

## Synthesis and Characterization of Metal Complex of an Azo Dye Based on Acid Orange 7

\*B. Myek, M. L. Batari, J. O. Oriajogun and M. A. Aboki

Received 20 May 2020/Accepted 29 June 2020/Published online: 30 June 2020

**Abstract:** Azo dye which serve as a ligand was prepared by diazotization of primary aromatic amine to form the diazonium salt. The relatively unstable diazonium salt thus formed was reacted with a coupling component. Complex of this ligand has been synthesized and characterized by IR spectroscopy and UV-Visible absorption spectroscopy. The absorption maximum of the ligand was at 483.50nm. Upon binding with the Fe(II) the band shifted to 479.50nm, indicates an interaction of the Fe(II) with the ligand. The ligand synthesized is soluble in water as well as its metal complex. The colour of the ligand is orange while that of the complex is brown. The prepared complex is stable at room temperature.

**Key Words:** Metal complex, azo dye, iron(II) salts, preparation, characterization

### B. Myek

Department of Chemistry,  
Kaduna State University, Kaduna State, Nigeria

Email: [myekbb@yahoo.com](mailto:myekbb@yahoo.com)

Orcid id: 0000-0001-8241-3236

### M. L. Batari

Department of Scientific and Industrial Research,  
NARICT, Zaria, Kaduna State, Nigeria

Email: [musalatayo@gmail.com](mailto:musalatayo@gmail.com)

Orcid id: 0000-0003-0980-3160

### J. O. Oriajogun

Department of Chemical Advanced Research  
Centre, SHESTCO Sheda, Abuja

Email: [joycejoseph06@yahoo.com](mailto:joycejoseph06@yahoo.com)

Orcid id: 0000-0001-7441-8184

### M. A. Aboki

Department of Scientific and Industrial Research,  
NARICT, Zaria, Kaduna State, Nigeria

Email: [mahmoudaboki@gmail.com](mailto:mahmoudaboki@gmail.com)

Orcid id: 0000-0003-2863-7065

### 1.0 Introduction

Azo dyes are usefully in several industries including textile, leather, plastics, paper, food and cosmetics industries (Cho and Zho, 2007; Somasiri *et al.*, 2006). They are usually strongly coloured compounds which can be intensely yellow, red, orange, blue or even green, depending on the chemical structure. As a result of their colour, azo compounds are tremendous importance as dyes and also as pigments for a long time (Ebenso *et al.*, 2008).

Metal complex dyes play a very important role in the textile industry. Hussain *et al.* (2017) synthesized and characterized metal-azo dye complexes for use in dyeing leather. They found that the fastness properties of unmetallised dyes are less than that of metal complexes dye because metal interacts strongly with leather. However, different metal dye complexes behave differently. For example, Hirdina *et al.* (2004) prepared some reactive mordant azo dyes and found that when dyed wool samples (combination of acid and reactive dyeing conditions) were treated (mordanted) with iron salts (Fe(II), Fe(III)) and a chromium salt (Cr (III)). The iron mordant dyeing showed acceptable wash fastness and light fastness comparable with chromium complexes dyes.

Cr (III) and Co (III) complexes are frequently used for dyeing of wool and synthetic polyamides. Metal complex dyes are applied to the wool either in the pre-metallised form or the complex is prepared "in situ" in the fibre by treatment of dyed wool with chromate or dichromate (Cr (VI)) salts (Zollinger, 1991). Metal complex dye is used in textile, lips, eye shadow, inks, leather finishing and colouring for metals and plastic. Many transition metal form complexes with azo dyes as ligand and have been widely studied in different application such as biological studies (Modhavadiya, 2011; Mamdough *et al.*, 2012), coordination polymers (Hemang *et al.*, 2013), textile industry (Hrdina *et al.*, 2004; Emel and Hamit, 2002), solvent extraction (Shawk *et al.*,

Available at <https://journalcps.com/index.php/volumes>

(Published by Faculty of Physical Sciences, University of Nigeria, Nsukka)

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)

Cobalt and chromium complexes are widely used in the dye industries because of their high degree of wash and light fastness. However, some iron (Fe(II), Fe(III)) complex dyes have been found to exhibit good fastness properties. Consequently, the use of iron salts as a replacement for cobalt and chromium salts can address the eco-friendly requirements needed in the dyeing (Reife *et al.*, 1997). Therefore, in this study, we seek to prepare iron-azo dye complex as a replacement for the more toxic azo dye complexes of chromium and cobalt.

