



## STUDIES ON METAL CHELATES OF HETEROCYCLIC AZO LIGAND DERIVED FROM BENZOESORCINOL

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### Abstract

Some new transition metal chelates have been synthesized through the coupling reaction between diazonium salt of 2-Amino-5-(furan-2-yl)-1,3,4-oxadiazol and benzoesorcinol in presence nitrosyl sulfuric acid. The synthesized compounds were characterized on the basis of IR, <sup>1</sup>H NMR, TGA, Reflectance spectral study and magnetic measurement data. Also the antifungal activity of all compounds suggests the good to moderate activity against the all four employed strains.

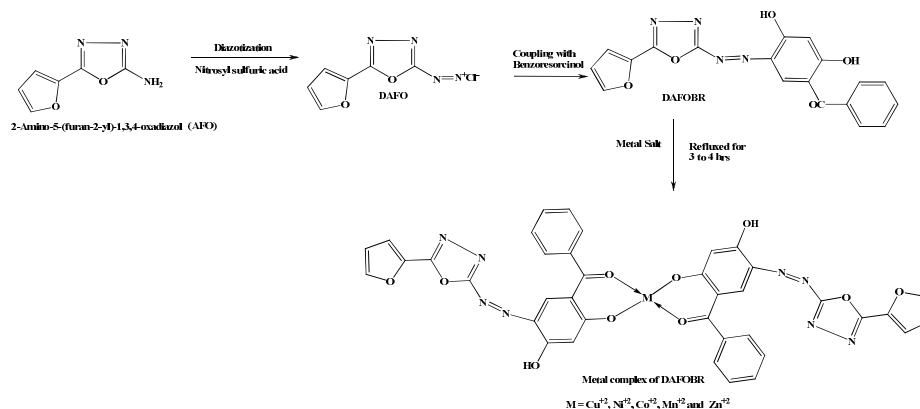
### Keywords

Oxadiazole, Benzoesorcinol, azo ligand, spectral studies, TGA and antifungal activity.

### Introduction

A large numbers of heterocyclic azo ligands have been formulated by many researchers.<sup>1-3</sup> Many of these compounds serve useful in field of thermal and optical properties. This ligand also widely applied in areas such as optical recording medium, food, cosmetics, toner, inkjet printing, biological activities and textile industries.<sup>1,4-8</sup> Also, the heterocyclic azo ligands considering interest due to their promising biological activities.<sup>7-9</sup> In recent years metal chelates of these azo ligands has assumed a new importance in organometallic and coordination metal chemistry.<sup>10-13</sup> These metal chelates have been given increasing interest due to their promising geometrical and electronic properties in field of molecular memory storage. Metal chelates of azo dyes are found more light-stable and thermally stable then its parent azo ligands which recommend the use of metal chelates over its parent heterocyclic azo ligands in the field of high-density optical recording materials.<sup>14,15</sup> Also the biological studies of the metal chelates suggest the advantage of coordination of metal ions to the heterocyclic azo ligands.<sup>16,17</sup>

Inspired by the above review and in continuation of our previous work<sup>18</sup> the present paper comprises a synthesis, characterization and chelating properties of metal chelates derived from heterocyclic azo ligand containing benzoesorcinol and oxidazole derivative. Also, antifungal assay was examined against four fungal strains using agar dilution technique.



**Scheme-1 Synthetic route of targeted metal chelates**

### Materials and methods

2-Amino-5-(furan-2-yl)-1,3,4-oxadiazol (**AFO**) was prepared according to reported method.<sup>19</sup> All other chemicals and solvents used were of laboratory grade. The elemental contents were determined by Thermo Finigen Flash1101 EA (Italy) the metals were determined volumetrically by Vogel's method.<sup>20</sup> To a 100 mg chelate sample, each 1 ml of HCl, H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> were added and then 1 g of NaClO<sub>4</sub> 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 **DAFOBR** was recorded on 60 MHz NMR spectrophotometer. Magnetic susceptibility measurement of the synthesized chelates was carried out on Gouy Balance at room temperature. Mercury tetrathiocyanatocobalate (II) Hg[Co(NCS)<sub>4</sub>] was used as a calibrant. The reflectance spectra of chelates in solid were recorded on at room temperature. MgO was used as reference. Antifungal activity of all the samples was monitored against various strains, following the method reported in literature.<sup>21</sup> The thermo gravimetric analyses (TGA) of sample have been done by using "PERKIN ELMER PYRIS 1 TGA" in a slow stream of air.

