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Studies on Transition Metal-azo Ligand Chelates

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ABSTRACT

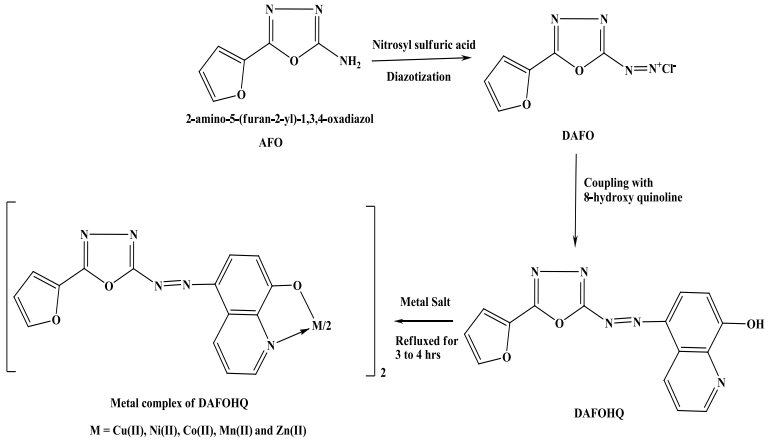
The new azo ligand chelates of Cu(II), Ni(II), Co(II), Mn(II), Zn(II) with 1,3,4-oxidazole and 8-hydroxyquinoline were synthesized and further characterized by FT-IR, elemental analysis and Metal: Ligand ratio as well as reflectance spectra and magnetic moment measurement. Earlier the synthesized ligand was characterized by using Mass, IR and NMR spectroscopy. Analysis of Metal: Ligand ratio suggest all complexes are found in 1:2 (M:L) ratio. The work also includes antifungal activity of the azo-ligand metal chelates was studied against four types of fungal strains which suggest the advantage of coordination to such type of heterocyclic azo-ligand.

Keywords: 2-amino-5-(furan-2-yl)-1,3,4-oxadiazol, 8-Hydroxyquinoline, Metal, Ligand ratio, Spectral studies, Conductivity measurement, Antifungal properties

INTRODUCTION

Azo ligands are generally synthesized by coupling reaction of diazonium salts with heterocyclic compounds [1-3]. Azo ligand containing O, N donor atoms well known for its superior chelating properties with the all types of metal ions and showed significant biological activities [4,5]. The interest around the azo compounds sustain due to their effortless procedure, cost-effectiveness and good fastness properties [6,7]. Furthermore, the coordination compounds of azo ligands have been studied extensively for their essential role in industry, life processes and also in technology field [8-10]. The coordinating ability of 8-HQ and its metal chelates has been well known from its existence and proven significant in the different field such as, biological, pharmacological, analytical and industrial [11-13].

In continuation of our previous works on azo-ligand metal chelates and their various properties [14-16], we have synthesized a new azo-ligand namely 5-((5-(furan-2-yl)-1,3,4-oxadiazol-2-yl)diazenyl)quinolin-8-ol (DAFOHQ) and characterized on the basis of elemental analysis, mass spectrometry, ^{1}H NMR spectral studies. Further the chelating and biological properties of all synthesized compounds were explored and discussed in detailed (Scheme 1).



Scheme 1: General synthesis of azo-ligand metal chelates

EXPERIMENTAL

2-Amino-5-(furan-2-yl)-1,3,4-oxadiazol (AFO) was prepared according to reported method [17]. All other chemicals and solvents used were of laboratory grade. The elemental contents were determined by Thermo Finigen Flash 1101 EA (Italy) the metals were determined volumetrically by Vogel's method [18]. 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 Ethylenediaminetetraacetic Acid (EDTA) solution. Infrared spectra of the synthesized compounds were recorded on Nicolet 760 FT-IR spectrometer. Nuclear Magnetic Resonance (NMR) spectrum of DAFOHQ was recorded on 400 MHz, NMR spectrophotometer. Magnetic susceptibility measurement of the synthesized chelates was carried out on Gouy Balance at room temperature. Mercury Tetrathiocynatocobalate (II) $Hg[Co(NCS)_4]$ 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 [19].

Synthesis of 5-((5-(furan-2-yl)-1,3,4-oxadiazol-2-yl)diazenyl)quinolin-8-ol

AFO (0.01 mol) was dissolved in a mixture of H_2SO_4 (12 ml) and water (15 ml) and cooled to 0°C in ice bath. To this solution a cold aqueous solution of sodium nitrite (0.04 mol) was added. The diazonium salt solution of AFO was filtered into a cooled solution of 8-hydroxyquinoline (0.01 mol) at 0-5°C. The resulting solid azo dye was washed with water, dried and recrystallized from, MeOH. Yield: 70%, M.P. 252-254°C (decompose) uncorrected. $C_{15}H_9N_5O_3$ (307), Elemental analysis (%): Cal. 58.63 (C), 2.95 (H), 22.79 (N); Found, 58.6 (C), 2.9 (H), 22.7 (N). IR Spectral Features (cm^{-1}): 3035 (Ar C-H), ~2950 (Ar C-C), 1628, 1572 (Azo group), 3410 (-OH), 1573 (C=N), 1325 (C-O-C). ^{1}HNMR (δ ppm): 6.58-8.92 (m, 8H, Ar-H), 5.28 (s, 1H, OH).

