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Studies on Transition Metal Chelates of Azo Ligand Containing Bon Acid

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ABSTRACT:

New azo ligand i.e. 3-hydroxy-4-((5-(furan-2-yl)-1,3,4-oxadiazol-2-yl)-2-naphthoic acid (**DAFOBA**) was prepared by coupling reaction between the diazonium salt of 2-amino-5-(furan-2-yl)-1,3,4-oxadiazol (**AFO**) and bon acid (**BA**). The structure of azo ligand was characterized on the basis of elemental analyses, NMR, FT-IR and UV-Vis spectroscopic techniques. Transition metal chelates of prepared azo ligand have been synthesized and characterized. The structure of metal chelates has been confirmed by using elemental Analysis along with metal content determination, FT-IR, reflectance spectra as well as magnetic susceptibility measurements. Analytical data revealed that all the complexes exhibited 1:2 metal-ligand ratios. Also the biological evaluation of all the synthesized compounds was carried out.

KEY WORDS: 2-amino-5-(furan-2-yl)-1,3,4-oxadiazol, Bon acid, Dyeing study, spectral study, Biological activities.

INTRODUCTION:

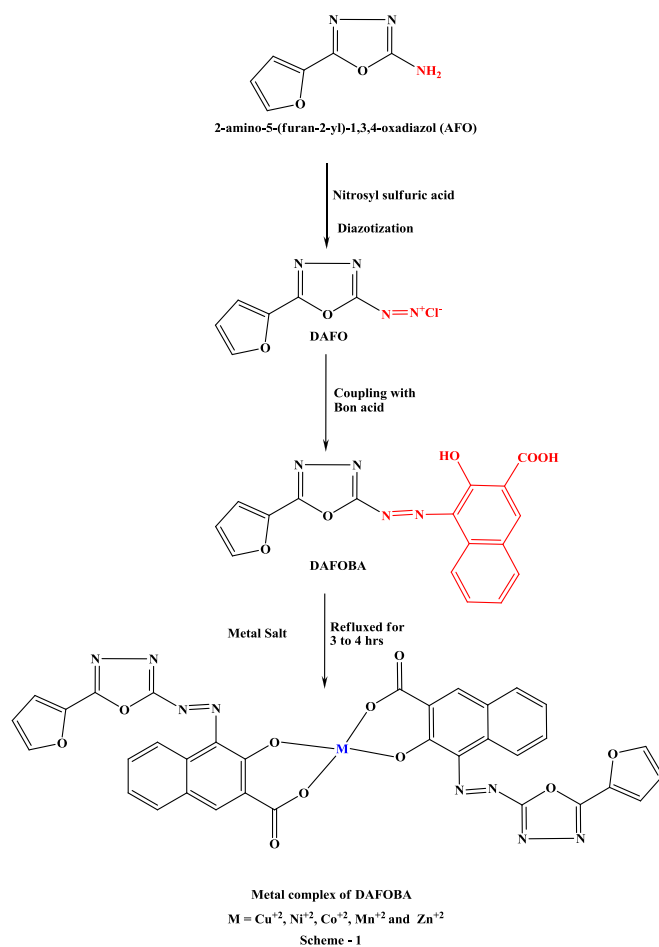
Numerous azo dyes are synthesized and established in different dyeing as well as other industries. Azo dyes are have been widely studied recently for the reason that of their ease of availability, affordable price and some useful applications^[1,2]. The wider applications of azo dyes results with several types of the heterocyclic compounds^[3-5]. More particularly their versatile application in various field, such as dyeing textile fiber, food, biomedical studies, in organic synthesis as well as in high technology areas such as laser, liquid crystalline displays, electro-optical devise and ink-jet printers, optical recording medium^[2, 6-8]. Recently azo metal chelates have been given growing interest due to their useful biological properties and enzymatic decolourization field^[9,10].

