

## Synthesis, Characterization and Antimicrobial Activity of Metal Chelates of 5-(4-N,N-Diphenylamino sulfonyl phenyl azo)-8-hydroxy Quinoline

A.U. PATEL

Department of Chemistry, Shree M.&N. Virani Science College,  
Yogidham, Kalawad Road, Rajkot-360 005, India  
E-mail: aup\_bhoolku@yahoo.co.in; kaushaloza@gmail.com

4-N,N-Diphenylamino sulfonyl phenyl amine was synthesized, diazotized and coupled with 8-hydroxyquinoline. The resultant 5-(4-N,N-diphenylamino sulfonyl phenylazo)-8-hydroxy quinoline (PSQ) was characterized by elemental analysis and spectral studies. The transition metal chelates viz.  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  of PSQ were prepared and characterized by metal-ligand (m:L) ratio. IR and reflectance spectroscopy and magnetic properties. The antifungal activity of PSQ and its metal chelates was screened against various fungi. The results show that all these samples are good antifungal agents.

**Key Words:** 8-Hydroxy quinoline, Metal chelates, Antifungal activity.

### INTRODUCTION

8-Hydroxyquinoline is well known as an analytical reagent<sup>1,2</sup>. Its various derivatives<sup>3</sup> 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<sup>4,6</sup>. Various derivatives based on quinolinol have also been reported for their chelating properties. The literature survey reveals that the azo dyes based on sulfonyl amide of 8-hydroxyquinoline have not been reported so far. The present paper deals with synthesis, characterization and chelating properties of 5-(4-N,N-diphenylamino sulfonyl phenylazo)-8-hydroxy quinoline (PSQ) towards transition metal ions.

### EXPERIMENTAL

4-(N,N-Diphenyl amino sulfonyl) aniline was prepared according to method reported in literature<sup>7</sup>. All other chemicals used were of laboratory grade.

**Synthesis of 5-[4-N,N-diphenylamino sulfonylphenylazo)-8-hydroxyquinoline (PSQ):** Diazotization of N,N-diphenyl amino sulfonyl aniline was carried out by usual method<sup>8</sup>. The diazosalt solution was then coupled with 8-hydroxy quinoline.

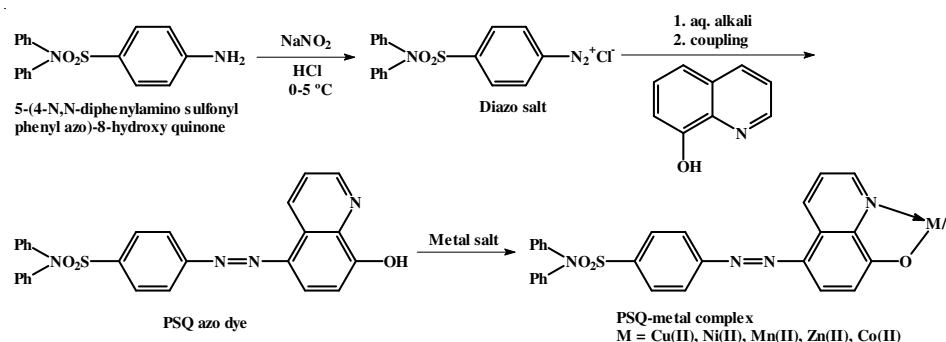
8-Hydroxyquinoline (0.01 mol) was dissolved in required amount of aqueous alkali and the solution was then cooled to 0-5 °C. To this well stirred solution the diazonium salt of N,N-diethyl phenyl aminosulfonyl aniline was added slowly so that the temperature did not rise above 5 °C. While maintaining 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 was filtered off. Washed with boiling water and then air dried. It is red amorphous powder and insoluble in common organic solvent but soluble only in formic acid and DMSO. It did not melt up to 225 °C.

**Synthesis of metal chelate of PSQ:** All the metal chelates of PSQ were prepared in two steps. The details are given as follows:

**Preparation of PSQ solution:** PSQ (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 PSQ. It was diluted to 100 mL.

