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Synthesis, Characterization, Biological and Industrial Applications of Co (II), Ni (II), Cu (II) and Zn (II) Complexes with Azo Dye Ligands

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Abstract: The largest class of synthetic colorants are azo dyes considered as effective ligands of transition metals generating complexes with improved properties relative to free dyes. This work discusses the characterization, synthesis and the applications regarding Ni (II), Co (II), Zn (II), and Cu (II) complex with azo dye ligands. FT-IR, NMR, thermal, X-ray diffraction, and UV-Vis techniques are commonly utilized for characterizing the complexes, which are usually prepared by diazotization–coupling followed by coordination with metal salts. Analytical results prove coordination through phenolic oxygen and azo nitrogen, which lead to stable structures with adjustable geometries and altered electronic transitions. The complexes have considerable cytotoxic, antioxidant and antimicrobial activities in the biology, with Cu (II) species giving the best. Their optical and electronic versatility finds application in the industry in advanced materials, textile dyeing, sensors, and catalysis. The findings indicate the viability of azo dye metal complexes in industry and biomedical fields and also the multifunctionality of the complex.

Keywords: Complexes, Azo Dye Ligands, Antimicrobial Activity, Spectroscopic Characterization, Textile Applications, Catalysis.

Research Paper

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INTRODUCTION

Azo dyes are considered as the largest class of synthetic organic dyes, and no less than 60 percent of all commercial colorants produced in the world are azo dyes. Such compounds are characterized through the existence regarding azo groups (-N=N-), at least one of them present in the molecular structure. These groups are not only good chelating sites to coordinate the metal but also impart vibrant colors. The coordination chemistry has revealed new directions due to the combination of transition metals and azo dyes creating metal complexes with various applications and better properties.

Transition metal complexes regarding Co (II)-Ni (II)-Cu (II)-Zn (II) were of great interest due to the differences in electronic configurations, variable oxidation states and different coordination geometries. Unlike their free ligands, the metals have remarkable characteristics including enhanced stability, change in electronic spectra, and increased biological activities when they form complexes with azo dye ligands.

In addition to the traditional use in the textile sector, azo dye metal complexes are important. Recent studies have demonstrated their potential as catalysts, antimicrobial agents, anticancer medications, functional materials in various technological applications. The flexibility of these complexes is due to the ability to change the metal center and the azo ligand structure to select the properties specifically for meeting the requirements regarding a certain application. Also, the figure 1 shows an example from the literature for the Complexes with Azo Dye Ligands synthesized by Gehad *et al.,* in 2020 [1].

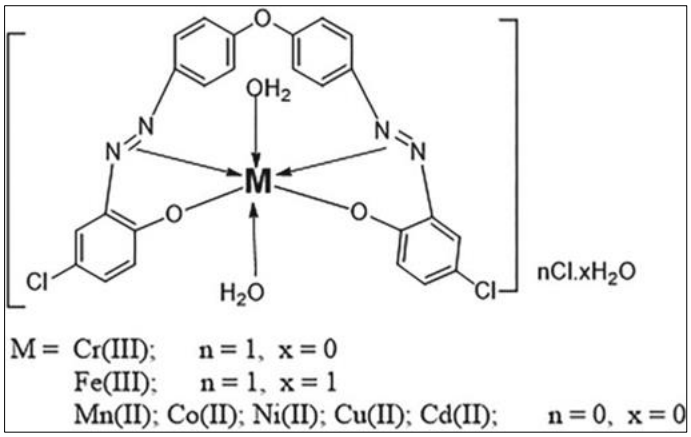


Figure 1: Gehad *et al.*, Complexes with Azo Dye Ligands [1]

Azo dyes are naturally colored substances that, when synthesized, take on a variety of colors, including orange, red, and yellow. Traditionally, azo dyes have been used to impart color to various goods, like apparel, paper, food, cosmetics, pharmaceuticals, and many more [2].

Containing an emphasis on synthesis approaches, characterization methods, also their industrial and biological applications, this study offers a thorough summary of the present state of knowledge of Co (II), Ni (II), Cu (II), and Zn (II) complexes containing azo dye ligands.