### Synthesis of (5-((5-(furan-2-yl)-1,3,4-oxadiazol-2-yl)diazenyl)-2,4-dihydroxyphenyl)(phenyl)methanone (**DAFOBR**)

2-Amino-5-(furan-2-yl)-1,3,4-oxadiazol (**AFO**) (0.01mole) was dissolved in a mixture of H<sub>2</sub>SO<sub>4</sub> (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 APO was filtered into a cooled solution of Benzoescorcinol (0.01mole) at 0-5°C. The resulting solid azo dye was washed with water, dried and recrystallized from, MeOH. Yield: 75%, M.P.270-271°C (decompose) uncorrected. C<sub>19</sub>H<sub>12</sub>N<sub>4</sub>O<sub>5</sub> (376), **Elemental Analysis (%)**: **Cal.** 60.64(C), 3.21(H), 14.89(N); **Found**, 60.6(C), 3.2(H), 14.8(N). **IR Spectral Features (cm<sup>-1</sup>)**: ~3030 (Ar C-C), 1630,1575(Azo group), 3450-3530 (-OH), 1735 (CO), 1320 (C-O-C). **<sup>1</sup>HNMR (δ ppm)**: 6.45-7.78 (m, 10H, Ar-H), 5.25 (s, 2H,OH).

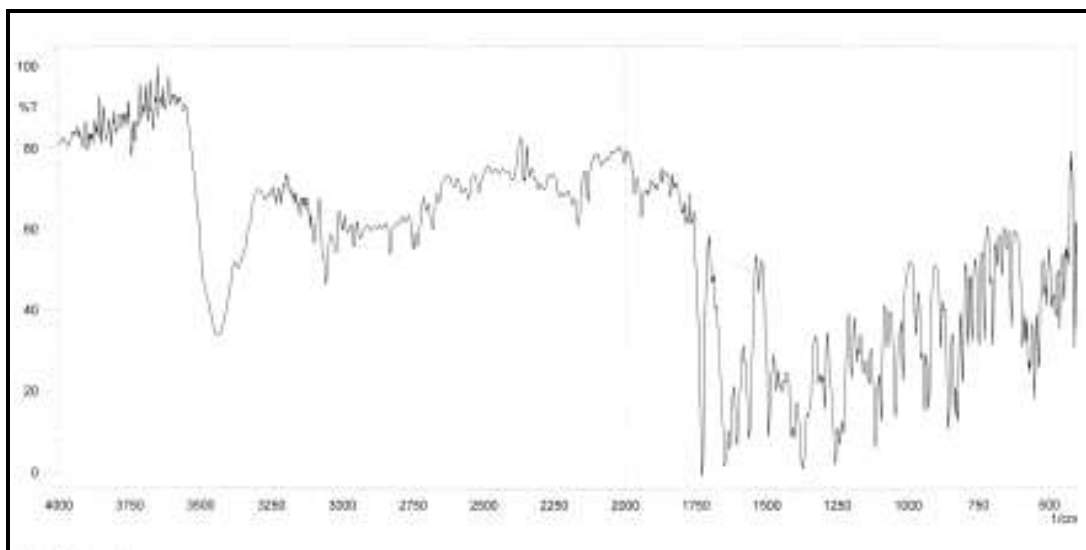


Figure-1 IR spectra of DAFOBR

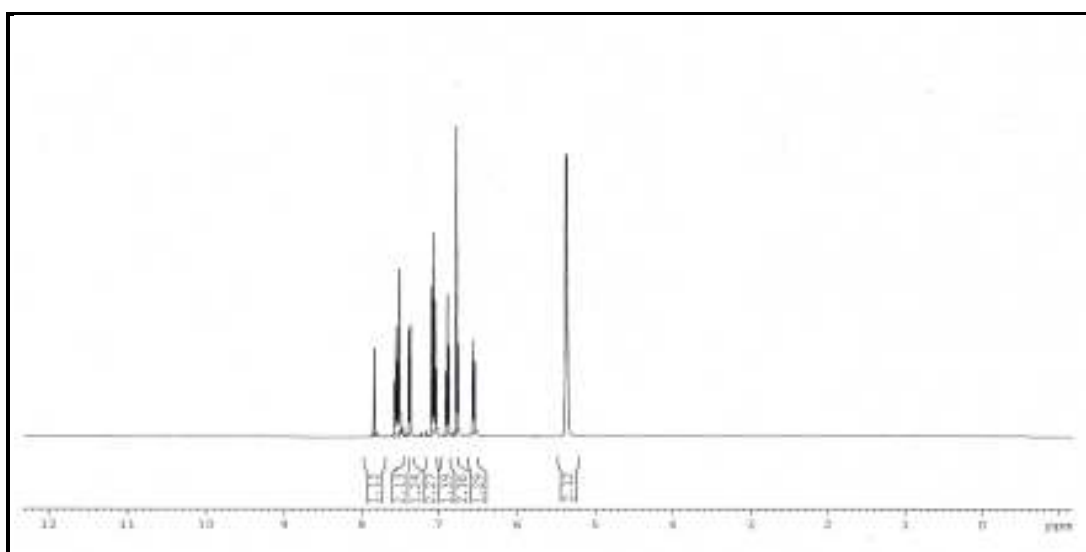


Figure-2 <sup>1</sup>H NMR spectra of DAFOBR

#### Synthesis of metal chelates of DAFOBR

The metal chelates of **DAFOBR** with Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) metal ions were prepared in two steps. The general procedure for the metal chelates is as follows;

##### (i) Preparation of DAFOBR solution

**DAFOBR** (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 **DAFOBR**. It was diluted to 100 ml.

##### (ii) Synthesis of DAFOBR-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 **DAFOBR** solution (i.e. containing 0.01 M **DAFOBR**) 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.

**Table-1: Physical and Elemental analysis of synthesized compounds**

Molecular Formula	Mol. Wt.	Yield (%)	Elemental Analysis							
			C%		H%		N%		M%	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$C_{19}H_{12}N_4O_5$	376	75	60.64	60.6	3.21	3.2	14.89	14.8	-	-