In previous studies, the one of the authors reported synthesis and characterization of various metal chelates containing azo dye compounds and their biological properties^[11,12]. In the present investigation the synthesis of azo dyes synthesized by coupling of oxidazole

derivative containing furan ring and bon acid. The transition metal chelates of new azo ligand were prepared and confirmed using different spectral studies. Also the biological evaluation was discussed for all synthesized compounds.

MATERIALS AND METHODS

The elemental contents were determined by Thermo Finigen Flash1101 EA (Italy) the metals were determined volumetrically by Vogel's method^[13]. To a 100 mg chelate sample, each 1 ml of HCl, H₂SO₄ and HClO₄ were added and then 1 g of NaClO₄ was added. The mixture was evaporated to dryness and the resulting salt was dissolved in double distilled water and diluted to the mark. From this solution the metal content was determined by titration with standard EDTA solution. Infrared spectra of the synthesized compounds were recorded on Nicolet 760 FT-IR spectrometer. NMR spectrum of DAFOBA was recorded on 60 MHz NMR spectrophotometer. Magnetic susceptibility measurement of the synthesized complexes was carried out on Gouy



Scheme-1 General synthetic procedure for DAFOBA and their metal chelates

Balance at room temperature. Mercury tetrathiocyanatocobalate (II) $\text{Hg}[\text{Co}(\text{NCS})_4]$ was used as a calibrant. The electronic spectra of complexes in solid were recorded on at room temperature. MgO was used as reference. Biological activity of all synthesized compounds was evaluated against various biological strains by following reported method^[14].

2-amino-5-(furan-2-yl)-1,3,4-oxadiazol (**AFO**) was prepared according to reported method^[15]. All other chemicals and solvents used were of laboratory grade.

Synthesis of 3-hydroxy-4-((5-(furan-2-yl)-1,3,4-oxadiazol-2-yl)-2-naphthoic acid (**DAFOBA**):

2-amino-5-(furan-2-yl)-1,3,4-oxadiazol (**AFO**) (0.01mole) was dissolved in a mixture of H_2SO_4 (12ml) and water (15ml) and cooled to 0°C in ice bath. To this solution a cold aqueous solution of sodium nitrite (0.04mole) was added. The diazonium salt solution of AFO was filtered into a cooled solution of Bon acid (**BA**,

0.01mole) at $0-5^\circ\text{C}$. The resulting solid azo dye was washed with water, dried and recrystallized from, MeOH. Yield: 72%, M.P.256-258 $^\circ\text{C}$ (decompose) uncorrected. The characterization data of **DAFOBA** ligand is described in following **Table-1**.

Preparation of metal chelates of 3-hydroxy-4-((5-(furan-2-yl)-1,3,4-oxadiazol-2-yl)-2-naphthoic acid (**DAFOBA**):

The metal chelates of DAFOBA with Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , and Zn^{2+} metal ions were prepared in two steps. The general procedure for the metal chelates is as follows;

(1) Preparation of DAFOBA solution:

DAFOBA (0.05 mol) was taken in 500 ml beaker and formic acid (85% v/v) was added up to slurry formation. To this slurry water was added till the complete dissolution of DAFOBA. It was diluted to 100 ml.

Synthesis of DAFOBA-metal-chelates:

In a solution of metal acetate (0.005 mol) in acetone: water (50:50 v/v) mixture (40 ml) the 20 ml of above mentioned DAFOBA solution (i.e. containing 0.01 M DAFOBA) was added with vigorous stirring at room temperature. The appropriate pH was adjusted by addition of sodium acetate for complete precipitation of metal chelate. The precipitates were digested on a boiling water bath. The precipitates of chelate were filtered off, washed by water and air-dried.

UV - Visible spectral analysis

UV - Visible spectra of DAFOBA was analysed for solution (1.0×10^{-3} mg/ml) prepared in acetone using SHIMADZU A-20 SPECTROPHOTOMETER. The concentration of the dye in the solution was 1.0×10^{-3} mg/ml. From the visible spectrum, the values of λ_{max} and the absorbance corresponding to the λ_{max} were read and molar extinction co-efficient (ϵ) values are estimated using Lambert-Beer's equation.