1. Inorganic Chemistry of Azo Dye Ligands

Two hybridized carbon atoms, which are often but not always a part of aromatic systems, are joined by an azo group—-N = N— in azo dyes [3]. An amine or phenol connected to a diazotized amine makes up azo dyes. Most azo dyes consist of one azo group, but others have two (disazo), three (trisazo), or even more. Based on the exact structure regarding molecule, azo dyes can be used to create a broad variety of hues [4]. Azo dye compounds could be found in the color's orange, yellow, brown, red, also blue. The degree of conjugation related to azo dye varies depending on which aromatic rings are substituted [5]. It is well known that molecule's ability to absorb visible light at specific wavelength depends on the size regarding its conjugated system. Take the next example: (longest π system) → yellow → orange → red → green → blue.

2. Synthesis Methods of Azo Dyes Ligands

Diazotization and coupling reactions are the two phases in the traditional azo dye preparation process. In the case when primary aromatic amines treated with the ice-cold nitrous acid in aqueous acid medium, diazonium salts—poor electrophiles and unstable—are created. Temperature is maintained between 0 and 5 degrees Celsius. Electrophilic substitution occurs in relation to coupling reactions with the electron-rich species, such as hydroxy or amino compounds, following the completion of diazotization. In order to give the diazonium salt the highest stability without deactivating nucleophile, the coupling usually takes place in the site related to electron-rich density, such as ortho or para position. For example, coupling with naphthalene or phenol requires alkaline medium with pH range between 7 and 11. However, coupling with aromatic amine requires pH range between 1 and 5 [6].

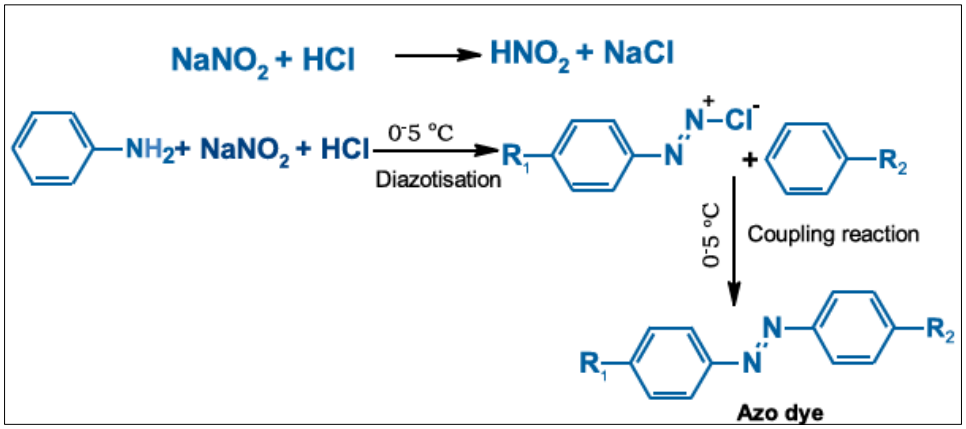


Fig. 2: Classical method of azo dye synthesis [6]

Bingtao Tang, Jinjing Qiu, Benzhi Ju, *et al.,* for creating dispersion azo dyes depending on 2,6-dibromo-4-nitroaniline, the authors created clean synthesis method. Large yields could be produced fast and

effectively with this safe, energy-efficient method. Solid diazonium salt that is stable and could be held with less sulfuric acid, is utilized throughout synthesis for preventing the production regarding waste inorganic salt as well as reducing system's heat output by 88.5%. The depletion regarding all distributed azo dyes is more than 96% in comparison with standard process of synthesis [7].