$C_{38}H_{22}CuN_8O_{10}$	814	72	56.06	56.0	2.72	2.7	13.76	13.7	7.80	7.7
$C_{38}H_{22}N_8NiO_{10}$	809	68	56.39	56.3	2.74	2.7	13.85	13.8	7.25	7.2
$C_{38}H_{22}CoN_8O_{10}$	809	68	56.38	56.3	2.74	2.7	13.84	13.8	7.28	7.2
$C_{38}H_{22}MnN_8O_{10}$	805	69	56.66	56.6	2.75	2.7	13.91	13.8	6.82	6.8
$C_{38}H_{22}N_8O_{10}Zn$	816	65	55.93	55.9	2.72	2.7	13.73	13.7	8.02	8.0

### Results and discussion

The reaction of **(5-((5-(furan-2-yl)-1,3,4-oxadiazol-2-yl)diazanyl)-2,4-dihydroxyphenyl)(phenyl)methanone (DAFOBR)** with the metal ions Co(II), Ni(II), Co(II), Mn(II) and Zn(II) gave different colored powdered compounds, depending on the nature of metal ion. The metal chelates were stable in air, insoluble in water, but soluble in some common organic solvents. All the metal chelates The results show that the metal: ligand (M:L) ratio for all divalent metal chelate is 1:2. The elemental analysis data (**Table-1**) of all compounds were consistent with the predicted structures as per **Scheme-1**.

The most important IR absorption bands corresponding to the ligand and the metal chelates are almost identical, only distinct bands were found in the spectra of metal chelates due to their respective metal-ligand coordination. In all compounds the appearance of a broad band around  $3450-3530\text{ cm}^{-1}$  in the spectra of the chelates suggests the presence of hydroxyl group. The observed band in the range  $1630, 1575\text{ cm}^{-1}$  is due to azo group of the ligand. The band around  $1320\text{ cm}^{-1}$  is due to C-O-C stretching of ligand. The band was observed in the range  $1730\text{ cm}^{-1}$ . Some bands in the range of  $500-550\text{ cm}^{-1}$  which are not present in the free ligand assigned to coordination bonding for respective metal ions.

