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SYNTHESIS, CHARACTERIZATION AND CHELATING PROPERTIES OF NOVEL METAL CHELATES DERIVED FROM RESACETOPHENONE CONTAINING AZO DYE

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ABSTRACT

Several transition metal chelates viz. Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Zn^{2+} of DAPORA ligands were synthesized and further characterized using metal-ligand (M:L) ratio, elemental analysis, IR and reflectance spectra and magnetic properties. The ligand used in synthesis of metal chelates i.e. 1-(2,4-dihydroxy-5--((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)phenyl)ethanone (DAPORA) was prepared by simple diazotization reaction between diazonium salt of 2-amino-5-phenyl-[1,3,4]-oxadiazole (APO) and resacetophenone (RA). The synthesized ligand was characterized by elemental analysis and spectral analysis. In addition, the antifungal activity of DAPORA and its metal chelates was examined against various fungi.

Key words: 2-Amino-5-phenyl-[1,3,4]-Oxadiazole, Resacetophenone, Electronic spectral analysis, Magnetic moment, Antifungal properties.

INTRODUCTION

Resacetophenone a well-known complexing agent is able to coordinate with wide number of metal ions. It is also well known as pharmaceutical agent[1-4]. Several resacetophenone derivatives are also reported for dyeing of textiles and other industrial applications[5,6]. Some of the ions exchanging resins of resacetophenone are also reported with good potentiality[7,8]. A number of heterocyclic compounds show the pharmaceutical as well as biological activity. Oxidazole has played a vital role in the preparation of various biologically active compounds as antimicrobial, antitubercular, antibacterial, anti-inflammatory[9-11]. One of the derivative say 2-amino-5-phenyl-[1,3,4]-oxadiazole (APO) is synthesized and studied extensively for number of derivatives[12,13]. The reaction of oxidazole derivative with resacetophenone has not been reported so far. Hence, such type of heterocyclic ring and resacetophenone into one molecule may afford good biological active compound. The present communications discuss about synthesizes, characterization and antifungal properties of metal chelates derived from 1-(2,4-dihydroxy-5--((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)phenyl)ethanone (DAPORA) ligand **(Scheme 1)**.

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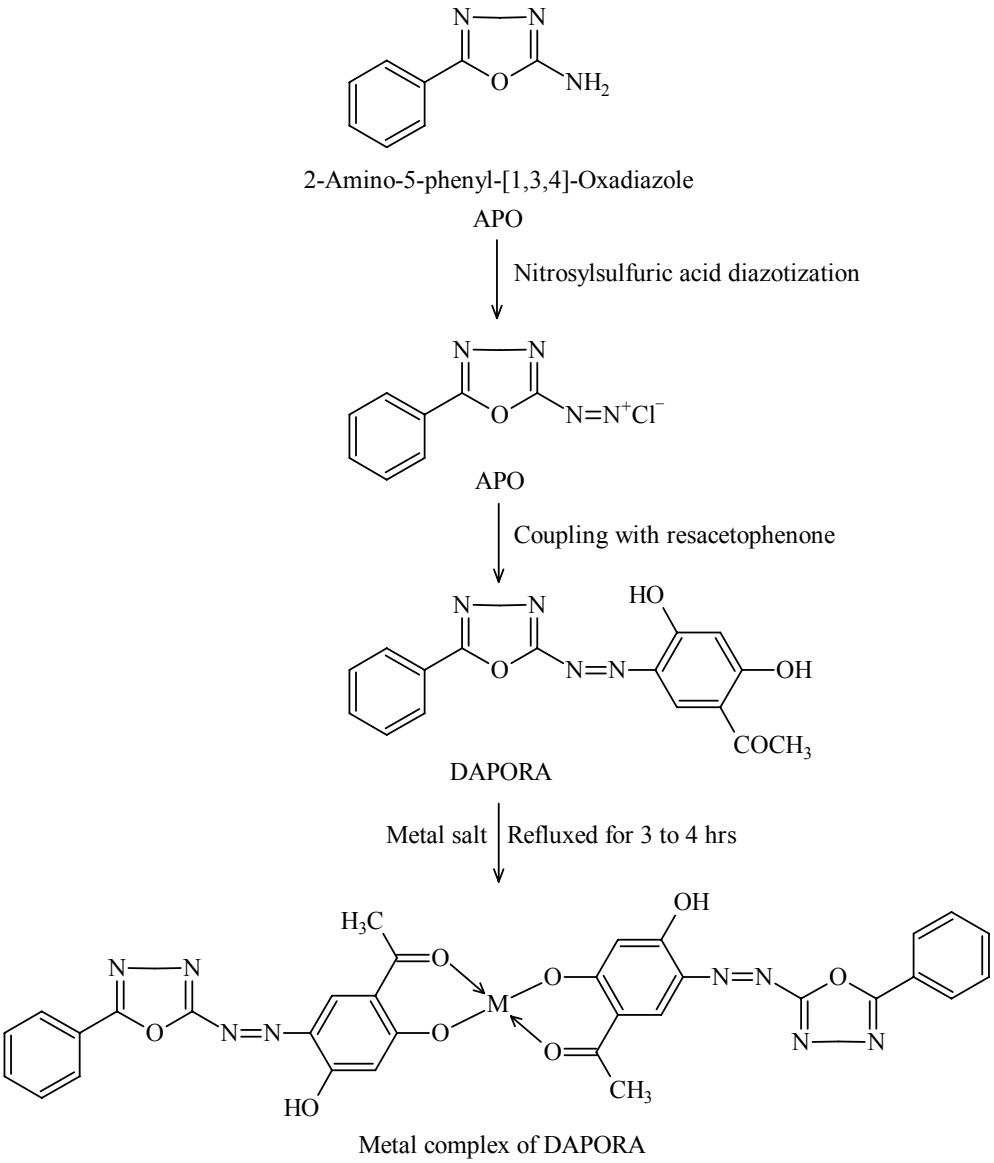