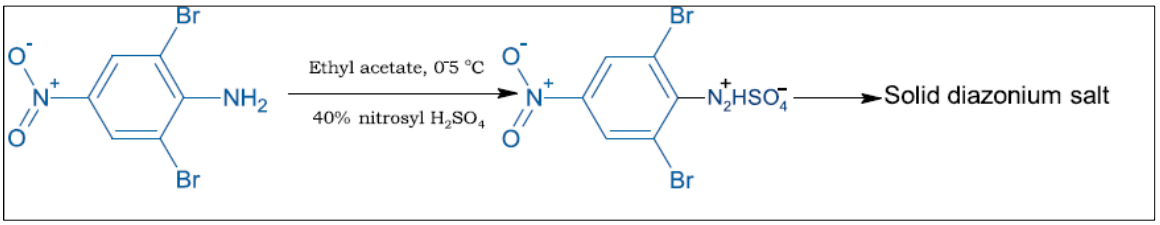


Fig. 3: Clean synthesis of disperse azo dyes depending on stable 2,6-dibromo-4-nitrophenyl diazonium salts [7]

Non-symmetrical azo dyes were developed. In the case when nitroarenes transformed into nitroso arenes, aromatic amines acting as reductant. Large amounts of a variety of water-soluble and dispersed azo hues are after that produced by combining the same aromatic amine with nitroso arenes. Thus, less expensive aniline derivatives are serving as coupling substrate and reductant, eliminating the need for expensive or hazardous metals. Aniline or electron-rich aromatic amines were used for quickly and efficiently create a variety regarding unsymmetrical azo dyes in up to 97% yields utilizing microwave (MW) approach.

The present approach related to the synthesis of azo dye is superior to several other methods now in use due to its catalyst-free environment, rapid reaction, absence regarding work-up as well as purification processes, using greener medium, also higher yields, figure 4 [8].

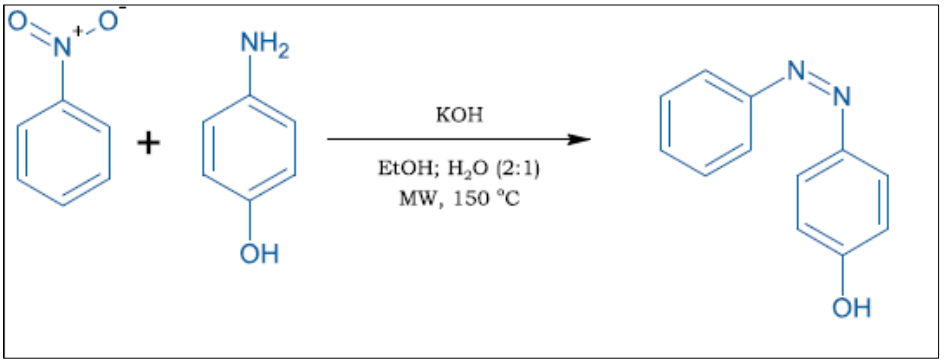


Fig. 4: Microwave assisted synthesis of azo dyes

Filimonov and associates have synthesized novel colors using the free grinding diazotization process. After three minutes of grinding a mixture of sodium nitrite, heterocyclic amine, and silica-supported boron trifluoride, they added deionized water and stirred for about two minutes at room temperature. For obtaining the dyes, they subsequently coupled heterocyclic coupling component while stirring continuously for two minutes. The resultant dye soaked in chloroform and filtered for removing the catalyst. Ethanol is used to recrystallize the resultant product. The newly developed grinding procedures are safe and environmentally beneficial. Additionally, it provides considerable selectivity, clarity, simplicity, ease of use, low time consumption, and good yield, Figure 5.