## 2.0 Materials and methods

### 2.1 Materials

Reagents used in the study were analytical grades and included 2-naphthol, hydrochloric acid, iron (II) sulphate, sulphanilic acid and sodium nitrite. The following apparatus/equipments were also used: weighing bottles, beakers, conical flasks, volumetric flasks, glass rod, thermometer, mettler analytical balance, UV, FTIR

### 2.2 Methods

#### 2.2.1 Preparation of the ligand

The dye was prepared with slight modification of the method reported by David (2008). 2-naphthol (0.02 mole) was weighed and dissolved in 20 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> sodium hydroxide solution contained in flask (A) and cooled below the temperature of 5°C using an ice bath. Sulphanilic acid (0.02 mole) was weighed and dissolved in 20 cm<sup>3</sup> of distilled water in a conical flask (B). The solution was also cooled in an ice bath to a temperature below, 5°C. Sodium nitrite (0.01 mole) was weighed and transferred into a test tube (C) and 5 cm<sup>3</sup> of distilled water was added and stirred. The solution of sodium nitrite in test tube (C) was transferred into sulphanilic acid solution in beaker (B). Crushed ice (10 g) was weighed and transferred into a 100 cm<sup>3</sup> beaker (D) and 3 cm<sup>3</sup> of concentrated HCl was added. The solution containing sulphanilic acid with sodium nitrite in flask (B) was transferred into beaker (D) and stirred to form the diazonium salt. The content in flask (A) was transferred into beaker (D) and stirred. The solution was then kept for 24 hours before it was filtered, washed and air dried. The dye was characterized using UV-vis and FTIR.

#### 2.2.2 Preparation of complex dye

The method reported by Ali and Abdul (2011) was adopted with slight modification. A 0.35g of unmetallized azo dye was weighed and transferred into a 100 ml beaker. 50ml of distilled water was added. A second solution was prepared by adding 0.50 g of FeCl<sub>2</sub> to 80ml of distilled water in a 100 ml beaker. The two solutions were mixed together and the pH was adjusted to 8 using NaOH (0.1M). The solution was stirred and then heated on a hot plate at 70°C for 30 minutes. The mixture was kept for 24 hours before it was filtered and then washed with methanol and dried.

## 3.0 Results and Discussion

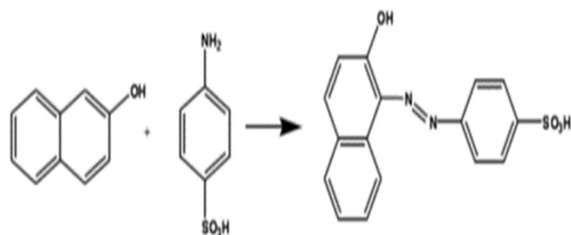
The ligand and its complex were analysed using IR and UV spectrophotometers. The IR- spectra of the ligand complex were recorded to confirm their structures. The vibration frequencies and the corresponding assignment for the ligand and transition metal complex are listed in Table 1. The infrared spectrum of the ligand showed bands at 3767.10 cm<sup>-1</sup>  $\nu$ (O-H). Upon binding to Fe (II) to form a complex, this band shifted to 3773.85 cm<sup>-1</sup> suggesting that there was an interaction of the Fe(II) ion via hydroxyl group (Regina *et al.*, 2007). The peaks observed at 3061.13 cm<sup>-1</sup> and 3020.50 are attributed to the aromatic C-H group in the ligand and in the complex respectively. The peak at 2266.43 cm<sup>-1</sup> is due to C=N in the ligand which slightly increased to 2275.11 cm<sup>-1</sup> in the complex.

**Table 1. Infrared signals of the ligand and its complex (cm<sup>-1</sup>)**

Functional group	Ligand	Complex
O-H	3767.10	3773.85
C-H	3061.13	3020.50
C=N	2266.43	2275.11
C-C	1396.51	1474.63

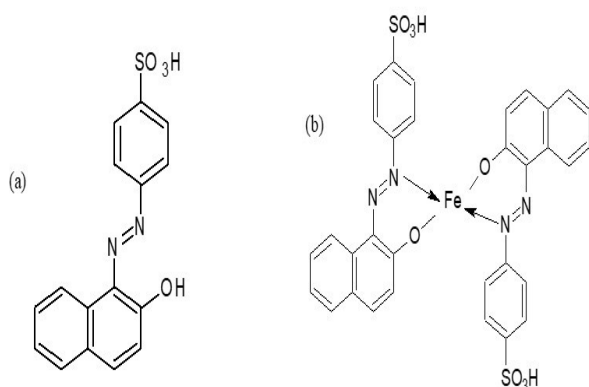
The ligand exhibited an absorption maximum at 483.50nm. However, upon formation of a complex with Fe(II), the maximum absorption band was shifted to 479.50 suggesting an interaction of the Fe(II) with the ligand. These results are in agreement with the result obtained by Regina *et al.* (2007) which indicates that this band shift is caused by the binding of the metal with the ligand.





