Synthesis, Characterization and Antimicrobial Activity of Metal Chelates of 5-(4-*N,N*-Diethylamino sulfonyl phenyl azo)-8-hydroxy quinoline

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Abstract: 4-*N,N*-Diethylamino sulfonyl phenyl amine was synthesized by diazotization and coupled with 8-hydroxyquinoline. The resultant 5-(4-*N,N*-diethylamino sulfonyl phenyl azo)-8-hydroxy quinoline (DSAQ) was characterized by elemental analysis and spectral studies. The transition metal chelates viz. Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺ and Zn²⁺ of DSAQ were prepared and characterized by metal-ligand (M:L) ratio. IR and reflectance spectroscopy and magnetic properties. The anti fungal activity of DSAQ and its metal chelates was screened against various fungi. The results show that all these samples are good antifungal agents.

Keywords: 8-Hydroxy quinoline, Magnetic moment, Metal chelates, Antifungal properties.

Introduction

8-Hydroxyquinoline is well known as an analytical reagent^{1,2}. It's various derivatives³ are also useful in pharmaceuticals. Several azo dyes based on 8-quinolinol (8-HQ) are also reported for dyeing of textiles as well as their chelating properties. Various derivatives based on quinolinol have also been reported for their chelating property. The literature survey reveals that the azo dyes based on sulfonyl imide of 8-HQ have not been reported so far. Hence considering the research gap, present paper deals with synthesis, characterization and chelating properties of 5-(4-*N,N*-diethylamino sulfonyl phenyl azo)-8-hydroxy quinoline (DSAQ). The research work is shown in Scheme 1.

Experimental

4-(*N,N*-Diethylamino sulfonyl) aniline was prepared according to the method reported in literature⁴. All other chemicals used were of laboratory grade.

*Synthesis of 5-[4-*N,N*-diethylamino sulfonyl phenylazo]-8-quinolinol*

Diazotization of *N,N*-diethylamino sulfonyl aniline was carried out by usual method⁵. The diazo salt solution was then coupled with 8-hydroxy quinoline. 8-HQ (0.01 mole) was dissolved in required amount of aqueous alkali and the solution was then cooled to 0-5 °C. To this well stirred solution, the diazonium salt of *N,N*-diethylamino sulfonyl aniline was added slowly, so that temperature did not rise above 5 °C. While maintaining pH 4.5-5.5 by the action of sodium acetate solution (10% w/v) the mixture was then stirred for 1 h at 0-5 °C. The resulting solid dye material was filtered off and washed with boiling water and then air dried. It was red amorphous powder. It is insoluble in common organic solvent but soluble only in formic acid and DMSO. It did not melt up to 230 °C

Synthesis of metal chelate of DSAQ

The metal chelates of DSAQ were prepared in two steps. All the metal chelates were prepared in an identical procedure. The details are given as follows.

Preparation of DSAQ solution

DSAQ (0.05 mol) was taken in 500 mL beaker. Formic acid was added up to slurry formation. To this slurry water was added till the complete dissolution of DSAQ. It was diluted to 100 mL.

Synthesis of DSAQ-metal Chelates

In a solution of metal acetate (0.005 mol) in acetone: water (50:50 v/v) mixture (40 mL), 20 mL of above mentioned DSAQ solution (*i.e* containing 0.01 M DSAQ) was added with vigorous stirring at room temperature. The appropriate pH was adjusted by the 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.

The elemental contents C, H, N were determined by thermo analyzer. The metals were determined volumetrically by Vogel's method. The sulfur content was determined by carius method⁶. To a 100 mg sample, each 1 mL of HCl (AR), H₂SO₄ and HClO₄ were added and then 1 g of NaClO₄ 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 compound were recorded on Nicolet 760 FT-IR spectrometers. NMR spectrum of DSAQ was recorded on 400 MHz NMR spectrometers. Magnetic susceptibility measurement of the synthesized complexes was carried out on Gouy balance at room temperature. The electronic spectra of complexes in solid were recorded at room temperature. MgO was used as reference. Antifungal activity of all the samples was monitored against various fungi, following the method reported in literature⁷.

Results and Discussion

The synthesis of 5-[4-*N,N*-diethylamino sulfonyl phenyl azo)-8-quinolinol (DSAQ) was performed by a simple azo dye formation process⁵. The resultant DSAQ ligand was an amorphous dark red powder. The C, H, N content of DSAQ is presented in Table 1. The data are consistent with the structure predicted (Scheme 1). The IR spectrum of DSAQ comprises the important bands due to 8-quinolinol. The bands were observed at 1630, 1575, 1500, 1470 and 750 cm⁻¹.

The broad band due to -OH group appeared at 3800-2700 cm⁻¹. In this band the inflections are observed at 2890, 2950 and 1350 cm⁻¹. These might be attributed due to CH₃. The NMR spectrum of DSAQ in DMSO indicates that the singlet at 2.4 ppm due to CH₃, while the singlet at 3.8 δ ppm due to -OH group. The aromatic portions are appeared in the form of multiplet between 6.5 to 7.2 δ ppm. The number of azo and hydroxyl groups of the ligands are found to be one⁷. Thus the structure of DSAQ is confirmed as shown in Scheme 1.