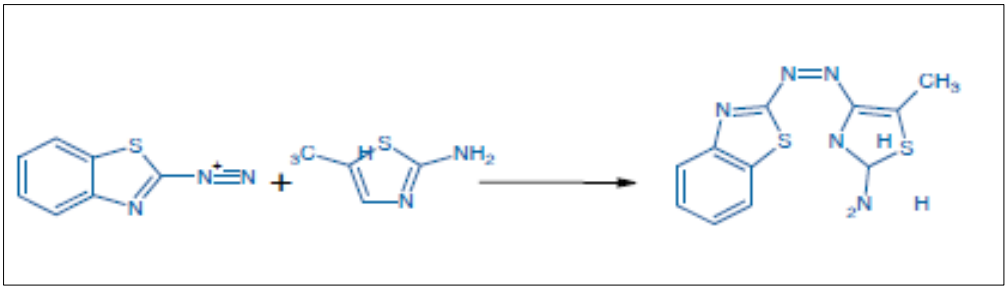


Fig. 5: One step facile synthesis of azo dyes

3. Synthesis of Azo Dye Complexes

4.1 General Synthetic Approach

The synthesis regarding transition metal complexes with the azo dye ligands follows a direct complexation method involving the reaction regarding hydrated metal salts with the organic ligand in appropriate solvents.[9] The general reaction can be represented as:

$$M^{2+} + nL \rightarrow [ML_n]^{2+}$$

where M = Co(II), Ni(II), Cu(II), or Zn(II), and L represents the azo dye ligand.

3.2 Solvent Systems and Reaction Conditions

For complex formation to be successful, the solvent system selection is essential. Typical solvents used are water-soluble azo dyes and metal salts can be used in aqueous systems. Media that contains alcohol: For moderate polarity requirements, methanol and ethanol are commonly utilized. Solvents in mixtures: For many systems, water-ethanol mixtures offer ideal conditions. In addition, for ligands that are not very soluble in traditional solvents, DMSO/DMF is utilized. Controlling the pH and temperature are important factors. Depending on the particular metal-ligand system, the majority of syntheses are carried out at temperatures between room temperature and 80°C, with pH values normally maintained between 6 and 9 [10].

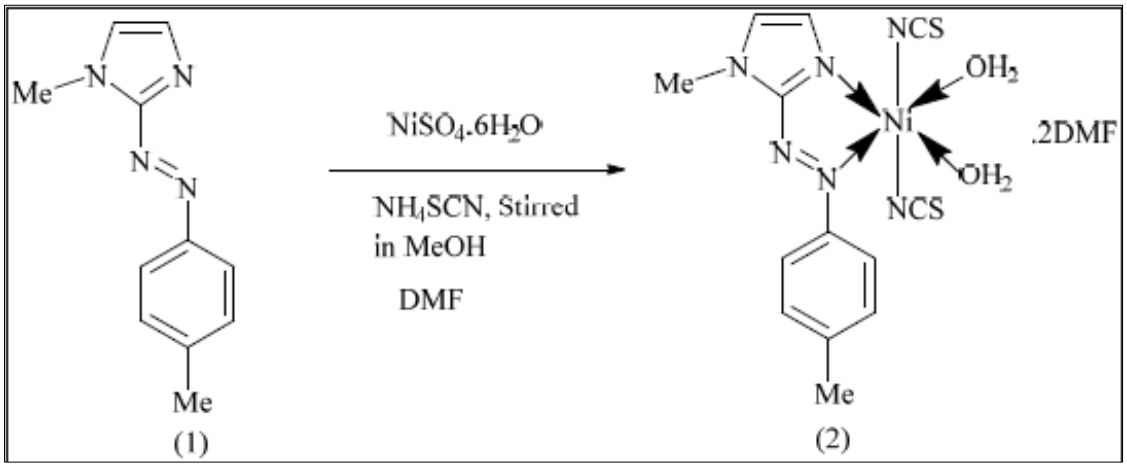
3.3 Metal Salt Selection

The choice of metal salt significantly influences the reaction outcome:

- **Chloride salts:** $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$
- **Nitrate salts:** $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$
- **Acetate salts:** Often preferred due to their buffering capacity and reduced tendency for hydrolysis.