RESULTS AND DISCUSSION

The resulted DAFOBA ligand was in form of amorphous powder. The C,H,N contents of DAFOBA their metal chelates along with metal content (**Table-1**) are consistent with the predicted structures as shown in **Scheme-1**.

The IR spectrum of the ligand DAFOBA (**Figure-1**) shows a broad OH stretching band in range 3200-3400 cm^{-1} . The free ligand IR spectrum shows a very stronger band at 1682 cm^{-1} due to stretching frequency for CO group of COOH. The IR spectrum of DAFOBA also shows the important bands at 1632 and 1578 cm^{-1} due to azo group. Also bands for aromatic carbon and C-O-C stretching of furan ring were found at 2850-2950 and 1357 cm^{-1} , respectively. In case of IR spectra of all transition metal chelates almost identical bands were found as its parent ligand, the only discrete band found due to formation of metal-ligand bonding that supports the coordination of metal to the respective ligand. Also all the metal chelates having absence of band characteristic for free -OH group support the metal chelate formation.

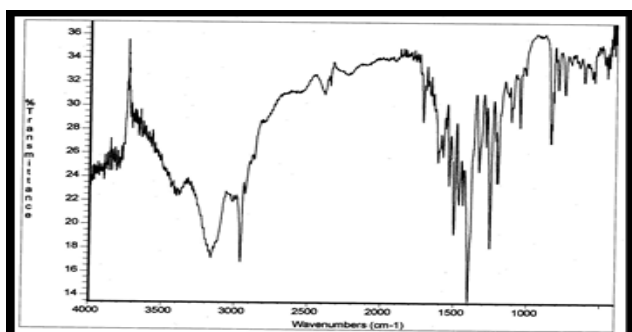


Figure-1 IR spectra of DAFOBA

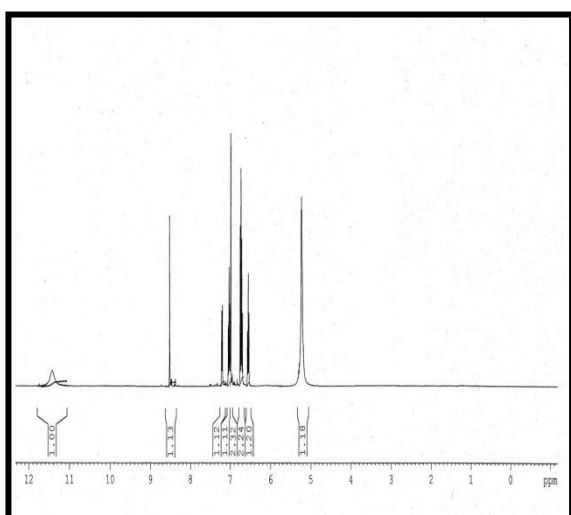


Figure-2 NMR spectra of DAFOBA

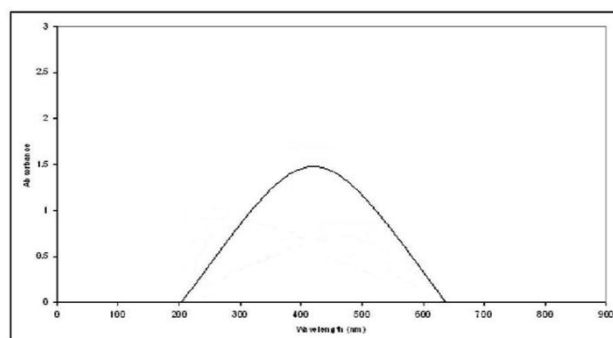


Figure-3 UV-Vis spectra of DAFOBA

NMR spectrum of ligand shows two singlets at 5.27 ppm and 11.48 ppm for -OH and -OH of COOH group, respectively. The remaining eight aromatic protons are appeared in multiplicity at δ 6.52-8.50 ppm. Thus the 1H protons confirm the structure of DAFOBA as shown in **Scheme-1**.