**Fig. 1: Reaction scheme showing the synthesis route of the ligand**

The synthesized ligand and its metal complex are soluble in water. The colour of the ligand is orange while that of the complex is brown. The prepared complex is stable at room temperature. It has a chemical formula of  $C_{34}H_{28}FeN_2O_8S_2$  while its formula weight is 740.58g. Calculated percentage composition of elements in the complex are C(55.14), H(3.81), Fe(7.54), N(7.57), H(3.81), Fe(7.54), N(7.57), O(17.28) and S(8.66).



**Fig. 2: structure of the ligand (acid orange 7), (a) and its complex (b)**

#### 4.0 Conclusion

We were able to synthesized iron complex azo dye using acid orange 7 as the ligand. This investigation shows that it is possible to prepared brown complex azo dye for fabres to replace Cr and other toxic metal complex azo dye. Results obtained from analysis indicate that the ligand can chelates with the complex and exhibit properties that are closely related to established textile dye metal complexes.

#### 5.0 References

Ali A. I. & Abdul Z. (2011). Synthesis, characterization and spectroscopic properties of

new azo-dyes and azo-metal complexes derived from 8-hydroxyquinoline. *Basrah Journal of Science*, 28, 1, pp. 15-36.

David, C. (2008). *Synthesis and use of Fabric Dyes*. Chemical, Environmental and Biotechnology Department, College of Applied Arts and Technology, Mohawk, Canada. pp 1-20.

Zollinger, H. (1991). *Color Chernistry-Synthesis, Properties and Applications of Organic dyes an Pigments*; 2nd Edition, VCH Weinheim, pp 108.

Modhavadiya, V. A. (2011). Synthesis, characterization and antimicrobial activity of metal complexes containing azo dye ligand of sulfa drugs. *Asian Journal of Biochemistry and Pharmaceutical Research*, 11,1,173-179.

Mamdouh, S. M., Sawsan, S. H., Alaa , E. A. & Nessma, M. N. (2012). Synthesis and spectroscopic characterization of gallic acid and some of its azo complexes. *Journal of Molecular Structure*, 1014, pp. 17-25.

Hemang, M. S., Yogesh, K. S.& Ashish, R. S. (2013). Synthesis, characterization and antimicrobial studies of coordination polymers. *Research Journal of Chemistry*, 3, 1, pp. 48-56.

Hrdina, R., Lustinec, D., Stolin, P., Burgert, L., Lunak, Jr S. &Holcapek, M, (2004). Iron complexes of reactive azo dyes. *Advanced Collour Science and Technology*, 7, 1, 6-17.

Hussain, G., Abass, N., Shabir, G., Athar, M., Saeed, A., Saleem, R., Ali, F. & Khan, M. A. (2017). New acid dyes and their metal complexes based on substituted phenols for leather: synthesis, characterization and optical studies. *Journal of Applied Research and Technology*, 15, 4, pp. 346-355.

Emel, Y., Hamit, B. (2002)."Synthesis of novel acidic mono azo and an investigation of their use in the textile industry. *Turkish Journal of Chemistry*, 26, pp. 897-903.

Shawket , K. J., Zainab, A. M. & Rafa, M. D. (2011). Solvent extraction of Co (II) from aqueous solutions by new ligand 2-[(4-chloro-2-methoxy phenyl)azo]-4,5-diphenyl imidazole. *Journal of the Thi-Quar University*, 7, 1, pp. 50-60.

Banjit, B. & Sudarsan, B. (2009). Spectrophotometric determination of zinc in blood serum of diabetic patients using bis-[2,6-(2-hydroxy-4-sulpho-1'-naphthylazo)] pyridine disodium salt". *Archives of Applied Science Research*, 1, 1, pp. 74-83.



- Girish, B. V. & Raksha, V. Z. (2011). Synthesis and analytical studies of some azo dyes as ligands and their metal chelates. *International Journal of Chemical Science*, 9, 1, pp. 87-94.
- Chauhan, O. S., Varma, Y. S., Ishwar, S., Garg, B. S. & Singh, R. P. (1980). Spectrophotometric determination of cadmium (II) and mercury (II) with water soluble pyridinalazo dyes. *Proceeding of the Indian Natural Science Academy*, 46, 4, pp. 369-373.
- Amer, J. J., Khalida, F. S. & Ahmed, L. H. (2010). Synthesis and spectroscopic studies of new heterocyclic azo dye and their complexes with selected metal ion". *Al- Mustansiriya. Journal of Science*, 21, 6, pp. 251-257
- Savic, J. & Vasic, V. (2006). Complex formation between pd(II) and immobilized imidazole azochromotropic acid. *Acta Chimica Solvanica*, 53, pp. 36-42.