4. Synthesis of Complexes with Azo Dye Ligands

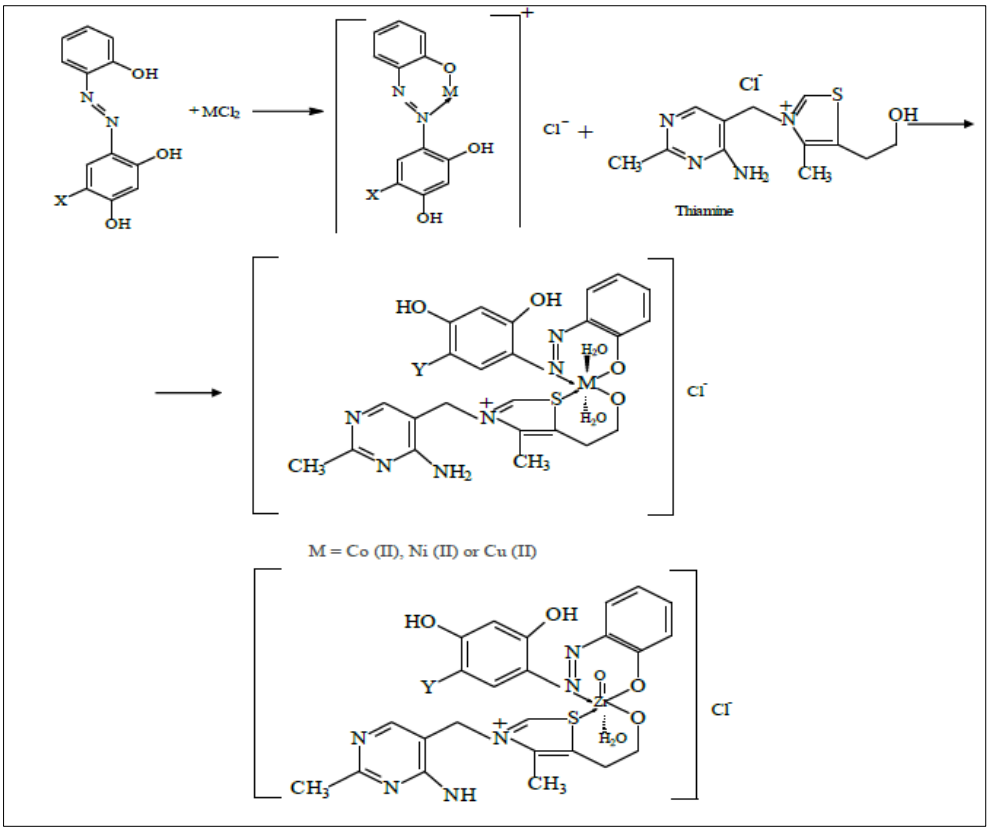
After isolating X-ray-quality crystals regarding complex in DMF solvent, C. Sinha *et al*., created a mononuclear bis-chelated Ni(II) complexes (2) by reacting NiSO4.6H2O and NH4HCN with 1-alkyl-2-(arylazo)imidazoles azo-imine ligand (1) earlier in 2005. The complex has been characterized using a variety of microanalytical methods, like magnetic and thermal analyses. According to the X-ray crystallographic data, the ligand (I) forms a deformed octahedral complex with the azo-N and imidazole-N atoms when it binds to the Ni(II) ion in benate mode, as seen in Scheme 1 [11].



Scheme 1: The synthetic route for mono-nuclear bis-chelate Ni(II) complex (2) with imidazole-based azo ligand (1)

Moustafa and Abdellattif in 2017 describe the characterization and synthesis regarding new mixed-ligand complexes that include metal ions Co(II), Ni(II), Cu(II), and Zr(IV) as secondary ligands, thiamine hydrochloride (vitamin B1) as primary ligand, also azo dye derivatives as secondary ligands.

The complexes have been prepared in 1:1:1 molar ratio (thiamine: azo dye: metal) and a description was made using thermal analysis (TGA), FT-IR, elemental analysis, UV-Vis spectroscopy, magnetic susceptibility tests, also molar conductivity. The complexes are reported to be octahedrally geometrical with azo dyes coordinating with oxygen/nitrogen (ON mode) and thiamine coordinating with sulfur (OS mode) [12].



