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Synthesis, characterization and chelating properties of ligand containing heterocyclic azo dyes

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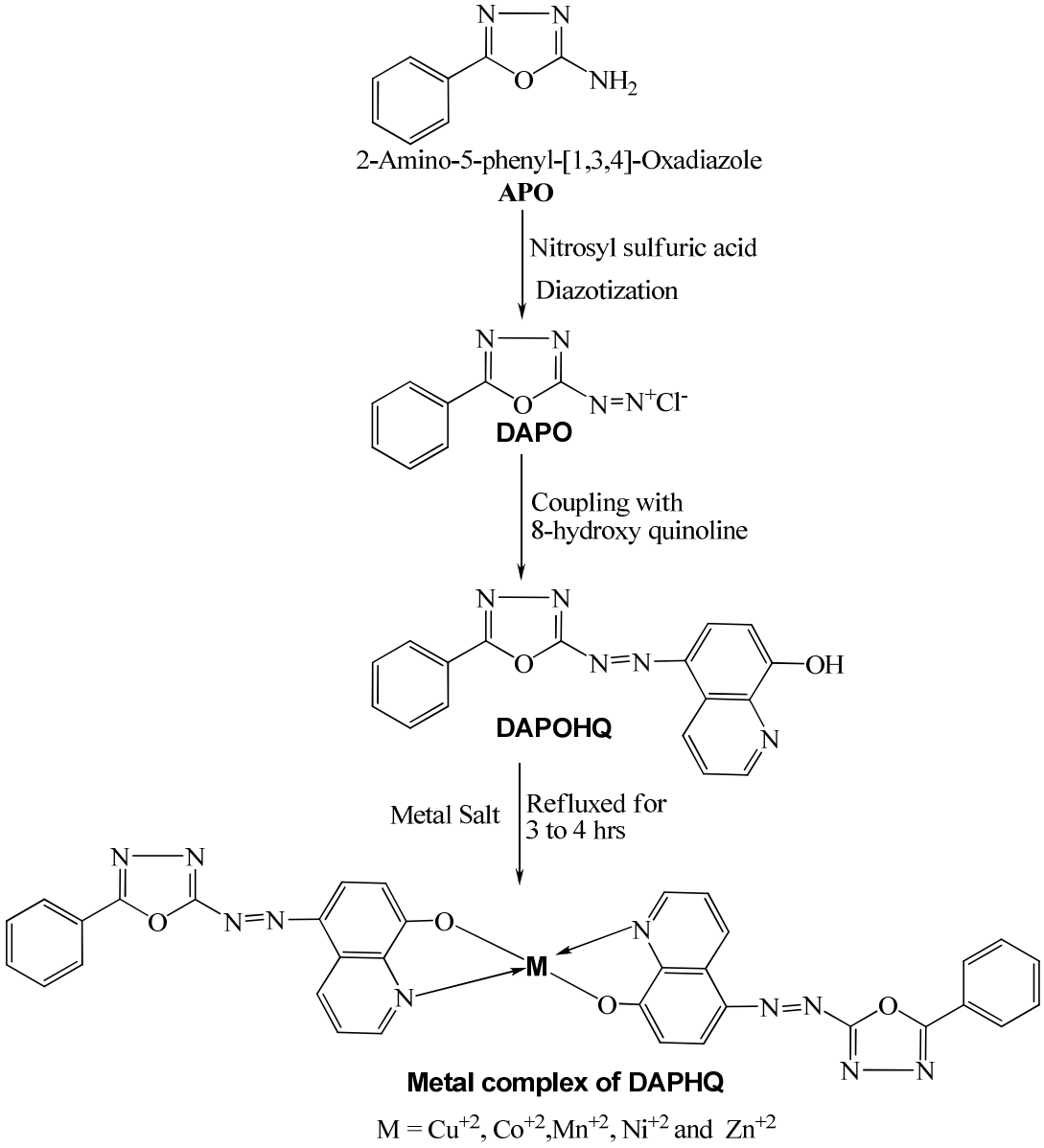
ABSTRACT

The 5-((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)quinolin-8-ol (DAPOHQ) was prepared by Diazotization reaction of diazonium salt of 2-Amino-5-phenyl-[1,3,4]-Oxadiazole (APO) and 8-hyroxyquinolinol (HQ).The novel ligand was characterized by elemental analysis and spectral studies. The transition metal chelates viz. Cu^{2+}, Ni^{2+} , Co^{2+} , Mn^{2+} and Zn^{2+} of DAPOHQ were prepared and characterized by metal-ligand (M:L) ratio, IR and reflectance spectroscopies and magnetic properties. The antifungal activity of DAPOHQ and its metal chelates was examined against various fungi.

Keywords: 2-Amino-5-phenyl-[1,3,4]-Oxadiazole, 8-hyroxy quinolinol, Magnetic moment, Spectroscopies study and Antifungal properties.