**Synthesis of PSQ-metal chelates:** In a solution of corresponding metal acetate (0.005 mol) in acetone: water (50:50 v/v) mixture (40 mL) the 20 mL solution of PSQ solution (*i.e.*, containing 0.01 M PSQ) 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 (**Scheme-I**).



**Scheme-I**

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 method<sup>9</sup>. To a 100 mg sample, each 1 mL of analR HCl, H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> were added and then 1 g of NaClO<sub>4</sub> 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 PSQ 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 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<sup>10</sup>.

## RESULTS AND DISCUSSION

The synthesis of 5-[4-N,N-diphenylamino sulfonylphenylazo)-8-hydroxyquinoline (PSQ) was performed by a simple azo dye formation process<sup>11</sup>. The resultant PSQ ligand was an amorphous red powder. The C, H, N content of PSQ (Table-1) are consistent with the structure predicted (**Scheme-I**). The IR spectrum of PSQ prides the important bands due to 8-hydroxyquinoline. The bands were observed at 1630, 1575, 1500, 1470 and 750 cm<sup>-1</sup>.

TABLE-1  
ANALYTICAL DATA OF PSQ LIGAND AND ITS METAL CHELATES

Compound (m.f.)	m.w. (g/mol) (Yield, %)	Elemental analysis (%): Calcd. (found)				
		C	H	N	S	M
PSQ (C <sub>27</sub> H <sub>20</sub> N <sub>4</sub> O <sub>3</sub> S)	480.00 (86)	67.50 (67.45)	4.16 (4.12)	11.66 (11.63)	6.66 (6.60)	–
[Cu PSQ(H <sub>2</sub> O) <sub>2</sub> ] (C <sub>54</sub> H <sub>38</sub> N <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Cu <sup>2+</sup> ·2H <sub>2</sub> O)	1025.54 (67)	61.27 (61.20)	3.59 (3.51)	10.59 (10.59)	6.05 (6.05)	6.00 (6.00)
[CuPSQ(H <sub>2</sub> O) <sub>2</sub> ] (C <sub>54</sub> H <sub>38</sub> N <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Co <sup>2+</sup> ·2H <sub>2</sub> O)	1079.62 (68)	61.54 (61.51)	3.60 (3.60)	10.63 (10.61)	6.07 (6.07)	5.59 (5.55)
[CuPSQ(H <sub>2</sub> O) <sub>2</sub> ] (C <sub>54</sub> H <sub>38</sub> N <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Ni <sup>2+</sup> ·2H <sub>2</sub> O)	1079.38 (77)	61.55 (61.52)	3.60 (3.59)	10.63 (10.59)	6.07 (6.07)	5.57 (5.56)
[CuPSQ(H <sub>2</sub> O) <sub>2</sub> ] (C <sub>54</sub> H <sub>38</sub> N <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Mn <sup>2+</sup> ·2H <sub>2</sub> O)	1075.62 (76)	61.77 (61.70)	3.62 (3.60)	10.67 (10.61)	6.10 (6.10)	5.23 (5.21)
[CuPSQ(H <sub>2</sub> O) <sub>2</sub> ] (C <sub>54</sub> H <sub>38</sub> N <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Zn <sup>2+</sup> ·2H <sub>2</sub> O)	1086.08 (67)	61.16 (61.10)	3.58 (3.51)	10.57 (10.51)	6.04 (6.04)	6.17 (6.10)