Scheme 2: Abdellattif and Moustafa method for synthesizing new Ni (II), Co (II), and Cu (II) Complexes with Azo Dye Ligands

5. Characterization Techniques

6.1. Infrared Spectroscopy (FTIR)

FTIR spectroscopy is also a very useful tool in the characterization of azo dye metal complexes, which can be used to provide a great deal of information regarding the coordination mode and bonding interactions. The typical characteristic azo stretching vibration (N=N ν) is observed in the 1450-1600 cm^{-1} range of free azo dyes. With the complexation, this band tends to move to lower frequencies because of the coordination regarding the azo nitrogen to metal center.

C=N stretching (1580-1650 cm^{-1}), C=C aromatic stretching (1400-1600 cm^{-1}), also C-O stretching in phenolic groups (1200-1300 cm^{-1}) are other significant vibrational modes. The formation of coordination bonds is justified by the appearance of new bands in the low-frequency region (200-600 cm^{-1}) related to M-N and M-O stretching vibrations.

The recent research has utilized FTIR spectroscopy as a technique to not only characterize the structure of the complexes, but also to study the stability of the complexes in various conditions. This method has been found to be especially useful in separation of various coordination modes of polydentate azo ligands.

6.2 Electronic Spectroscopy (UV-Vis)

The UV-Vis spectroscopy offers very important data concerning electronic structure as well as coordination geometry regarding azo dye metal complexes. The spectra normally contain strong bands in the visible range, which are a result of π→π* transition of the azo chromophore, metal centered d-d transitions as well as charge transfer bands.

The extension of the conjugated system during the process of coordination usually results in the red-shift of λmax values of azo dye complexes relative to their free ligands. Their position and intensity are sensitive to the coordination environment and can be used to determine the geometry and electronic configuration of metal center.

In the case of Cu (II) complexes, square planar geometry d-d transitions can be observed at about 600-700 nm, and tetrahedral geometry d-d transitions can be observed at about 800-900 nm. There are typical bands of Ni (II) complexes of 400-500 nm (octahedral) or 600-700 nm (tetrahedral). Spin-orbit coupling causes Co (II) complexes to have many bands within the visible region.

6.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H NMR as well as ^{13}C NMR spectroscopy can give comprehensive structural data on the organic structure of azo dye ligands and complexes. In the case of diamagnetic complexes (e.g. complexes with Zn (II)) the NMR spectroscopy may be used to display the

change in chemical shifts and in the patterns of the couplings induced by the coordination.

The aromatic protons of the azo dye ligands are normally observed in the range of 7-8 ppm whereas the azo bridge protons are observed to exhibit characteristic chemical shifts about 8-9 ppm. When complexed, these signals can undergo major changes owing to effects of magnetic anisotropy of the metal center.

The [13]. C NMR spectroscopy has found application especially in determining the coordination sites of multidentate azo ligands. The carbon atoms next to coordinating nitrogen and oxygen atoms exhibit typical downfield shifts upon metal binding.

X-ray Diffraction (XRD)

The most conclusive method of establishing the molecular structure and coordination geometry of azo dye metal complexes is single crystal X-ray diffraction. The technique gives accurate bond lengths, bond angles and intermolecular interactions, which are vital in understanding the structure-property relationships.

Powder X-ray diffraction is widely used to identify phases and determine purity of bulk samples. Depending on the polymorphic form, the technique can be used to distinguish between various forms and the presence of impurities or unreacted starting materials.

The recent crystallographic observations have shown some interesting structural characteristics which include π-π stacking interactions, hydrogen bonding networks and supramolecular assemblies in azo dye metal complex. These non-covalent interactions are also important in determining the properties of the solid state and possible uses of these materials.

3.5 Thermal Analysis

Thermal analysis approaches, like DTA), TGA, and DSC are useful in giving information on the thermal stability and decomposition behavior regarding azo dye metal complexes.

The presence of coordinated water molecules is usually detected in TGA studies, and they are lost at temperatures of about 100-150 Celsius. The decomposition of the organic ligands typically takes place at higher temperatures (250-400 Celsius) followed by metal oxide formation as final residues. Complexes tend to have better thermal stability than free ligands because the coordination of the metal provides stability.