Table 1. Analytical data of DSAQ ligand and its metal chelates.

Compound	Emperical Formula	Mol. Cal g/mole	Yield, %	Elemental Analysis, %									
				C		H		N		S		M	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
DSAQ	$C_{19}H_{20}N_4O_3S$	384	83	59.37	59.30	5.20	5.10	14.58	14.52	8.33	8.31	-----	-----
[Cu DSAQ (H ₂ O) ₂]	$C_{38}H_{38}N_8O_6S_2Cu^{2+}2(H_2O)$	865.54	71	52.68	52.60	4.39	4.30	12.93	12.90	7.39	7.31	7.34	7.31
[Co DSAQ (H ₂ O) ₂]	$C_{38}H_{38}N_8O_6S_2Co^{2+}2(H_2O)$	860.93	66	52.96	52.90	4.41	4.40	13.00	13.00	7.45	7.40	6.83	6.82
[Ni DSAQ (H ₂ O) ₂]	$C_{38}H_{38}N_8O_6S_2Ni^{2+}2(H_2O)$	858.69	70	53.10	53.10	4.42	4.40	13.04	12.93	7.43	7.41	6.84	6.81
[Mn DSAQ (H ₂ O) ₂]	$C_{38}H_{38}N_8O_6S_2Mn^{2+}2(H_2O)$	856.93	74	53.08	53.08	4.43	4.40	13.06	13.00	7.46	7.41	6.41	6.40
[Zn DSAQ (H ₂ O) ₂]	$C_{38}H_{38}N_8O_6S_2Zn^{2+}2(H_2O)$	897.39	66	50.81	50.80	4.23	4.20	12.48	12.35	7.13	7.10	7.28	7.20

Scheme 1

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

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 DSAQ. The other bands are almost at their respectable positions as appeared in the spectrum of parent-DSAQ 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 spectrum data are shown in Table 2. Magnetic moments of metal chelates are given in Table 2. The diffuse electronic spectrum of Cu^{2+} chelate shows two broad bands around 15000 and 23000 cm^{-1} .

The first band may be due to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ 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 chelate⁹⁻¹⁰. 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 22719 and 15254 cm^{-1} which can be assigned ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$, transition, respectively^{11,12}. These absorption bands and the μ_{eff} value indicate an octahedral configuration of the Co^{2+} metal chelate¹¹. The spectrum of Mn^{2+} polymeric chelate comprised two bands at 18340 cm^{-1} and 23854 cm^{-1} . The latter does not have a very long tail. These bands may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{2g}(4G)$, and ${}^6A_{1g} \rightarrow {}^4A_{2g}({}^4E_g)$, 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 measurements of magnetic moment it is difficult to attach any significance to this. As the spectrum of the metal chelate of Ni^{2+} show two distinct bands a 22570 cm^{-1} and 15360 cm^{-1} are assigned as ${}^3A_{1g}(F) \rightarrow {}^3T_{1g}(P)$, and ${}^3A_{1g} \rightarrow {}^3T_{1g}(F)$ transition respectively suggested the octahedral environment for Ni^{2+} ion. The observed μ_{eff} values in the range 3.01-3.2 B.M are consistent with the above moiety^{8,9}.

Table 2. Spectral features and magnetic moment of DSAQ metal chelates.

Metal Chelates	μ_{eff} , BM	Electronic spectral data, cm^{-1}	Transition	IR spectral features common for all, cm^{-1}	
DSAQ- Cu^{2+}	2.10	23245 15869	Charge transfer ${}^2B_{1g} \rightarrow {}^2A_{1g}$	1640 1570 1503 1460	Quinoline moiety
DSAQ- Ni^{2+}	3.29	22570 15360	${}^3A_{1g} \rightarrow {}^3T_{1g}(P)$ ${}^3A_{1g} \rightarrow {}^3T_{1g}(F)$	2920 2852 1431	CH_2
DSAQ- Co^{2+}	4.65	22719 15252 8935	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$	1110 502	C-O-M & O-M bands
DSAQ- Mn^{2+}	5.40	23854 18340 16814	${}^6A_{1g} \rightarrow {}^6A_{2g}({}^4E_g)$ ${}^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ ${}^6A_{1g} \rightarrow {}^4T_{1g}(PG)$	710- 750	Ar-Cl
DSAQ- Zn^{2+}	Diamag.		-----	-----	-----

The results of the examination of antifungal activity of DSAQ 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+} chelates is more toxic against fungi.

Table 3. Antifungal activity of DSAQ ligand and its metal chelates.

Sample	Zone of inhibition of fungus at 1000 ppm, %						
	PE	BT	N	T	RN	AN	TL
DSAQ	55	54	53	63	63	67	70
DSAQ- Cu^{2+}	83	78	77	83	81	81	85
DSAQ- Zn^{2+}	75	64	63	77	83	83	84
DSAQ- Ni^{2+}	80	77	75	75	73	81	80
DSAQ- Co^{2+}	65	75	75	73	78	79	85
DSAQ- Mn^{2+}	79	74	73	75	80	77	83

PE=Penicillium expansum; BT= Bortydepladia thiobromine; N= Nigrospora sp.; AN= Asperginus niger T= Trichothesium sp.; RN= Rhizopus nigricans; TL= Trichoderma lignorum

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