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# Synthesis, Spectral and Thermogravimetric Investigation of Zinc(II) Complex of 8-Hydroxyquinoline-5-sulphonic Acid

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Zinc(II) complex of 8-hydroxyquinoline-5-sulphonic acid is synthesized by the reaction of zinc(II) ion with this ligand at the pH of 4.5. The yellow crystalline complex thus formed is characterized by elemental analysis, thermogravimetric and spectral studies *viz.*, UV-Vis, FTIR, $^1$H NMR and $^{13}$C NMR. 8-Hydroxyquinoline-5-sulphonic acid acts as a neutral bidentate ligand coordinating through N- and O-atoms. The complex is diamagnetic and tetrahedral. The structure and geometry of the complex is discussed.

**Key Words: Zinc(II) complex, 8-Hydroxyquinoline-5-sulphonic acid, Spectral and thermogravimetric analysis.**

## INTRODUCTION

8-Hydroxyquinoline-5-sulphonic acid (8HQS) is used as a reagent for the determination of transition metal ions[1-6]. This paper reports the synthesis and characterization of *bis*(8-hydroxyquinoline-5-sulphonic acid)zincate (II) complex.

## EXPERIMENTAL

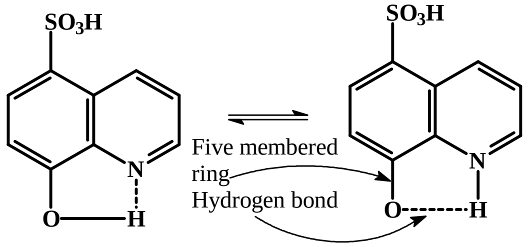
Elemental analysis is done using a Perkin Elmer 2400 series Elemental analyzer. FTIR spectra are recorded in KBr pellets on a Bomen NB series spectrometer. Proton NMR and $^{13}$C NMR spectra scanned on Bruker Avence series spectrometer at 300 MHz and 75 MHz. The thermogravimetric analysis of the complex is done in air using TGA 50H Shimadzu, Japan.

8-Hydroxyquinoline-5-sulphonic acid is obtained from Aldrich and all other chemicals used are of AR grade.

**Synthesis of zinc-8-hydroxyquinoline-5-sulphonic acid complex:** 2.87 g of $ZnSO_4\cdot 7H_2O$ is dissolved in 5 mL of water. To this solution, 6.75 g of 8HQS in 150 mL of 25 % $NH_4OH$ is added and the pH of the mixture is adjusted to 4.5 using sulphuric acid. A yellow crystalline complex separated when the mixture is stirred for about 5 min at room temperature. The filtered solid is washed several times with water and recrystallized with $NH_4OH$ (pH 4.5). Elemental analysis % found (calcd): C 38.96 (39.34); H 3.11 (2.91); N 4.83 (5.10); S 10.65 (10.97), m.p. 370ºC.

## RESULTS AND DISCUSSION

In the UV-Vis spectra of the free ligand, a peak at 310 nm is observed. This is assigned to the quinoline group. In the complex, a new band at 370 nm in addition to the band at 310 nm indicates formation of the complex. The FTIR spectra of 8-hydroxyquinoline-5-sulphonic acid gives a sharp OH stretching band at 3516 $cm^{-1}$ in addition to an intramolecular hydrogen bonded band at 3397 $cm^{-1}$ (**Scheme-I**). Intramolecular hydrogen bonding in 8-hydroxyquinolines has been studied by Roossotti and Rossotti[7] and Badger and Moritz[8]. Thus in 8 HQS, hydrogen forms readily between the phenolic OH group and the heterocyclic N-atom and the OH stretching frequency shift is high[9]. The peaks at 1043 $cm^{-1}$ and at 1200 $cm^{-1}$ are assigned to the ν($SO_3H$) and ν(S=O) stretching, respectively. An asymmetric stretching frequency of sulphonic acid is assigned[10] to the band at 1350 $cm^{-1}$. However, 8HQS very readily hydrates and exists as hydroxonium sulphonates ($Ar\text{-}SO_3^-\cdot H_3O^+$) and this has been confirmed due to the formation of a band at 1231 $cm^{-1}$, similar to that of acid salt[11]. The sharp band found at 1632 $cm^{-1}$ is due to the stretching of ν(OH) of $SO_3H$ group[12]. The bands at 1387 and 1319 $cm^{-1}$ are stretching vibrations of (C–N–C) of the pyridine ring, the first being asymmetrical and the second symmetrical[13]. The bands *ca.* 1607 and 3084 $cm^{-1}$ are respectively due to ν(C=C) and ν(C–H) stretching vibrations of aromatic ring. The mode of bonding of ligands in the complex has been assigned by comparing the characteristic FTIR spectral bands of the complex with those of the free lignad. In the complex, the ν(NH) band has completely disappeared upon chelation and the phenolic stretching band is drastically lowered due to the replacement of phenolic hydrogen by $Zn^{2+}$. Then $SO_3H$ stretching of the reagent and that of the complex occur at the same frequency of 1045 $cm^{-1}$ confirming its non-participation in bond formation. Appearance of a new band at 552 $cm^{-1}$ in the complex is due to (Zn–O) bond formation[14].