Phase transitions, melting points and crystallization processes can be detected by DSC analysis. Applications that need high-temperature stability or special processing requirements are significant in these thermal properties.

6. Biological Activity of Co(II), Ni(II), Cu(II), and Zn(II) Complexes with Azo Dye Ligands

Strong antimicrobial, antioxidant, cytotoxic, and DNA-binding qualities are among the many biological activities displayed by azo dye metal complexes. Due to the synergistic effects regarding the metal center and azo ligand, their antimicrobial efficacy frequently outperforms that of free ligands and some common antibiotics. Cu(II) complexes exhibit special promise against strains that are resistant to multiple drugs [13]. Through metal chelation, lipid peroxidation inhibition, and radical scavenging, they also exhibit noteworthy antioxidant activity that typically outperforms that of free ligands. DNA binding/cleavage, apoptosis induction, ROS generation, and enzyme inhibition are the mechanisms by which cytotoxic and anticancer studies demonstrate selective toxicity toward cancer cells (HepG2, MCF-7, A549, and HCT-116) with activity on par with that of well-known medications. Viscosity changes, fluorescence quenching, and spectroscopic shifts all support the intercalative and groove-binding modes confirmed by DNA-binding studies, underscoring their potential as diagnostic and therapeutic agents [13].

7. Industrial Applications of Ni(II), Co(II), Zn(II), and Cu(II) Complexes with Azo Dye Ligands

Azo dye metal complexes have wide-ranging industrial applications because of their stability, tunable electronic properties, and multifunctionality. They serve as effective, recyclable catalysts for polymerization, oxidation, and C–C coupling reactions in catalysis; complexes of Cu(II), Co(II), Ni(II), and Zn(II) exhibit special promise in controlled and environmentally friendly synthesis. By enhancing color fastness, adding antimicrobial activity, and enabling functional textiles with conductivity, flame retardancy, or UV protection, they improve dye performance in the textile industry [14].

Also, due to their optical responsiveness, they may find application in sensor applications as selective detectors for gases, pH changes and dangerous metals. The azo dye complexes in materials science underlie the advanced technologies of liquid crystals, magnetic systems, and nonlinear optical materials, used in data storage, photonics, and displays. Their multiple applications highlight the importance of their application as multi-purpose, sustainable materials in modern industry [15].

CONCLUSIONS

In conclusion, Ni (II), Co (II), Zn (II), and Cu (II) complexes with azo dye ligands exhibit the excellent structural, biological, and industrial interest. Stable coordination through azo nitrogen as well as oxygen donor atoms is established through spectroscopy and thermal analysis in comparison to free ligands, resulting in better stability and adjustable geometries. The

complexes possess significant antioxidant and antimicrobial properties, and Cu (II) species has the highest bioefficacy.

Besides their biological potential, these complexes have diverse industrial applications, including dyeing of textiles, catalysis, also functional materials for photonic and sensing technologies. Altogether, the versatility of azo dye metal complexes highlights their possible multi-purpose agents in both industrial and biomedical fields, and they should be further explored to be applicable in more advanced applications.