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

The metal chelates of DAFOHQ with Cu(II), Ni(II), Co(II), Mn(II), Zn(II) metal ions were prepared in two steps. All the metal chelates were prepared in an identical procedure.

Preparation of DAFOHQ solution

DAFOHQ (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 DAFOHQ. It was diluted to 100 ml.

Synthesis of DAFOHQ-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 DAFOHQ solution (i.e. containing 0.01 M DAFOHQ) 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: Analysis of DAFOHQ ligand and its metal chelates

Empirical formula	Yield (%)	Elemental analysis							
		C%		H%		N%		M%	
		Cald	Found	Cald	Found	Cald	Found	Cald	Found
DAFOHQ	70	58.63	58.6	2.95	2.9	22.79	22.7	-	-
$(DAFOHQ)_2Cu(II)$	68	53.3	53.2	2.39	2.3	20.72	20.7	9.4	9.3
$(DAFOHQ)_2Ni(II)$	64	53.68	53.6	2.4	2.3	20.87	20.8	8.74	8.7
$(DAFOHQ)_2Co(II)$	66	53.66	53.6	2.4	2.3	20.86	20.8	8.78	8.7
$(DAFOHQ)_2Mn(II)$	67	53.98	53.9	2.42	2.4	20.99	20.9	8.23	7.2
$(DAFOHQ)_2Zn(II)$	61	53.15	53.1	2.38	2.3	20.66	20.6	9.65	9.6

RESULTS AND DISCUSSION

The azo ligand, DAFOHQ was prepared by reacting 8-hydroxyquinoline with AFO. The structure of the DAFOHQ was demonstrated by an analytical, IR, NMR, CMR and Mass spectral Studies. The ligand coordinates to the metal ion in N_2O_2 manner through Metal: Ligand (1:2) ratio for all metal chelates. The elemental analysis of all compounds is given in Table 1, which consist with theoretically expected value supports their structural composition.

Table 2: Magnetic moment and reflectance spectral data of DAFOHQ metal chelates

Metal Chelates	μ_{eff} (BM)	Electronic spectral data (cm^{-1})	Transition
DAFOHQ-Cu(II)	2.45	23415 13240	Charge transfer $^2B_{1g} \rightarrow {}^2A_{1g}$
DAFOHQ-Ni(II)	3.68	22617 15384	$^3A_{1g} \rightarrow {}^3T_{1g}(P)$ $^3A_{1g} \rightarrow {}^3T_{1g}(F)$
DAFOHQ-Co(II)	4.75	23735 19120 8974	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$
DAFOHQ-Mn(II)	5.51	23256 19030 16862	$^6A_{1g} \rightarrow {}^6A_{2g}\ {}^4E_g$ $^6A_{1g} \rightarrow {}^4T_{2g}$ (4G) $^6A_{1g} \rightarrow {}^4T_{1g}(PG)$
DAFOHQ-Zn(II)	Diamag.	-	-

The ligand spectrum revealed a broad band at 3410 cm^{-1} corresponding to the vibration of the O–H group present in the structure. The band observed at 3035 cm^{-1} and 2950 cm^{-1} are due to the presence of aromatic C-H and C-C bonds in the structure, respectively. Especially, the band observed at 1628, 1572 cm^{-1} indicates the azo (-N=N-) group, which was not present in the starting material but forms as resulting product of the diazotization reaction. This band is shifted in the metal chelates toward lower frequencies because of the coordination of the nitrogen to the metal ion. The peak at 3410 cm^{-1} in the spectrum of the ligand corresponding to the OH group was disappeared in the spectrum of all metal chelates suggest coordination at OH of quinoline derivative. The peaks attributed to C=N also suggest the coordination by low value found for the same group in spectra of all metal chelates. The peaks appearing attributed to the M–O and M–N groups found for all metal chelates at their respective positions.

The ^{1}H-NMR spectrum of the azo-ligand showed peaks at δ-5.28 ppm attributed to -OH group, while, the multiple peaks appearing in the range δ-6.58-8.92 ppm are attributed to remaining aromatic protons.