Scheme 1

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

EXPERIMENTAL

2-Amino-5-phenyl-[1,3,4]-oxadiazole (APO) was prepared according to reported method[14]. All other chemicals and solvents used were of laboratory grade.

Synthesis of 1-(2,4-dihydroxy-5-((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)phenyl)ethanone (DAPORA)

2-Amino-5-phenyl-[1,3,4]-oxadiazole (APO) (0.01 mole) was dissolved in a mixture of H_2SO_4 (12 mL) and water (15 mL) and cooled to 0^oC in ice bath. To this solution, a cold aqueous solution of sodium nitrite (0.04 mole) was added. The diazonium salt solution of APO was filtered into a cooled solution of Resacetophenone (0.01 mole) at O-5^oC. The resulting solid azo dye was washed with water, dried and recrystallized from, MeOH. Yield: 68%, M.P. 270-271^oC (decompose) uncorrected.

Analysis

Elemental analysis	C (%)	H (%)	N (%)
$C_{16}H_{12}N_4O_4$ (324)			
Calculated	59.26	3.73	17.28
Found	59.2	3.7	17.2
IR Spectral features	2950-2850		Ar C-C
(cm^{-1})	1630, 1575		Azo group
	3200-3600		OH
	1350		C-O-C
	1750		CO

NMR : δ ppm 6.45-8.05 (m, 7H, Ar-H), 5.32 (s, 1H, OH), 2.38 (s, 3H, CH_3).

Synthesis of metal chelates of 1-(2,4-dihydroxy-5-((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)phenyl) ethanone (DAPORA)

The metal chelates of DAPORA 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 DAPORA solution

DAPORA (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 DAPORA. It was diluted to 100 mL.

Synthesis of DAPORA-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 DAPORA solution (i.e. containing 0.01 M DAPORA) 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 Flash 1101 EA (Itally) the metals were determined volumetrically by Vogel's method[15]. 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 DAPORA 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[16].

Table 1: Elemental analysis of DAPORA ligand and its transition metal chelates

Empirical formula	Mol. wt.	Yield (%)	Elemental analysis							
			C (%)		H (%)		N (%)		M (%)	
			Cald.	Found	Cald.	Found	Cald.	Found	Cald.	Found
DAPORA	324	68	59.26	59.2	3.73	3.7	17.28	17.2	-	-
$(DAPORA)_2Cu^{2+}$	710	66	54.12	58.1	3.12	3.0	15.78	15.7	8.95	8.9
$(DAPORA)_2Co^{2+}$	705	65	54.48	54.4	3.14	3.1	15.88	15.8	8.35	8.3
$(DAPORA)_2Mn^{2+}$	701	60	54.79	59.7	3.16	3.1	15.97	15.9	7.83	7.8
$(DAPORA)_2Ni^{2+}$	705	62	54.50	54.4	3.14	3.1	15.89	15.8	8.32	8.2
$(DAPORA)_2Zn^{2+}$	711	63	53.98	53.9	3.11	3.0	15.74	15.7	9.19	9.1

RESULTS AND DISCUSSION

The synthesis of 1-(2,4-dihydroxy-5--((5-phenyl-1,3,4-oxadiazol-2-yl)diazenyl)phenyl)ethanone (DAPORA) was performed by a simple reaction of diazonium salt of 2-amino-5-phenyl-[1,3,4]-oxadiazole (APO) and resacetophenone (RA). The resulted DAPORA ligand was in form of amorphous powder. The C, H, N contents of DAPORA (Table 1) are consistent with the structure predicted **(Scheme 1)**. The IR spectrum of DAPORA comprises the important bands due to CO of acetyl group at around 1750 cm^{-1}. The broad band due to –OH group appeared at around 3650 cm^{-1}. In this band the inflections are observed at 2968, 2925 and 2841 cm^{-1}. The NMR spectrum of DAPORA in DMSO indicates that the singlet of 1 H at 5.32 δ ppm due to –OH group. Also the important signal for $–CH_3$ found at their respective position i.e. 2.38 δ ppm. Rest of the aromatic protons are appeared in multiplicity at δ 6.45-8.05 ppm. Thus the structure of DAPORA is confirmed as shown in **Scheme 1**.