The  $^1\text{H NMR}$  spectra (**Figure-2**) of **DAFOBR** in DMSO indicates that the spectrum display singlet of two protons at  $5.25\text{ }\delta$  ppm due to -OH group present in ligand, while the remaining aromatic protons are appeared in multiplicity in the range  $6.45-7.78\text{ }\delta$  ppm. Thus the structure of **DAFOBR** is confirmed as shown in **Scheme-1**.

The reflectance spectra of the ligand and all the chelates were recorded in ethanol at room temperature. The Cu(II) chelate exhibited a magnetic moment value of 2.3 BM suggesting the

possibility of an distorted octahedral geometry. In the reflectance spectra of Cu(II) chelate shows two broad bands around 13245 and 23450  $\text{cm}^{-1}$  due to  ${}^2B_{1g} \rightarrow {}^1A_{1g}$  transition, and charge transfer, respectively. The Ni(II) chelate also gave two bands at 15,325 and 22,630  $\text{cm}^{-1}$  were attributed to  ${}^3A_{1g} \rightarrow {}^3T_{1g}(P)$  and  ${}^3A_{1g} \rightarrow {}^3T_{1g}(F)$ . The magnetic moment observed for Ni(II) chelate lies at 3.5 BM, which is consistent with the octahedral geometry of the chelate. The Co(II) chelate gave three bands at 8970, 19210 and 23615  $\text{cm}^{-1}$ , which may be assigned to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$  transitions along with observed magnetic moment 4.82 BM suggest typical octahedral geometry. The reflectance data of Mn(II) metal chelate shows two bands at 19124  $\text{cm}^{-1}$  and 23210  $\text{cm}^{-1}$  attributed to  ${}^6A_{1g} \rightarrow {}^4T_{2g(G)}$  and  ${}^6A_{1g} \rightarrow {}^4A_{2g(G)}$  transitions, respectively. The high intensity of the bands suggests that they may have some charge transfer character. This has been further corroborated by the observed magnetic moment at 5.56 BM corresponds to a high spin octahedral Mn(II) chelate.<sup>22-25</sup> In case of reflectance spectra of Zn(II) metal chelate no d-d transition is possible due to its diamagnetic nature.

In view of industrial application of azo dyes, it has been worthwhile to study thermal behavior of ligand. The brief account of the thermal behavior of ligand in air is given below: Examination of the TG curve of DAFORA reveals that degradation takes place in two steps. The first stage of degradation up to 200° to 230°C indicate the weight loss around 13.5%, while the second degradation stage is rapid and loss upto 75% compound at 300°C.

The antifungal activity of the ligand (DAFOBR) and their metal chelates against four fungal strains was measured and tabulated in **Table-2**. All of tested compounds exhibited remarkable antifungal activity against tested fungus. A comparative study of the antifungal activity data of the ligand and their chelates suggest that the all metal chelates exhibited higher antifungal activity compared to its free ligand.

**Table-2: Antifungal activity of synthesized compounds**

Compound	Zone of inhibition of fungus at 1000 ppm (%)			
	<i>Nigrospora Sp.</i>	<i>Botrydeplaiia thiobromine</i>	<i>Asperginus niger</i>	<i>Rhisopus Nigricans</i>
DAFOBR	52	50	55	47
DAFOBR- Cu(II)	70	68	74	65
DAFOBR- Ni(II)	62	58	66	54
DAFOBR- Co(II)	64	61	69	57
DAFOBR-Mn(II)	66	65	71	60
DAFOBR-Zn(II)	65	63	67	58

#### Conclusion:

The ligand BPPD acts as a bidentate ligand and formed stable chelates with all employed metal ions. The metal chelates showed a higher efficiency than its parent ligand, while amongst the all metal chelates the Cu(II) chelate showed higher antifungal activity against the all employed fungus.

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