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Advances in Applied Science Research, 2015, 6(7):165-170

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ISSN: 0976-8610
CODEN (USA): AASRFC

Studies on Bon-acid based azo dyes and its metal chelates

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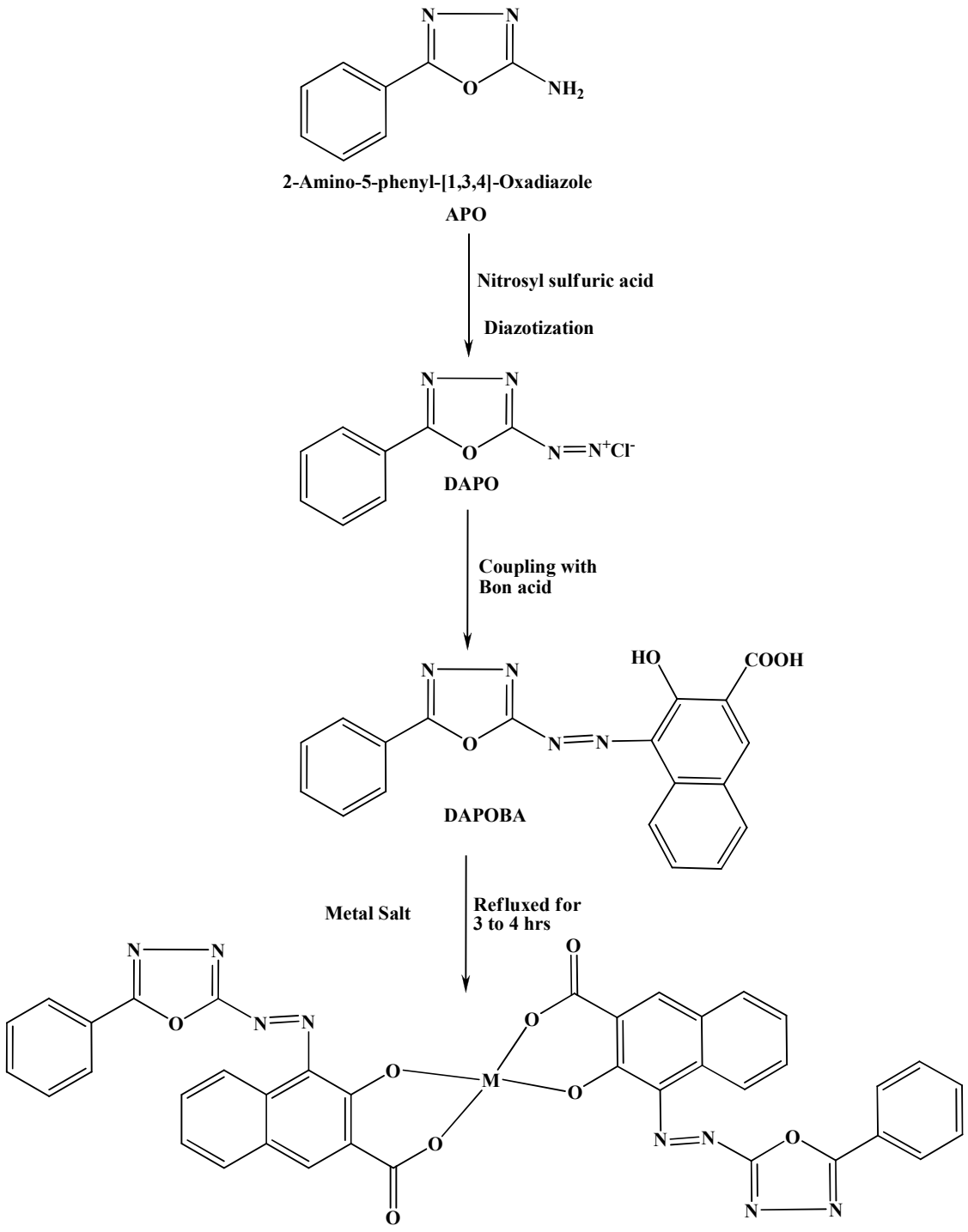
ABSTRACT

New ligand i.e. 3-hydroxy-4--((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)-2-naphthoic acid (DAPOBA) was synthesized by diazotization reaction of diazonium salt of 2-Amino-5-phenyl-[1,3,4]-Oxadiazole (APO) and Bon acid (BA). The synthesized novel ligand was further investigated by means of their physical properties, elemental analysis and spectral studies. The transition metal chelates of DAPOBA were prepared and characterized by metal-ligand (M:L) ratio and IR spectral studies. Furthermore, geometry of metal chelates confirmed through the reflectance spectral study and magnetic values. The antifungal activity of DAPOBA and its metal chelates was examined against various fungi shows clear enhancement in the activity of metal chelates upon coordination.