TABLE-2  
SPECTRAL FEATURUES AND MAGNETIC MOMENT OF PSQ METAL CHELATES

Metal chelates	$\mu_{\text{eff}}$ (BM)	Electronic spectral data (cm <sup>-1</sup> )	Transition	IR spectral features common for all (cm <sup>-1</sup> )
PSQ-Cu <sup>2+</sup>	2.12	23241 15869	Charge transfer <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub>	1640 1570 1503 1460 Quinoline moiety
PSQ-Ni <sup>2+</sup>	3.36	22571 15377	<sup>3</sup> A <sub>1g</sub> → <sup>3</sup> T <sub>1g</sub> (P) <sup>3</sup> A <sub>1g</sub> → <sup>3</sup> T <sub>1g</sub> (F)	2920 2852 1431 CH <sub>2</sub>
PSQ-Co <sup>2+</sup>	4.61	22719 15255 8929	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (F) <sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (P) <sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (P)	1110 502.0 C-O-M & O-M bands
PSQ-Mn <sup>2+</sup>	5.49	23856 18341 16822	<sup>6</sup> A <sub>1g</sub> → <sup>6</sup> A <sub>2g</sub> <sup>4</sup> E <sub>g</sub> <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> (4G) <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (PG)	710- 750 Ar-Cl
PSQ-Zn <sup>2+</sup>	Diamag.	–	–	–

The broad band due to –OH group appeared at 3800-2700  $\text{cm}^{-1}$ . In this band the inflections are observed at 2891, 2952, and 1352  $\text{cm}^{-1}$ . These might be attributed to  $\text{CH}_3$ . The NMR spectrum of PSQ in DMSO indicates that the singlet at 2.40  $\delta$  ppm due to  $\text{CH}_3$ . While the singlet at 3.8  $\delta$  ppm due to –OH group. The aromatic portions are appeared in form of multiplet between 6.5 to 7.2  $\delta$  ppm. The number of azo and hydroxyl groups of the ligand were found to be one.

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 PSQ. The other bands are almost at their respectable positions as appeared in the spectrum of parent-PSQ ligand. However, the band due to  $\nu(\text{M-O})$  band could not be detected as it may appeared below the range of instrument used. The important IR spectrum data are given in Table-2. The magnetic and electronic data of the metal complexes are given in Table-2. the antifungal activity of the ligand (PSQ) and its metal chelates are given in Table-3.

TABLE-3  
ANTIFUNGAL ACTIVITY OF PSQ LIGAND AND ITS METAL CHELATES

Sample	Zone of inhibition of fungus at 1000 ppm (%)						
	PE	BT	N	T	RN	AN	TL
PSQ	51	52	50	63	63	62	70
PSQ-Cu <sup>2+</sup>	83	83	79	81	81	84	86
PSQ-Zn <sup>2+</sup>	73	63	63	76	83	81	82
PSQ-Ni <sup>2+</sup>	79	71	74	77	73	80	79
PSQ-Co <sup>2+</sup>	62	78	72	73	78	78	80
PSQ-Mn <sup>2+</sup>	78	71	71	73	80	71	83

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

## REFERENCES

1. A.I. Vogel's, A Textbook of Quantitative Chemical Analysis, Revised by J. Besselt. R.C. Denny, J.H. Jeffery and J. Mendham, ELBS, edn. 5 (1996).
2. V.M. Ivanor and T.F. Metkina, *Ah. Anal. Khim.*, **33**, 2426 (1978).
3. J.H. Bruckhalter, V.C. Stephars, H.C. Searberough, W.S. Briniger and W.E. Dergton, *J. Am. Chem. Soc.*, **76**, 4902 (1954).
4. A. Sayed, A. Manieh and A. Mohamed, *Adv. Colour Sci. Technol.*, **3**, 65 (2000).
5. A.M.S. Youssef, M.Y. Mohamed, *Indian J. Chem.*, **37B**, 948 (1998).
6. A.F. Shoair, A.A. El-Bindary, A.Z. El-Sonabati, R.M. Younes, *Egypt. Polym. J. Chem.*, **74**, 1047 (2000).
7. H.S. Patel and V.K. Patel, *Indian. J. Heterocycl. Chem.*, **12**, 253 (2003).
8. A.I. Vogel, Elementary Practical Organic Chemistry Part-3 CBS Publisher & Distributors, India (1987).
9. S. Bance, Hand book of Practical Organic Microanalysis, Ellis Horwood Limited, New York (1980).
10. A.L. Barry, The Antimicrobial Susceptibility Test, Principal and Practice, Lea & Febiger Philadelphia (1976).
11. A.I. Vogel, Elementary Practical Organic Chemistry, Part-3, CBS Publisher & Distributors, India (1987).

(Received: 1 January 2009; Accepted: 12 October 2009) AJC-7951