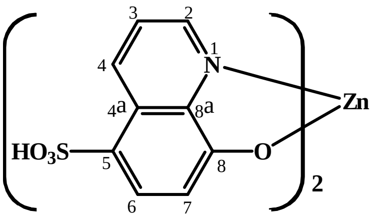
Scheme-I

**NMR spectra of the ligand:** In the $^1H$ NMR spectrum of the free ligand, the protons at $C_2$ and $C_4$ positions are less shielded due to electron withdrawal by nitrogen atom and hence resonates, respectively at 89.07

and 89.76 as doublets while the proton of $C_3$ resonates as a triplet at 88.13. As the nitrogen atom deactivates the pyridine ring, the phenyl ring having high electron density and hence the proton signals of this ring show upfield shift. Since, the OH group is *o*- and *p*-directing and $SO_3H$ group is *m*-directing, $C_7$ proton experience high shielding and hence the signal appeared at 87.32 as a doublet while the $C_6$ proton of $SO_3H$ group and the signal around 83.97 is due to the proton of OH group[15,16]. The carbon chemical shift of the reagent predicted are 149.69 ($C_2$) 122.97 ($C_3$), 135.95 ($C_4$), 145.7 ($C_5$), 128.8 ($C_6$), 114.02 ($C_7$), 126.6 ($C_8$), 130.1($C_{4a}$) and 144.70 ($C_{8a}$)[17,18].

**NMR spectra of the complex:** $^1H$ NMR signals of the complex are relatively sharp because the fluctuating magnetic fields are sufficiently rapid and hence the nucleus sees only an average effect so that its relaxation times are not severely shortened[19]. Disappearance of the signal around 83.97 of the oH group indicates the formation of (Zn–O) bond and the existence of a signal around 810.5 reveals the non-participation of $SO_3H$ group in coordinate bond formation with $Zn^{2+}$. All the proton signals in the complex are largely shifted to high field due to the electronic current induced by the applied magnetic field[20] and also due to the delocalization of the *p*-electrons by a $d\pi$-$p\pi$ mechanism. Due to Zn–N bond formation, the proton signal of $C_2$ carbon vicinal to nitrogen is broad to the extent that the coupling constant cannot be obtained fromo the peak. Moreover, the proton bonded to nitrogen as a result of intramolecular hydrogen bonding being acidic in nature, readily undergoes proton exchange. As a result of this rapid exchange, $C_2$ proton sees only an average for the spin state of N-proton and hence coupling is not observed between $C_2$ proton and proton bonded to the hetero atom. The peak intensity of the proton bonded to the hetero atom is reduced due to the exchange of proton with the deuterium. Instead a new peak due to HOD appears in the spectrum at 83.93. The $C_3$ proton appears as a quartet due to spin coupling with the $C_2$, $C_4$ and $SO_3H$ protons. Formation of only a single signal for the same protons of the ring indicates that the complex exists in *cis*- form having *cis*-$ZnN_2O_2$ chromophore. The complex, $Zn(8HQS)_2$ is tetrahedral[21] and being symmetric, gives rise to fewer resonances. The magnetic susceptibilities as determined at room temperature have been found to be negative. This confirms the diamagnetic nature of the complex as expected for diavalent zinc ion with $d^{10}$ configuration, having tetrahedral geometry.

$^{13}C$ NMR chemical shift of the complex is determined by the orbital geometry of the complex than on the neighbouring environment. Thus the carbon-13 shifts of pyridine ring decrease in 8a and 7 but increase in 4a, 5 and 6 positions upon complexation. Shielding in the 8a and 7 positions in attributed to the change of the N-C-8a bond order (**Scheme-II**). Deshielding at 4a and 6 and particularly at 5 arises from an increased electron withdrawal of the positively charged nitrogen and also due to deshielding bond order arising from delocalization of multiple bonds in aromatic system on complexation. Moreover, heavy atom substitution at $C_8$ position due to complexation also causes a significant upfield shift called the high field complexation shift. This is attributed to the increased diamagnetic shielding caused by the large number of electrons introduced by the heavy atom. Thus carbon-13 resonances of the complex assigned are 110.58 ($C_2$, $C_7$), 139.23 ($C_3$, $C_5$) 147.09 ($C_4$), 137.13 ($C_{4a}$), 127.64 ($C_6$), 122.41 ($C_8$), 126.23 ($C_{8a}$).



Scheme-II

**Thermogravimetric analysis:** The thermal stability of complex was studies by TGA in air in the temperature range 300 to 1172 K. When heated, it decomposes in several steps. The complex shows a distinct weight loss between 300 and 383 K. The shape of the thermogram indicates the presence of loosely bound water possibly in the form of adsorbed water and the loss in weight is 1.27%. The loss in weight between 383 to 468 K corresponds to two molecules of water present in the complex. The onset of melting starts at 643 K which is followed by decomposition at 893 K. Finally zinc oxide is obtained at 1172 K. Considering the temperature at which the dehydration process takes place and the way by which it proceeds, it may be assumed that the molecules of water are in the outer sphere of complex coordination. According to Singh *et al.*[22] water eliminated below 313-423 K can be considered as water of crystallization and water eliminated above 423 K may be one coordinated to the central ion. In the present investigation water is eliminated below 468 K and FTIR study also revealed it to be of water of crystallization. From the TG curve the activation energies of dehydration reaction is calculated with Fatieev and Pletniev method[22] using the equation

$$E_a = RT^2_{max/} m_0 . \Delta m / \Delta T$$

where, R: gas Constant; $T_{max}$: temperature of maximum of the weight loss; $m_0$: weight loss at $T_{max}$; m: the weight loss at temperature T. The value of activation energy connected with the loss of water molecules is 21.03 KJ mol$^{-1}$ and this value of $E_a$ indicates that the water molecules are weakly bound in the outer coordination sphere and hence the formula $[Zn(8HQS)_2]\cdot 2H_2O$ is assigned for Zn-8HQS complex.

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