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Research Article

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

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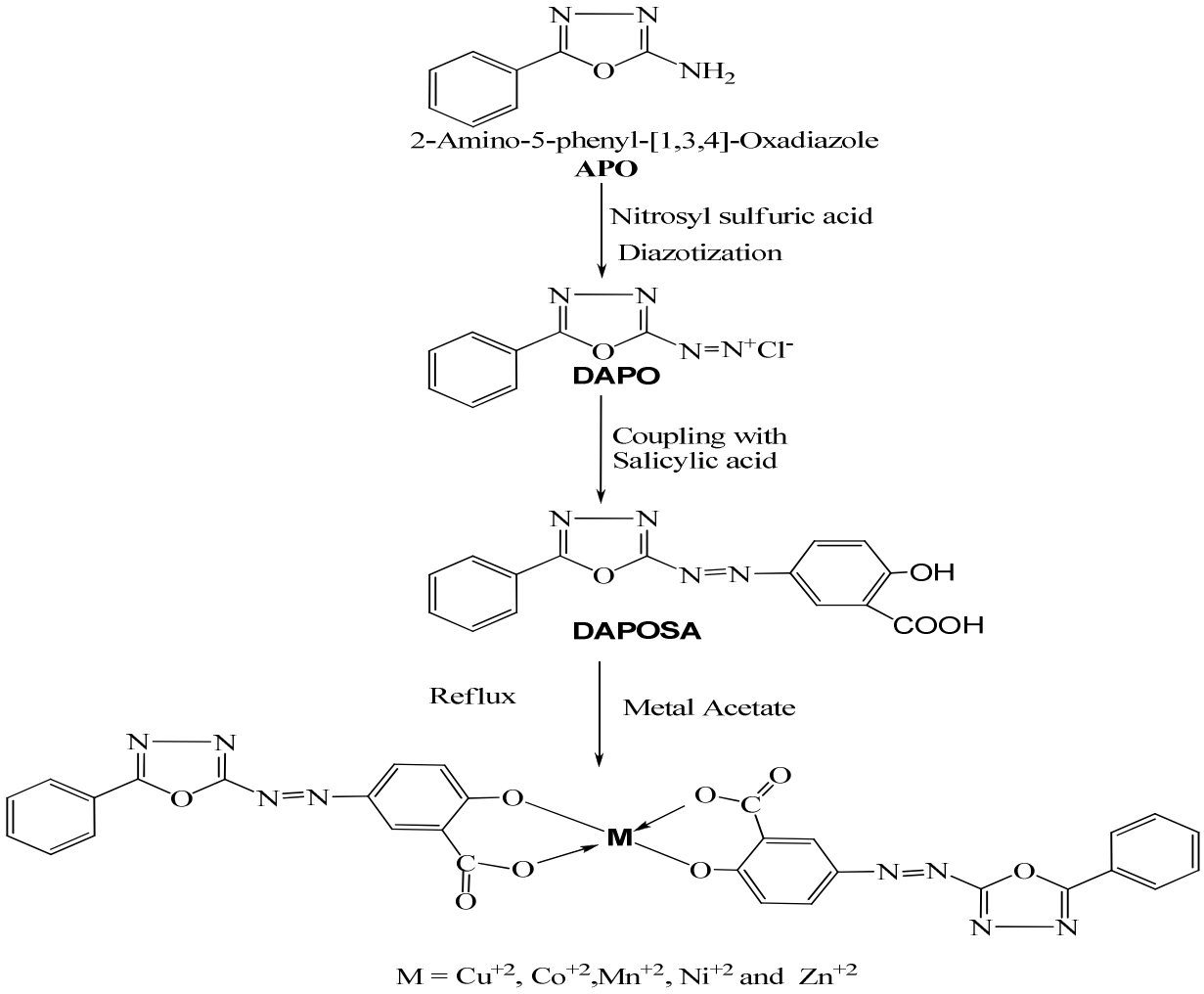
ABSTRACT

The diazotization reaction between diazonium salt of 2-Amino-5-phenyl-[1,3,4]-Oxadiazole (APO) and Salicylic acid (SA) was give 2-hydroxy-5-((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl) benzoic acid (DAPOSA). 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 DAPOSA were prepared and characterized by metal-ligand (M:L) ratio, IR and reflectance spectroscopies and magnetic properties. The antifungal activity of DAPOSA and its metal chelates was examined against various fungi.

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

INTRODUCTION

Metal ligands are becoming of commercial importance because they maintain the quality of industrial products analytically [1]. Novel ligands are continuously under investigation, for possible analytical and industrial applications. Salicylic acid and its bi-substituted derivatives are well known complexing agent. [2,3] Water insoluble metal complexes of 4-aminosalicylic acid (PAS) have been reported and investigated for tuberculolstatic effect [4,5]. They also show antibacterial as well as antifungal activity. [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 Salicylic acid has not been reported so far. Hence, it was thought that oxadiazole and Salicylic acid into one molecule may afford good biological active compound. The present article discuss about synthesizes and characterization and of 2-hydroxy-5-((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl) benzoic acid (DAPOSA) (Scheme-1).



Scheme - 1

Metal complex of DAPSA

EXPERIMENTAL SECTION

All other chemicals used were of laboratory grade. 2-Amino-5-phenyl-[1,3,4]-Oxadiazole was prepared by reported method[12].