INTRODUCTION

8-Hydroxyquinoline is well known as an analytical reagent[1]. It's various derivatives are also useful in pharmaceuticals. Several azo dyes based on 8-quinolinol are also reported for dyeing of textiles as well as their chelating properties [2]. One of the derivative say 8- hyroxy quinolinol (HQ) can be synthesize easily and studied extensively for number of derivatives [3]. Some of the ions exchanging resins are also reported with good potentiality [4-6]. The no of heterocyclic compounds shows the pharmaceutical as well as biological activity [7,8]. The oxadiazole and their derivatives show diverse biological activities like antituberculostic, antiinflamatory, analgesic, antibacterial and antifungal activity[9-11]. The reaction of oxadiazole derivatives with HQ has not been reported so far. Hence, it was thought that oxadiazole and 8-HQ into one molecule may afford good biological active compound. The present article discuss about synthesizes and characterization and of 5-((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)quinolin-8-ol(DAPOHQ) (Scheme-1).



Scheme - 1

MATERIALS AND METHODS

2-Amino-5-phenyl-[1,3,4]-Oxadiazole (APO) was prepared by reported method[12].

All other chemicals and solvents used were of laboratory grade.

Synthesis of 5-((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)quinolin-8-ol (DAPOHQ):
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 8-hydroxyquinoline (0.01mole) at O-5°C. The resulting solid azo dye was washed with water, dried and recrystallized from, MeOH. Yield: 67%, M.P.266-269°C (decompose) uncorrected.

ANALYSIS:

ElementalAnalysis

		C%	H%	N%
$C_{17}H_{11}N_5O_2$ (317)				
Calculated	:	64.35	3.49	22.07
Found	:	64.3	3.4	22.04
IR Spectral Features:		2950- 2850		Ar C-C
(cm^{-1})		1630, 1575,		Azo group
		1647, 1500, 1470		8-HQ and Oxadiazole
		1350		C-O-C

NMR : δ ppm 8.06-8.87 (m,4H, Ar-H), 7.05-7.63 (m,6H, Ar-H), 5.32 (s,1H,OH).

Synthesis of metal chelates of 5-((5-phenyl-1,3,4-oxadiazol-2-yl) diazenyl)quinolin-8-ol (DAPOHQ):

The metal chelates of DAPOHQ with Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, and Ni^{2+} metal ions were prepared in two steps. All the metal chelates were prepared in an identical procedure.

(1) Preparation of DAPOHQ solution:

DAPOHQ (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 DAPOHQ. It was diluted to 100 ml.

Table-1: ANALYSIS OF DAPOHQ LIGAND AND ITS METAL CHELATES

Empirical Formula	Yield (%)	Elemental Analysis							
		C%		H%		N%		M%	
		Cald	Found	Cald	Found	Cald	Found	Cald	Found
DAPOHQ	67	64.35	64.3	3.49	3.4	22.07	22.0	-	-
$(DAPOHQ)_2Cu^{2+}$	64	55.77	55.7	3.28	3.2	19.14	19.1	8.69	8.6
$(DAPOHQ)_2Co^{2+}$	63	56.13	56.1	3.30	3.2	19.26	19.2	8.11	8.0
$(DAPOHQ)_2Ni^{2+}$	61	56.14	56.1	3.30	3.2	19.26	19.2	8.08	8.0
$(DAPOHQ)_2Mn^{2+}$	63	56.44	56.4	3.32	3.3	19.37	19.3	7.60	7.5
$(DAPOHQ)_2Zn^{2+}$	60	55.63	55.6	3.27	3.2	19.09	19.0	8.91	8.8

Synthesis of DAPOHQ-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 DAPOHQ solution (i.e. containing 0.01 M DAPOHQ) 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.

Measurements:

The elemental contents were determined by Thermo Finigen Flash1101 EA (Itally) the metals were determined volumetrically by Vogel's method [13]. 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 DAPOHQ 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 [14].

RESULTS AND DISCUSSION

The synthesis of 5-((5-phenyl-1,3,4-oxadiazol- 2-yl)diazenyl)quinolin-8-ol (DAPOHQ) was performed by a simple reaction of diazonium salt of 2-Amino-5-phenyl-[1,3,4]-Oxadiazole (APO) and 8-hyroxyquinolinol (HQ). The resulted DAPOHQ ligand was an amorphous brown powder. The C,H,N contents of DAPOHQ (Table-1) are

consistent with the structure predicted (Scheme-1). The IR spectrum of DAPOHQ comprises the important bands due to 8-quinolinol. The bands were observed at 1640, 1575, 1475, and 755 cm^{-1}.