The stoichiometric study of all metal chelates suggest that the metal: ligand (M:L) ratio for all divalent metal chelate is 1:2. The molar extinction coefficient (ϵ) of the DAFOBA is of the order of 10^4 . It has been revealed that the ligand absorbs at higher wavelength around 475 nm and $\log \epsilon$ value found around 3.64.

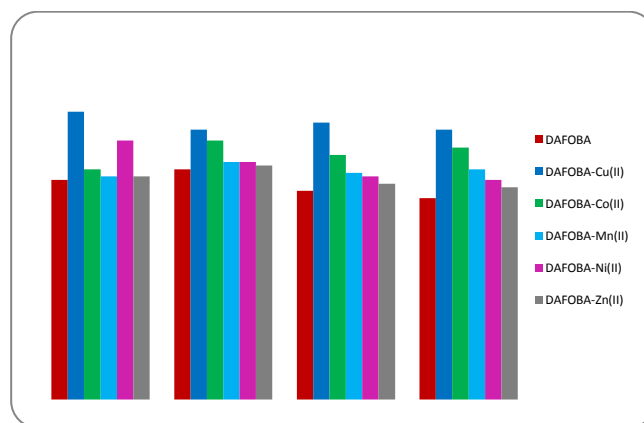


Figure-4 Antifungal activity of compounds

In present study, the magnetic moment (μ_{eff}) of Cu^{+2} chelate is found at 2.45 BM indicating the distorted octahedral geometry for the metal chelate. These finding are in agreement with reported data and further supported by the reflectance spectral study of particular chelate [16,17]. The two absorption bands are observed in the region 13728 cm^{-1} and 23878 cm^{-1} , in electronic spectra of Cu^{+2} metal chelate of each of the ligand many assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ and charge transfer transition respectively. These results reveal the distorted octahedral

geometry for Cu(II) chelate. The magnetic moment of Ni⁺² chelate is found at 3.24 BM, which indicate octahedral distorted structure of Ni⁺² chelates. Further, the diffuse reflectance spectra of Ni⁺² shown two band at 15625 and 22471 assigned to the transitions ³A_{1g} (F) → ³T_{1g} (F) and ³A_{1g} (F) → ³T_{1g} (P) respectively suggesting octahedral geometry for Ni⁺² chelate. It is observed that magnetic moment found at 4.7 BM for Co(II) chelate. These values indicate the possibility of octahedral complexes. Examination of the electronic spectral data shows that transitions observed at 8550 cm⁻¹ are assigned ⁴T_{2g} (F) → ⁴T_{1g} (P) transition and another bands in the region 19120 cm⁻¹ and 23115 cm⁻¹ may be attributed to ⁴T_{2g} (F) → ⁴T_{1g} (P) and ⁴T_{2g} (F) → ⁴T_{2g} (F) transitions respectively. Thus, on the basis of magnetic moment (μ_{eff}) and electronic spectra data octahedral structure can be interpreted for the Co⁺² chelate. The magnetic moment of Mn⁺² chelate found at 5.6 BM. The low magnetic moment values of the present chelate may be due to either arial oxidation of Mn⁺² → Mn⁺³ or due to spin exchange in the solid state. The absorption bands of the chelate is found to occur around 19,220 cm⁻¹ attributed to ⁶A_{1g} → ⁴T_{1g} (G) and around 23950 cm⁻¹ due to ⁶A_{1g} → ⁴T_{2g} (G) transition. From the study of these data reveals that Mn⁺² chelat has an octahedral structure^[16-19]. Zn⁺² metal chelate is diamagnetic in nature and its electronic spectra do not furnish any characteristic d-d transitions.

CONCLUSION

The screening results of biological activities revealed that the all compounds showed significant antifungal activity. In particular compounds showed moderate to good antifungal activities against all employed strains. The all metal chelates showed higher activity than its free ligand may be due to the coordination with the metal ion. Amongst all the metal chelates the Cu²⁺ chelate is found more toxic against employed strains.