REFERENCES

1. Ra, U.; Mahendiran, D.; Kumar, R.; Rahiman, K., Metal complexes of tetradentate azo-dye ligand derived from 4, 4′-oxydianiline: Preparation, structural investigation, biological evaluation and MOE studies. *Appl. Organomet. Chem* 2019, *33* (7), e4946-4966.
2. Eltaboni, F.; Bader, N.; El-Kailany, R.; Elsharif, N.; Ahmida, A., Dyes: A comprehensive review. *J. Chem. Rev* 2022, *4* (4), 313-330.
3. Tasli, P. T.; Atay, Ç. K.; Demirturk, T.; Tilki, T., Experimental and computational studies of newly synthesized azo dyes based materials. *Journal of Molecular Structure* 2020, *1201*, 127098.
4. Mezgebe, K.; Mulugeta, E., Synthesis and pharmacological activities of azo dye derivatives incorporating heterocyclic scaffolds: a review. *RSC advances* 2022, *12* (40), 25932-25946.
5. Al-Rufaie, M., Synthesis and analytical studies of 3-((4-acetyl-3-hydroxyphenyl) diazenyl)-4-amino-n-(5-methylisoxazol-3-yl) benzene sulfonamide. With some metals. *Australian Journal of Basic Applied Sciences* 2016, *10* (6), 9-14.
6. Khanum, R.; Ali, R. S.; Rangaswamy, H.; Kumar, S. S.; Prashantha, A.; Jagadisha, A., Recent review on Synthesis, spectral Studies, versatile applications of azo dyes and its metal complexes. *Results in Chemistry,* 2023, *5*, 100890.
7. Qiu, J.; Tang, B.; Ju, B.; Zhang, S.; Jin, X., Clean synthesis of disperse azo dyes based on peculiar stable 2, 6-dibromo-4-nitrophenyl diazonium sulfate. *Dyes Pigments,* 2020, *173*, 107920.
8. Thakuri, A.; Banerjee, M.; Chatterjee, A., Microwave-assisted rapid and sustainable synthesis of unsymmetrical azo dyes by coupling of nitroarenes with aniline derivatives. *Iscience* 2022, *25* (6).
9. Maurya, M. R.; Khurana, S.; Shailendra; Azam, A.; Zhang, W.; Rehder, D., Synthesis, Characterisation and Antiamoebic Studies of Dioxovanadium (V) Complexes Containing ONS Donor Ligands Derived from S-Benzyldithiocarbazate. *European Journal of Inorganic Chemistry* 2003, *2003* (10), 1966-1973.
10. Refat, M. S.; Al-Maydama, H. M.; Al-Azab, F. M.; Amin, R. R.; Jamil, Y. M., Synthesis, thermal and spectroscopic behaviors of metal–drug complexes: La (III), Ce (III), Sm (III) and Y (III) amoxicillin trihydrate antibiotic drug complexes. *Spectrochimica Acta Part A: Molecular Biomolecular Spectroscopy,* 2014, *128*, 427-446.
11. Ray, U.; Banerjee, D.; Liou, J.-C.; Lin, C.-N.; Lu, T.-H.; Sinha, C., Iron (II) and nickel (II)-thiocyanato complexes of 1-alkyl-2-(arylazo) imidazole: single crystal X-ray structure of [Fe (MeaaiEt) 2 (NCS) 2](MeaaiEt= 1-ethyl-2 (p-tolylazo) imidazole) and [Ni (MeaaiMe)(NCS) 2 (H2O) 2]· 2DMF (MeaaiMe= 1-methyl-2 (p-tolylazo) imidazole). *Inorganica chimica acta,* 2005, *358* (4), 1019-1026.
12. Moustafa, I.; Magda, H., Synthesis, spectroscopic studies and biological evaluation of Co (II), Ni (II), Cu (II) and Zr (IV) complexes of azo dyes and thiamine hydrochloride as antimicrobial agents. *Mod. Chem. Appl,* 2017, *5*, 1000202.
13. Al-Hassani, R. A., Synthesis, Characterization, Antimicrobial and Theoretical Studies of V (IV), Fe (III), Co (II), Ni (II), Cu (II), and Zn (II) Complexes with Bidentate (NN) Donar Azo Dye Ligand. *Baghdad Science Journal,* 2016, *13* (4), 25.
14. Al-Hassani, R. A., Synthesis, Characterization, Antimicrobial and Theoretical Studies of V (IV), Fe (III), Co (II), Ni (II), Cu (II), and Zn (II) Complexes with Bidentate (NN) Donar Azo Dye Ligand. *Baghdad Science Journal,* 2016, *13* (4), 25.
15. Ozkan, G.; Kose, M.; Zengin, H.; McKee, V.; Kurtoglu, M., A new Salen-type azo–azomethine ligand and its Ni (II), Cu (II) and Zn (II) complexes: Synthesis, spectral characterization, crystal structure and photoluminescence studies. *Spectrochimica Acta Part A: Molecular Biomolecular Spectroscopy,* 2015, *150*, 966-973.