Keywords: 2-Amino-5-phenyl-[1,3,4]-Oxadiazole, Bon acid, Reflectance spectral study, Magnetic moment, Antifungal activity.

INTRODUCTION

Recently, metal chelates of Schiff base containing Bon acid (i.e. 3-hydroxy-2-naphthoic acid) (BA) were reported and studied for their chelating properties [1-3]. Bon acid and its derivatives are extensively evaluated for their biological activity [4-6]. Several azo dyes based on bon acid are also reported for dyeing of textiles as well as their chelating properties [7,8]. The no of heterocyclic compounds containing oxadiazole shows diverse biological activities like antibacterial, antifungal, antituberculosis, antiinflammatory, analgesic activity [9-11]. The reaction of oxadiazole derivatives with Bon acid has not been reported so far. Hence, it was thought that oxadiazole and Bon acid into one molecule may afford good biological active compound. In this study, some metal chelates of 3-hydroxy-4--((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)-2-naphthoic acid (DAPOBA) **(Scheme-1)** derived from 2-Amino-5-phenyl-[1,3,4]-Oxadiazole (APO) and 3-hydroxy-2-naphthoic acid (i.e. Bon acid), were synthesized to screen for their chelating properties and antimicrobial activity. The structures of these chelates were elucidated using elemental analysis, reflectance spectra and magnetic moment values. Also ligand and their metal chelates were tested for their antifungal activity.



Metal complex of DAPOBA

M = Cu^{+2}, Co^{+2},Mn^{+2}, Ni^{+2} and Zn^{+2}

Scheme - 1

MATERIALS AND METHODS

2-Amino-5-phenyl-[1,3,4]-Oxadiazole (APO) was prepared according to reported method [11]. 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 [12]. To a 100 mg chelate sample, each 1 ml of HCl, H_2SO_4 and $HClO_4$ were added and then 1 g of $NaClO_4$ 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 DAPOBA was recorded on 60 MHz NMR spectrophotometer. Magnetic susceptibility measurement of the synthesized complexes was carried out on Gouy Balance at room temperature. Mercury tetrathiocynatocobalate (II) $Hg[Co(NCS)_4]$ was used as a calibrant. The electronic spectra of complexes in solid were recorded on at room temperature. MgO was used as reference. Antifungal activity of all the samples was monitored against various fungi, following the method reported in literature [13].

Synthesis of 3-hydroxy-4--((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)-2-naphthoic acid (DAPOBA):
2-Amino-5-phenyl-[1,3,4]-Oxadiazole (APO) (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 APO was filtered into a cooled solution of Bon acid (0.01mole) at O-5°C. The resulting solid azo dye was washed with water, dried and recrystallized from, MeOH. Yield: 70%, M.P.282-284°C (decompose) uncorrected.

Analysis:
ElementalAnalysis

	C%	H%	N%
$C_{19}H_{12}N_4O_4$ (360)			
Calculated:	63.33	3.36	15.55
Found :	63.3	3.3	15.5

IR Spectral Features: (cm^{-1})	2950- 2850	Ar C-C
	1630, 1575	Azo group
	1675	CO of COOH
	3200-3600	OH
	1350	C-O-C

NMR : δ ppm 7.35-8.65 (m, 10H, Ar-H), 5.31 (s, 1H, OH), 11.52 (s, 1H, COOH).

Synthesis of metal chelates of 3-hydroxy-4--((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)-2-naphthoic acid (DAPOBA):
The metal chelates of DAPOBA with Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, and Ni^{2+} metal ions were prepared in two steps. The general procedure for the metal chelates is as follows;

(1) Preparation of DAPOBA solution:
DAPOBA (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 DAPOBA. It was diluted to 100 ml.

