *Orient J Chem* **1** 33

[7] Gaffer H E 2019 Antimicrobial sulphonamide azo dyes *Coloration Technology* **135** 484-500

[8] Halve A and Goyal A 1996 Potential Bacteriostats: Synthesis of New Azo Schiff Bases *Oriental Journal of Chemistry* **12** 87-8

[9] Hassanin H M, Abd Elmoneam W R and Mostafa M A 2019 Synthesis and antitumor activity evaluation of different 2, 5-dialkylazolopyrano[3, 2-c] quinolinone derivatives *Medicinal Chemistry Research* **28** 28-38

[10] Benkhaya S, M'Rabet S and El Harfi A 2020 Classifications, properties, recent synthesis and applications of azo dyes *Heliyon* **6** e03271

[11] Benkhaya S, M' rabet S and El Harfi A 2020 A review on classifications, recent synthesis and applications of textile dyes *Inorganic Chemistry Communications* **115** 107891

[12] Fahad T A, Ali A A and Baty A H 2018 SYNTHESIS, CHARACTERIZATION AND ANALYTICAL STUDIES OF SOME NEW AZODYES DRIVEN FROM O-VANILLIN *World Journal of Pharmaceutical Research* **8** 707-15

[13] Abdallah S M 2012 Metal complexes of azo compounds derived from 4-acetamidophenol and substituted aniline *Arabian Journal of Chemistry* **5** 251-6

[14] Li X, Wu Y, Gu D and Gan F 2010 Spectral, thermal and optical properties of metal(II)-azo complexes for optical recording media *Dyes and Pigments* **86** 182-9

[15] Abe T, Mano S, Yamaya Y and Tomotake A 1999 Termal Dye Transfer Printing with Chelate Compounds *Journal of Imaging Science and Technology* **43** 339-44

[16] Chhowala T N and Desai K R 2015 Synthesis of Cu(II) and Ni(II) Azo Complex Dyes, their Application on Silk Fabrics and their Application for Antibacterial Activity *International Journal of Science and Research* **4** 901-5

[17] El-Wakiel N A, Rizk H F and Ibrahim S A 2017 Synthesis and characterization of metal complexes of azo dye based on 5-nitro-8-hydroxyquinoline and their applications in dyeing polyester fabrics *Applied Organometallic Chemistry* **31** e3723

[18] Daniel V P, Murukan B, Kumari B S and Mohanan K 2008 Synthesis, spectroscopic characterization, electrochemical behaviour, reactivity and antibacterial activity of some transition metal complexes with 2-(N-salicylideneamino)-3-carboxyethyl-4,5-dimethylthiophene *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **70** 403-10

[19] Sultan H A, Dhumad A M, Hassan Q M A, Fahad T, Emshary C A and Raheem N A 2021 Synthesis, characterization and the nonlinear optical properties of newly synthesized 4-((1,3-
Dioxo-1-phenylbutan-2-yl)diazenyl)benzenesulfonamide *Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy* 251 119487

[20] Dhumad A M, Hassan Q M A, Fahad T, Emshary C A, Raheem N A and Sultan H A 2021 Synthesis, structural characterization and optical nonlinear properties of two azo-β-diketones Journal of Molecular Structure 1235 130196

[21] Chun H, Yizhong W and Hongxiao T 2001 Preparation and characterization of surface bond-conjugated TiO2/SiO2 and photocatalysis for azo dyes Applied Catalysis B: Environmental 30 277-85

[22] Venugopal N, Krishnamurthy G, Bhojya Naik H S and Manohara J D 2020 DNA Binding, Molecular Docking and Antimicrobial Evaluation of Novel Azo Dye Ligand and Their Metal Complexes Journal of Inorganic and Organometallic Polymers and Materials 30 2608-25

[23] Andersen F A and Jensen K A 1980 Infrared spectra of transition metal coordination compounds with the formaldoximate ion Journal of Molecular Structure 60 165-71

[24] Shah R, Alharbi A, Hameed A M, Saad F, Zaky R, Khedr A M and El-Metwaly N 2020 Synthesis and Structural Elucidation for New Schiff Base Complexes; Conductance, Conformational, MOE-Docking and Biological Studies Journal of Inorganic and Organometallic Polymers and Materials 30 3595-607

[25] Mahmoud W H, Omar M M and Sayed F N 2016 Synthesis, spectral characterization, thermal, anticancer and antimicrobial studies of bidentate azo dye metal complexes Journal of Thermal Analysis and Calorimetry 124 1071-89

[26] Al-Khuzaie M G A and Al-Majidi S M H 2020 Synthesis and characterization of new azo compounds linked to 1,8-naphthalimide as new fluorescent dispersed dyes for cotton fibers *AIP Conference Proceedings* 2290 030011

[27] Wahba M A, El-Saied F A, Al-Hakimi A N and Shakdofa M M 2017 Preparation, Characterization and Antimicrobial Activities of N’-(3-(hydroxyimino) butan-2-ylidene)-2 (phenylamino) acetoxyhydrizide and Its Metal Complexes *Egypt. J. Chem* 60 1-24

[28] Ali I, Wani W A and Saleem K 2013 Empirical Formulae to Molecular Structures of Metal Complexes by Molar Conductance *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry* 43 1162-70

[29] Abou-Hussein A A and Linert W 2014 Synthesis, spectroscopic, coordination and biological activities of some organometallic complexes derived from thio-Schiff base ligands *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 117 763-71

[30] Turan N, Adiguzel R, Buldurun K and Bursal E 2016 Spectroscopic, Thermal and Antioxidant Properties of Novel Mixed Ligand-Metal Complexes Obtained from Saccharinate Complexes and Azo Dye Ligand (mnppa) *International Journal of Pharmacology* 12 92-100

[31] Sekerci M and Yakuphanoglu F 2004 Thermal analysis study of some transition metal complexes by TG and DSC methods *Journal of Thermal Analysis and Calorimetry* 75 189-95

[32] A. Ali A, A. Fahad T and A. Al-muhsein A 2020 Preparation and Spectroanalytical Studies of Two New Azo Dyes Based on Luminol *IOP Conference Series: Materials Science and Engineering* 928 052007

[33] Sami Abd ali, mohammed, Shaker Hussein, A., & mohammed hadi, H. (2020). Study The Current Density-Voltage (J-V) Characteristics of α-Fe2O3 Thin Film Prepared by Spray Pyrolysis Technique. Al-Qadisiyiah Journal Of Pure Science, 25 (1), Phys 1-7.