TABLE-2: SPECTRAL FEATRUES AND MAGNETIC MOMENT OF DAPOHQ METAL CHELATES

Metal Chelates	μ_{eff} (BM)	Electronic spectral data (cm^{-1})	Transition
DAPOHQ-Cu^{2+}	2.56	23446 13208	Charge transfer $^2B_{1g} \rightarrow {}^2A_{1g}$
DAPOHQ-Ni^{2+}	3.72	22591 15365	$^3A_{1g} \rightarrow {}^3T_{1g}(P)$ $^3A_{1g} \rightarrow {}^3T_{1g}(F)$
DAPOHQ-Co^{2+}	4.78	23728 19098 8918	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$
DAPOHQ-Mn^{2+}	5.56	23228 19028 16835	$^6A_{1g} \rightarrow {}^6A_{2g}\ {}^4E_g$ $^6A_{1g} \rightarrow {}^4T_{2g}$ (4G) $^6A_{1g} \rightarrow {}^4T_{1g}$(PG)
DAPOHQ-Zn^{2+}	Diamag.		---------

The broad band due to –OH group appeared at 3650 cm^{-1}. In this band the inflections are observed at 2970, 2930 and 2850cm^{-1}. The NMR spectrum of DAPOHQ in DMSO indicates that the singlet of 1 H at 3.8 δ ppm due to –OH group. The aromatic protons are appeared in multiplicity at 6.80-9.03 δ. Thus the structure of DAPOHQ is confirmed as shown in Scheme-I.

The metal and C,H,N contents of metal chelates of DAPOHQ (Table-I) 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-3: ANTIFUNGAL ACTIVITY OF DAPOHQ LIGAND AND ITS METAL CHELATES

Sample	Zone of inhibition of fungus at 1000 ppm (%)			
	Nigrospora Sp.	***Botrydeplaia thiobromine***	***Asperginus niger***	***Rhisopus Nigricans***
DAPOHQ	56	60	47	57
DAPOHQ-Cu^{2+}	75	75	69	72
DAPOHQ-Co^{2+}	68	74	69	66
DAPOHQ-Ni^{2+}	63	71	67	69
DAPOHQ-Mn^{2+}	72	61	63	65
DAPOHQ-Zn^{2+}	76	74	58	75

The infrared spectra of all the chelates are identical and suggest the formation of all the metalocyclic compound by the absence of band characteristic of free –OH group of parent DAPOHQ. The other bands are almost at their respectable positions as appeared in the spectrum of parent-DAPOHQ ligand. However, the band due to (M-O) band could not be detected as it may appear below the range of instrument used. The important IR Spectral data are shown in Table-2.

Magnetic moments of metal chelates are given in Table-2. The diffuse electronic spectrum of Cu^{2+} chelates shows two broad bands around 13222 and 23460 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. The first band shows structures suggesting a distorted octahedral structure for the Cu^{2+} metal chelates. The higher value of the magnetic moment of the Cu^{2+} chelate supports the same. The Co^{2+} metal chelate gives rise to two absorption bands at 23742 and 19112cm^{-1}, which can be assigned $^4T_{1g} \rightarrow {}^2T_{2g}$, $^4T_{1g} \rightarrow {}^4T_{1g}(P)$transitions, respectively. These absorption bands and the µeff value indicate an octahedral configuration of the Co^{2+} metal chelate [15]. The spectrum of Mn^{2+} polymeric chelate comprised two bands at 19042cm^{-1} and 23242cm^{-1}. The latter does not have a very long tail. These bands may be 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 magnetic moment is found to be lower than normal range. In the absence of low temperature measuremet of magnetic moment it is difficult to attach any significance to this. The observed µeff values in the range 2.58-5.58 B.M are consistent with the above moiety[15].

The examination of antifungal activity of DAPOHQ ligand and its all chelates (Table-3) 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.

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REFERENCES

[1] Shah P J and Dave B P, *Der Chemica Sinica*, **2012,** 3(6),1343-1347.
[2] Philips J P, *Chem. Review*,**1984**,56, 271.
[3] Barkhater J H and Teib R I, *J.Org.Chem*.,**1968**,26,4078.
[4] Kenichiro A, Zaaea T and Sakurasaaea T, *seni Gakkaiski*,**2001**,57,229.
[5] Gosai D R, Nimavat K S and Vyas K B,*Der Chemica Sinica*,**2011**,3(4),491-500.
[6] Patel D K, and Singh A,*E-journal of chemistry*,**2009**,6(4),1017.
[7] Shah P J, Patel H S and Patel B P,*Bulgarian Chemical Communications*,**2010**, 42(4),474-478.
[8] Shah P J, Patel H S and Patel B P*Journal of Saudi Chemical Society*,**2013**,17, 307.
[9] Kumar K A,Jayaroopa P,Kumar G V, *International Journal of ChemTech Research*, **2012**, 4(4)4,1782.
[10] Chandra T,Garg N,Lata S,Saxena K K,Kumar A, *European Journal of Medicinal Chemistry*,**2010**,45,1772.
[11]Shah P J, *Oct. Jour. Env. Res*.,**2013**,1(3),205.
[12]Oza K K, Patel H S,*Bulgarian Chemical Communications*,**2010**,42(2),103.
[13]Vogel A I,*Textbook of Quantitative Chemical Analysis*, ELBS 5th Edn. London, **1996**.
[14]Baily W R and Scott E G, *Diagnostic Microbiology*, The C. V. Moshy Co. St. Lovis,**1966**, pp.257.
[15]Patil B.R., *Oriental J.Chem*.,**2006**,18,547.