Synthesis of DAPOBA-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 DAPOBA solution (i.e. containing 0.01 M DAPOBA) 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 properties and Elemental analysis of DAPOBA ligand and their transition metal chelates

Empirical Formula	Mol. Wt.	Yield (%)	Elemental Analysis							
			C%		H%		N%		M%	
			Cald	Found	Cald	Found	Cald	Found	Cald	Found
DAPOBA	360	70	63.33	63.3	3.36	3.3	15.55	15.5	-	-
$(DAPOBA)_2Cu^{2+}$	780	68	58.50	58.4	2.58	2.5	14.36	14.3	8.15	8.1
$(DAPOBA)_2Co^{2+}$	775	66	58.85	58.8	2.60	2.5	14.45	14.4	7.60	7.5
$(DAPOBA)_2Mn^{2+}$	771	65	59.15	59.1	2.61	2.5	14.52	14.4	7.12	7.0
$(DAPOBA)_2Ni^{2+}$	775	63	58.87	58.8	2.60	2.5	14.45	14.4	7.57	7.5
$(DAPOBA)_2Zn^{2+}$	782	64	58.36	58.3	2.58	2.5	16.37	16.3	8.36	8.3

RESULTS AND DISCUSSION

The synthesis of 3-hydroxy-4--((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)-2-naphthoic acid (DAPOBA) was performed by a simple reaction between diazonium salt of 2-Amino-5-phenyl-[1,3,4]-Oxadiazole (APO) and Bon acid (BA). The resulted DAPOBA ligand was in form of amorphous powder. The C,H,N contents of DAPOBA and their metal chelates **(Table-1)** are consistent with the predicted structure **(Scheme-1)**.

The IR spectrum of the ligand DAPOBA shows a broad OH stretching band in between 3460 and 3520 cm^{-1}. The free ligand IR spectrum shows a very stronger band at 1675 cm^{-1} due to stretching frequency for CO group of COOH. The IR spectrum of DAPOBA also comprises the important bands due to azo group at 1630 and 1575 cm^{-1}. Also bands for aromatic carbon and C-O-C stretching were found at their respective positions. On the other side infrared spectra of all the chelates are found identical as its parant ligand, the only difference found that formation of all the metal chelates having absence of band characteristic for free –OH group. Also, the band due to (M-O) bonding found for the respective metal-ligand bonding supports the coordination in all metal chelates.

NMR spectrum of ligand shows singlet at 5.31 ppm and 11.52 ppm for –OH and –COOH respectively, rest of the aromatic protons are appeared in multiplicity at δ 7.35-8.65 ppm. Thus the structure of DAPOBA is confirmed as shown in **Scheme-1**.

The metal and C,H,N contents of metal chelates of DAPOBA **(Table-1)** are also consistent with the predicted structure. The results show that the metal: ligand (M:L) ratio for all divalent metal chelate is 1:2.

Table-2: Electronic spectral featrues and magnetic moment of $(DAPOBA)_2$-metal chelates

Metal Chelates	μ_{eff} (BM)	Electronic spectral data (cm^{-1})	Transition
DAPOBA-Cu^{2+}	2.52	23396 13224	Charge transfer $^2B_{1g} \rightarrow {}^2A_{1g}$
DAPOBA-Co^{2+}	4.73	23733 19110 8911	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$
DAPOBA-Mn^{2+}	5.58	23236 19045 16851	$^6A_{1g} \rightarrow {}^6A_{2g}\ {}^4E_g$ $^6A_{1g} \rightarrow {}^4T_{2g}$ (4G) $^6A_{1g} \rightarrow {}^4T_{1g}$(PG)
DAPOBA-Ni^{2+}	3.75	22574 15361	$^3A_{1g} \rightarrow {}^3T_{1g}(P)$ $^3A_{1g} \rightarrow {}^3T_{1g}(F)$
DAPOBA-Zn^{2+}	Diamag.		---------

Table-3: Antifungal activity of DAPOBA ligand and their metal chelates

Sample	Zone of inhibition of fungus at 1000 ppm (%)			
	Nigrospora Sp.	*Botrydeplaia thiobromine*	*Asperginus niger*	*Rhisopus Nigricans*
DAPOBA	59	61	57	55
DAPOBA-Cu^{2+}	77	78	73	71
DAPOBA-Co^{2+}	64	73	69	68
DAPOBA-Mn^{2+}	61	68	62	59
DAPOBA-Ni^{2+}	70	65	64	62
DAPOBA-Zn^{2+}	65	70	66	64