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REFERENCES

- [1]. Ventura-Camargo BC and Marin-Morales MA. Azo Dyes: Characterization and Toxicity— A Review, *Textiles and Light Industrial Science and Technology (TLIST)*, 2013; 2(2):85-103.
- [2]. Bafana A, Devi SS and Chakrabarti T, Azo dyes: past, present and the future, *Environmental Reviews*, 2011; 19(NA):350-371.
- [3]. Anitha C, Sheela CD, Tharmaraj P and Sumathi S. Spectroscopic studies and biological evaluation of some transition metal complexes of azo Schiff-base ligand derived from (1-phenyl-2,3-dimethyl-4-aminopyrazol-5-one) and 5-((4-chlorophenyl)diazanyl)-2-hydroxybenzaldehyde, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2012; 96: 493-500.
- [4]. Anderson RG and Nickless G, Heterocyclic azo dyestuffs in analytical chemistry. A review, *Analyst*, 1967; 92: 207-238.
- [5]. Ispir E. The synthesis, characterization, electrochemical character, catalytic and antimicrobial activity of novel, azo-containing Schiff bases and their metal complexes, *Dyes and Pigments*, 2009; 82(1):13-19.
- [6]. Yamjala K, Nainar MS and Ramiseti NR. Methods for the analysis of azo dyes employed in food industry-A review, *Food Chemistry*, 2016; 192:813-824.
- [7]. Banat IM, Nigam P, Singh D and Marchant R, Microbial decolorization of textile-dyecontaining effluents: A review, *Bioresource Technology*, 1996; 58(3):217-227.
- [8]. Ewelina WT and Lukasz G. Azo dyes-biological activity and synthetic strategy, *Chemik*, 2012; 66(12): 1298-1307.
- [9]. Kumar S, Dhar DN and Saxena PN. Applications of metal complexes of Schiff bases-A review, *Journal of scientific and industrial research*, 2009; 68(3): 181-187.
- [10]. Singh RL, Singh PK and SinghRP. Enzymatic decolorization and degradation of azo dyes-A review, *International Biodeterioration & Biodegradation*, 2015; 104:21- 31.
- [11]. Patel BK and Patel SD. Synthesis, characterization and chelating properties of novel heterocyclic azo dyes containing ligand, *Journal of Chemical and Pharmaceutical Research*, 2014; 6(11):364-368.

- [12]. Patel BK and Patel SD. Studies on Bon-acid based azo dyes and its metal chelates, *Advances in Applied Science Research*, 2015; 6(7):165-170.
- [13]. Vogel AI. Textbook of Quantitative Chemical Analysis, ELBS, London, Fifth Edition, 1996.
- [14]. Baily WR and Scott EG. Diagnostic Microbiology, The C.V. Mosby Co. St. Louis, 1966:257.
- [15]. Oza KK and Patel HS. Antimicrobial activity of novel 3-substituted- 5-(pyridine-4-yl)-3H-1,3,4-oxadiazole-2-thione derivatives, *Bulgarian Chemical Communications*, 2010; 42(2): 103-106.
- [16]. Balhausen CJ. Introduction to ligand fields, McGraw Hill, New York, 1962.
- [17]. Figgs BN and Hitchman MA. Ligand Field Theory and Its Applications, Wiley- VCH, New York, 2000.
- [18]. Patel JC, Dholariya HR, Patel KS, Bhatt J and Patel KD. Cu (II) and Ni (II) complexes of coumarin derivatives with fourth generation flouroquinolone: synthesis, characterization, microbicidal and antioxidant assay, *Medicinal Chemistry Research*, 2014; 23(8):3714-3724.
- [19]. Chauhan GR, Patel KD, Dholariya HR, Patel JC and Tiwari KK, synthesis, electronic spectra and antimicrobial significance of novel drug based complexes, *International Journal of Health and Pharmaceutical Sciences*, 2012; 1(1):83-88.