Table 3: Antifungal activity of DAFOHQ metal chelates

Sample	Zone of inhibition of fungus at 1000 ppm (%)			
	***Nigrospora* sp.**	***Botryodiplodia theobromae***	***Asperginus niger***	***Rhizopus nigricans***
DAFOHQ	58	52	60	48
DAFOHQ-Cu(II)	75	73	78	70
DAFOHQ-Ni(II)	68	65	69	63
DAFOHQ-Co(II)	71	70	74	68
DAFOHQ-Mn(II)	70	69	71	64
DAFOHQ-Zn(II)	63	62	65	58

The reflectance spectra along with magnetic moment value suggest the geometry for all metal chelates respectively. Cu(II) metal chelate shows two broad bands around 13.240 cm^{-1} and 23.415 cm^{-1} may be due to $^2B_{1g}\rightarrow{}^2A_{1g}$ transition and charge transfer transition, respectively, which suggest a distorted octahedral structure [20-23]. Ni(II) metal chelate also shows two transition at 22617 and 15384 cm^{-1} attributed to $^3A_{1g}\rightarrow{}^3T_{1g}(P)$ and $^3A_{1g}\rightarrow{}^3T_{1g}(F)$ suggest the octahedral geometry [20,21] Co(II) and Mn(II) give three absorption bands respectively at 23735, 19120 and 8974 cm^{-1} and at 23256, 19030 and 16862 cm^{-1} which can be assigned respectively to $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$, $^4T_{1g}(F)\rightarrow{}^4T_{2g}$, $^4T_{1g}(F)\rightarrow{}^4T_{2g}(P)$ and $^6A_{1g}\rightarrow{}^6A_{2g}$ ^4E_g, $^6A_{1g}\rightarrow{}^4T_{2g}$ (4G), $^6A_{1g}\rightarrow{}^4T_{1g}(PG)$ transitions [21,22]. These absorption bands and the values of magnetic moment given in Table 2 indicate an octahedral configuration for all the metal chelates except the Zn(II) metal chelates which is not shown any d-d transition due to its diamagnetic nature.

The antifungal activity of the new azo-ligand (DAFOHQ) and their metal chelates were tested by the agar dilution method. The antifungal activities of the compounds against four funguses, namely *Viz. Nigrospora* sp., *Botrydeplaia thiobromine, Asperginus niger, Rhizopus nigricans* are presented in Table 3.

In conclusion, the results showed that the compounds exhibited good to moderate activity against all the tested fungus among which they found highest activity against *Asperginus niger*. However, the Cu(II) chelate showed the highest effect against all the tested fungi.

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REFERENCES

[1] C.T.K. Kumar, J. Keshavayya, T. Rajesh, S.K. Peethambar, *Int. J. Pharm. Pharm. Sci*., **2013**, 5, 296.
[2] C.J. Patil, C.A. Nehete, *Int. J. Pharm. Sci. Rev. Sci*., **2015**, 33, 248.
[3] S.A. Sharma, M. Kasem, E. Ali, M. E. Moustafa, *J. Basic Env. Sci*., **2014**, 1, 76.
[4] H.D. Raj, Y.S. Patel, *Adv. Appl. Sci. Res*., **2015**, 6, 11.
[5] C.T.K. Kumar, J. Keshavayya, T.N. Rajesh, S.K. Peethambar, A.R.S. Ali, *Org. Chem. Int*., **2013**, 1.
[6] D.R. Waring, G. Hallas, Springer, US, **1990**, 30.
[7] K. Hunger, Wiley & Sons, **2003**.
[8] G.B. Kauffin, Springer Verlag, Berlin, **1966**.
[9] F.A. Cotton, *J. Chem. Soc. Dalton Trans*., **2000**, 1961.
[10] M.M. El-Ajaily, F.I. Abdallh, M.S. Suliman, R.A. Akasha, *J. Adv. Chem. Sci*., **2015**, 1, 21.
[11] V. Prachayasittikul, S. Prachayasittikul, S. Ruchirawat, V. Prachayasittikul, *Drug Des. Devel. Ther*., **2013**, 7, 1157.
[12] Y. Song, H. Xu, W. Chen, P. Zhan, X. Liu, *Med. Chem. Commun*., **2015**, 6, 61.
[13] A. Marella, O.P. Tanwar, R. Saha, M.R. Ali, S. Srivastava, M. Akhter, M. Shaquiquzzaman, M.M. Alam, *Saudi Pharm. J*., **2013**, 21, 1.
[14] B.K. Patel, S.D. Patel, *Der. Chemi. Sin*., **2014**, 5, 27.
[15] B.K. Patel, S.D. Patel, *Adv. Appl. Sci. Res*., **2015**, 6, 165.
[16] B.K. Patel, S.D. Patel, *J. Chem. Pharm. Res*., **2015**, 7, 676.
[17] K.K. Oza, H.S. Patel, *Bul. Chem. Comm*., **2010**, 42, 103.
[18] A.I. Vogel, ELBS, London, **1996**.
[19] W.R. Baily, E.G. Scott, C.V. Moshy, Lovis, **1966**, 257.
[20] B.N. Figgs, M.A. Hitchman, Wiley VCH, NY, USA, **2000**.
[21] C.J. Balhausen, McGraw Hill, NY, USA, **1962**.
[22] G.R. Chauhan, K.D. Patel, H.R. Dholariya, J.C. Patel, K.K. Tiwari, *Int. J. Health Pharm. Sci*., **2012**, 1, 83.
[23] J.C. Patel, H.R. Dholariya, K.S. Patel, J. Bhatt, K.D. Patel, *Med. Chem. Res*., **2014**, 23, 3714.