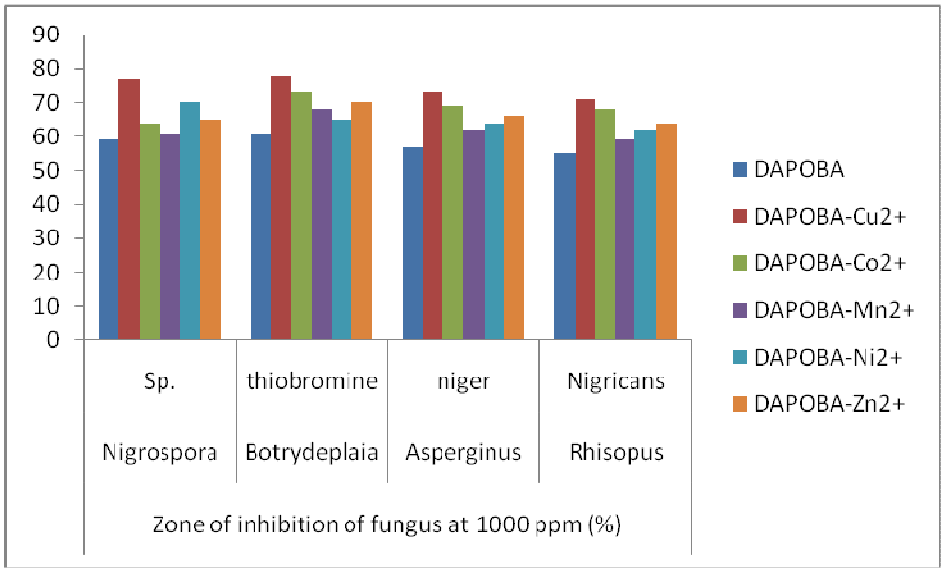


Fig.1. Antifungal activity comparision between ligand and their metal chelates

Electronic spectral data and magnetic susceptibility measurements gave adequate support to determine the geometry of metal chelates. Electronic spectral data and Magnetic moments of metal chelates are exhibit in **Table-2**. The diffuse electronic spectrum of Cu^{2+} chelates shows two broad bands around 13224 and 23396 cm^{-1}. The first band may be due to a $^2B_{1g} \rightarrow {}^1A_{1g}$ transition, while the second band may be due to charge transfer. This support the distorted octahedral Cu(II) chelates which was usual in the d^9 system [14]. Also higher magnetic moment value at 2.52 BM falls within the range normally observed for octahedral Cu(II) chelates supports the same. The Co^{2+} metal chelate shows to two absorption bands at 23733 and 19110 cm^{-1}, which can be assigned $^4T_{1g} \rightarrow {}^2T_{2g}$, $^4T_{1g} \rightarrow {}^4T_{1g}$(P) transitions, respectively, as expected for an octahedral Co^{2+} chelate. These absorption bands along with µeff value suggest an octahedral geometry for the Co^{2+} metal chelate [15]. The spectrum of Mn^{2+} chelate comprised two bands at 19045 cm^{-1} and 23236 cm^{-1} assigned 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. The observed µeff value 5.58 is consisting with expected spin only value for Mn^{+2} chelate [16]. The electronic spectra of the Ni^{2+} chelate display two bands at 15361 cm^{-1} and 22574 cm^{-1} assign to $^3A_1g \rightarrow {}^3T_1g$ (P) and $^3A_1g \rightarrow {}^3T_1g$ (F), respectively. The spectral bands are well within the range observed for octahedral distortion. The µeff values are also in the range as expected for six coordinated Ni^{+2} chelates [17]. Zn^{+2} metal chelate is diamagnetic in nature and its electronic spectra do not furnish any characteristic d-d transitions.

CONCLUSION

The examination of antifungal activity of DAPOBA ligand and its all chelates **(Table-3 and Fig. 1)** reveals that the ligand is moderately toxic against fungi, while all the chelates are more toxic than ligand. Among all the chelates the Cu^{2+} chelate is more toxic against fungi, as expected because the copper salts are mostly used as fungicides.

Acknoledgement
Thanks to Dr. V. G. Patel, Principal, Bhavan's Science College, Dakor, Gujarat for providing research facilities.

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