The metal and C, H, N contents of metal chelates of DAPORA (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: Spectral features and magnetic moment of DAPORA metal chelates

Metal chelates	μ_{eff} (BM)	Electronic spectral data (cm^{-1})	Transition
DAPORA-Cu^{2+}	2.54	23425	Charge transfer
		13196	$^2B_{1g} \rightarrow {}^2A_{1g}$
DAPORA-Co^{2+}	4.80	23736	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
		19102	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$
		8917	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$
DAPORA-Mn^{2+}	5.60	23214	$^6A_{1g} \rightarrow {}^6A_{2g}\ {}^4E_g$
		19012	$^6A_{1g} \rightarrow {}^4T_{2g}$ (4G)
		16841	$^6A_{1g} \rightarrow {}^4T_{1g}(PG)$
DAPORA-Ni^{2+}	3.70	22584	$^3A_{1g} \rightarrow {}^3T_{1g}(P)$
		15374	$^3A_{1g} \rightarrow {}^3T_{1g}(F)$
DAPORA-Zn^{2+}	Diamag.		---------

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 DAPORA. The other bands are almost at their respectable positions as appeared in the spectrum of parent-DAPORA 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.

Table 3: Antifungal activity of dapora ligand and its metal chelates

Sample	Zone of inhibition of fungus at 1000 ppm (%)			
	Nigrospora Sp.	***Botrydeplaia thiobromine***	***Asperginus niger***	***Rhisopus Nigricans***
DAPORA	56	60	55	53
DAPORA-Cu^{2+}	74	75	70	68
DAPORA-Co^{2+}	61	71	67	64
DAPORA-Mn^{2+}	68	63	62	60
DAPORA-Ni^{2+}	58	69	61	55
DAPORA-Zn^{2+}	62	69	64	58

Magnetic moments of metal chelates are given in Table 2. The diffuse electronic spectrum of Cu^{2+} chelates shows two broad bands around 13196 and 23425 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[17]. The Co^{2+} metal chelate gives rise to two absorption bands at 23736 and 19102 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 [18]. The spectrum of Mn^{2+} polymeric chelate comprised two bands at 19012 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 2.58-5.58 B.M are consistent with the above moiety[19]. 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[20]. Zn^{+2} metal chelate is diamagnetic in nature and its electronic spectra do not furnish any characteristic d-d transitions.

The examination of antifungal activity of DAPORA 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. K. S. Bhatki, Rev. Anal. Chem., **8**, 211 (2011).
2. V. K. Reddy, S. M. Reddy, P. R. Reddy and T. S. Reddy, Ind. J. Chem., **39A**, 557 (2000).
3. S. Baluja, A. Solanki and N. Kachhadia, J. Iranian Chem. Soc., **3**, 312 (2006).
4. M. S. S. Babu, K. H. Reddy and P. G. Krishna, Polyhedron., **26**, 572 (2007).
5. A. Kaur and U. Gupta, Ele. J. Envir., Agric. Food Chem., **9**, 1334 (2010).
6. S. G. Kadarmandalgi, J. Chem. Educ., **41**, 438 (1964).
7. N. Kavitha and P. V. A. Lakshmi, J. Saudi Chem. Soc., doi:10.1016/j.jscs.2015.01.003 (2015).
8. S. Lenka, A. Parija and P. L. Nayak, Poly. Int., **29**, 103 (2007).
9. N. Jaiswal, A. K. Singh, D. Singh and T. Ahmad, Int. Res. J. Pharm., **3**, 83 (2012).
10. D. S. Musmade, S. R. Pattan and M. S. Yalgatti, Int. J. Pharm. Chem., **5**, 11 (2015).
11. M. K. Bharty R. K. Dani, P. Nath, A. Bharti, N. K. Singh, O. Prakash, R. K. Singh and R. J. Butcher, Polyhedron., **98**, 84 (2015).
12. M. Faizi, S. Dabirian, H. Tajali, F. Ahmadi, E. R. Zavareh, S. Shahhosseini and S. A. Tabatabai, Bioorg. Med. Chem., **23**, 480 (2015).
13. A. Johnsoa and Wilcox, Lab. Exp. Org. Chem., The Macmillan Company, Collier Macmillan Limited, London (1969) p. 219.
14. K. K. Oza and H. S. Patel, Bulg. Chem. Comm., **42**, 103 (2010).
15. A. I. Vogel, Textbook of Quantitative Chemical Analysis, ELBS 5th Ed., London (1996).
16. W. R. Baily and E. G. Scott, Diagnostic Microbiology, The C. V. Moshy Co. St. Lovis (1966) p. 257.
17. J. C. Patel, H. R. Dholariya, K. S. Patel, J. Bhatt and K. D. Patel, Med. Chem. Res., **23**, 3714 (2014).
18. B. R. Patil, Oriental J. Chem., **18**, 547 (2006).
19. G. R. Chauhan, K. D. Patel, H. R. Dholariya, J. C. Patel and K. K. Tiwari, Int. J. Health Pharm. Sci., **1**, 83 (2012).
20. C. J. Balhausen, Introduction to Ligand Fields, McGraw Hill, New York (1962).