Synthesis of 2-hydroxy-5-((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl) benzoic acid (DAPOSA):
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 Salicylic acid (0.01mole) at 0-5°C. The resulting solid azo dye was washed with water, dried and recrystallized from, MeOH. Yield: 63%, M.P.242-244°C (decompose) uncorrected.

ANALYSIS:
ElementalAnalysis

		C%	H%	N%
$C_{15}H_{10}N_4O_4$ (310)	Calculated:	58.07	3.25	18.06
	Found :	58.05	3.22	18.03

IR Spectral Features: 2950- 2850 Ar C-C
(cm^{-1}) 1680 cm^{-1} CO of COOH
3200-3600 cm^{-1} OH
NMR : δ ppm 6.21-8.06 (m,8H Ar-H), 5.4 (s,1H,OH),11.7(s,1H,COOH)

Synthesis of metal chelates of 2-hydroxy-5-((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl) benzoic acid (DAPOSA):
The metal chelates of DAPOSA 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 DAPOSA solution:
DAPOSA (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 DAPOSA. It was diluted to 100 ml.

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

Empirical Formula	Yield (%)	Elemental Analysis							
		C%		H%		N%		M%	
		Cald	Found	Cald	Found	Cald	Found	Cald	Found
DAPOSA	63	58.07	58.05	3.25	3.22	18.06	18.03	-	-
$(DAPOSA)_2Cu^{2+}$	61	47.77	47.75	3.45	3.44	14.86	14.84	8.43	8.40
$(DAPOSA)_2Co^{2+}$	65	48.07	48.06	3.47	3.46	14.95	14.92	7.87	7.85
$(DAPOSA)_2Ni^{2+}$	62	48.08	48.07	3.47	3.45	14.96	14.94	7.84	7.82
$(DAPOSA)_2Mn^{2+}$	64	48.33	48.33	3.49	3.48	15.03	15.01	7.38	7.36
$(DAPOSA)_2Zn^{2+}$	63	47.66	47.64	3.44	3.43	14.83	14.80	8.66	8.64

Synthesis of DAPOSA-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 DAPOSA solution (i.e. containing 0.01 M DAPOSA) 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 DAPOSA 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 2-hydroxy-5-((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl) benzoic acid (DAPOSA) was performed by a simple reaction of diazonium salt of 2-Amino-5-phenyl-[1,3,4]-Oxadiazole (APO) and Salicylic acid(SA). The resulted DAPOSA ligand was an amorphous brown powder. The C,H,N contents of DAPOSA (Table-1) are consistent with the structure predicted (Scheme-1). The IR spectrum of DAPOSA comprises the important bands due to Salicylic acid. The bands were observed at 1680 cm^{-1} for CO of COOH and 3200-3600 cm^{-1} for OH group.

The broad band due to –OH group appeared at 3200-3600cm^{-1}. The NMR spectrum of DAPOSA in DMSO indicates that the singlet of 1 H at 5.4 δ ppm due to –OH group. The aromatic protons are appeared in multiplicity at 6.21-8.06 δ. Thus the structure of DAPOSA is confirmed as shown in Scheme-I.

The metal and C,H,N contents of metal chelates of DAPOSA (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-2: SPECTRAL FEATRUES AND MAGNETIC MOMENT OF DAPOSA METAL CHELATES

Metal Chelates	μ_{eff} (BM)	Electronic spectral data (cm^{-1})	Transition
DAPOSA-Cu^{2+}	2.54	23432 13194	Charge transfer $^2B_{1g} \rightarrow {}^2A_{1g}$
DAPOSA-Ni^{2+}	3.7	22577 15351	$^3A_{1g} \rightarrow {}^3T_{1g}(P)$ $^3A_{1g} \rightarrow {}^3T_{1g}(F)$
DAPOSA-Co^{2+}	4.76	23714 19084 8904	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$
DAPOSA-Mn^{2+}	5.55	23214 19014 16821	$^6A_{1g} \rightarrow {}^6A_{2g}\ {}^4E_g$ $^6A_{1g} \rightarrow {}^4T_{2g}$ (4G) $^6A_{1g} \rightarrow {}^4T_{1g}$(PG)
DAPOSA-Zn^{2+}	Diamag.		---------

TABLE-3: ANTIFUNGAL ACTIVITY OF DAPOSA LIGAND AND ITS METAL CHELATES

Sample	Zone of inhibition of fungus at 1000 ppm (%)			
	Nigrospora Sp.	***Botrydeplaia thiobromine***	***Asperginus niger***	***Rhisopus Nigricans***
DAPOSA	53	58	44	53
DAPOSA-Cu^{2+}	72	73	66	68
DAPOSA-Co^{2+}	65	72	66	62
DAPOSA-Ni^{2+}	60	69	64	65
DAPOSA-Mn^{2+}	69	59	60	61
DAPOSA-Zn^{2+}	73	72	55	71

The infrared spectra of all the chelates are identical and suggest the formation of the entire metalocyclic compound by the absence of band characteristic of free –OH group of parent DAPOSA. The other bands are almost at their respectable positions as appeared in the spectrum of parent-DAPOSA 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 13194 and 23432 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 23714 and 19084 cm^{-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 19014 cm^{-1} and 23214 cm^{-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 2.54-5.55 B.M are consistent with the above moiety[15].

The examination of antifungal activity of DAPOSA 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.

CONCLUSION

In present paper we reported about the synthesis and characterization of new ligand which contain heterocyclic azo dye moiety. The new synthesized all compound DAPOSA and its metal chelates was examined for their antifungal activity against various fungi. They showed that 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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