

## Zn(II) Complexes Of Thiazolylazo Dye: Synthesis, Spectral Characterization And Luminescence Properties

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### Abstract

zinc complexes of the type  $[M(L_1 \text{ or } L_2)(PPh_3)_2(N_3)_2]$  (1a-2a) and  $[M(L_1 \text{ or } L_2)(PPh_3)_2(NCS)_2]$  (1b-2b) (where  $L_1 = 4\text{-}(4'\text{-phenyl}, 2'\text{-thiazolylazo})$  nitrobenzene,  $L_2 = 4\text{-}(4'\text{-phenyl}, 2'\text{-thiazolylazo})$  anisole) have been prepared and characterized on the basis of their micro analytical data, spectroscopic and photo physical properties. On the basis of electronic spectra octahedral geometry has been proposed for the complexes. Complexes exhibit blue green emission with high quantum yield.

**Keywords:** Thiazolylazo complexes, spectral studies, luminescence spectra,

### 1. Introduction

**A**rylazo compounds and their complexes with transition metals have attracted much attention because of their physico-chemical properties and applications in various fields. Due to presence of the azo (-N=N-) group these compounds possess several distinctive properties including aggregation, optical data storage and tautomerism which define as a distinct class of dyestuffs [1, 2]. They are involved in many biological reactions [3, 4]; and in analytical chemistry as complexing agents for the determination of some metal ions spectrophotometrically [5, 6]. They have been widely studied for their excellent thermal and optical properties in applications such as photo switching, nonlinear optics, dyes, chemical analysis and pharmaceuticals [7-10]. They are also important in drugs and exhibit variety of interesting biological activities including antimicrobial [11, 12], anti-inflammatory [13], pesticidal activities [14] etc. Azo group is photochromic, redox sensitive, pH responsive; stabilizes low valent metal oxidation states due to the presence of low-lying azo-centered  $\pi^*$ -molecular orbital, serves as a molecular switch, is used as a metal ion indicator in complexometric titration, dyes and pigments in textile industries [15-17].

### 2. Experimental

#### 2.1. Materials and physical measurements

All the chemicals used were pure and of analytical grade. Solvents were purified and dried according to the standard procedure.  $Cu(NO_3)_2 \cdot 4H_2O$  (E-Merk India),  $NaN_3$  (Aldrich, USA),  $NH_4NCS$  (Aldrich, USA),  $PPh_3$  (Aldrich, USA) were purchased from the respective concerns and were used as received.

Microanalysis (C, H, N and S) were performed on a Thermo Finnigan FLASH EA-112 CHNS analyzer. Electronic spectra were recorded on a Shimadzu UV-visible-NIR spectrophotometer. Molar conductance ( $\Lambda_M$ ) was measured on the ELICO (CM-185) conductivity bridge using ca  $10^{-3}$  M solution in DMF. Infrared spectra were recorded on Perkin-Elmer FT-IR spectrometer as KBr pellets in the  $4000\text{-}400\text{ cm}^{-1}$  spectral range. Luminescence properties were measured using a JASCO F.P.750 fluorescence spectrophotometer equipped with quartz cuvette of  $1\text{ cm}^3$  path length at room temperature.

#### 2.2. Synthesis of thiazolylazo ligands

The thiazolylazo ligands 4-(4'-phenyl, 2'-thiazolylazo) nitrobenzene ( $L_1$ ) and 4-(4'-phenyl, 2'-thiazolylazo) anisole ( $L_2$ ) were prepared by diazotization of 4-phenyl-2-aminothiazole as procedure reported earlier [18]. These were characterized by elemental analysis, Infrared and UV-Visible spectral studies.

**2.3. Preparation of Zinc (II) complexes:** Zinc(II) complexes **1a-2a** were prepared from the Zinc (II) nitrate using the mole ratio (1:1:2:2) of metal,  $L_1/L_2$ ,  $PPh_3$  and azide. Complexes **1b-2b** was prepared from Zinc (II) nitrate using mole ratio of 1:1:2:2 with

$L_1/L_2$ ,  $PPh_3$  and thiocyanate. Typical synthesis is described below.

### 2.3.1. Zinc (II) azido complexes

A methanolic solution of (5ml) azo dye ligand (1 mmol, 0.310g  $L_1$ ; 1 mmol, 0.295 g,  $L_2$ ) was added dropwise to a solution (5 ml) of  $Zn(NO_3)_2 \cdot 4H_2O$  (1 mmol, 0.297 g) in the same solvent followed by  $PPh_3$  (2 mmol, 0.524 g) and  $NaN_3$  (2 mmol, 0.130 g) in warm methanol. The resultant mixture was stirred for 2h where upon the solid complexes were precipitated which were collected by filtration, washed several times with 1:1 ethanol: water mixture and dried under vacuum over  $CaCl_2$ .

**1a** Yield 69%; M.P. 186<sup>o</sup>C; Anal. calc. for  $C_{51}H_{40}N_{10}P_2SO_2Zn$ ; C, 62.19; H, 4.09; N, 12.28; found: C, 62.28; H, 4.18; N, 12.20; IR (KBr,  $cm^{-1}$ )  $\nu(C=N)$  1592;  $\nu(N=N)$  1435;  $\nu(PPh_3)$  1476, 744, 690;  $\nu(N_3)$  2172;  $\Lambda_m$  (DCM,  $\Omega^{-1}cm^2mol^{-1}$ ): 16.73; UV-Vis (DCM,  $\lambda_{max}$  nm): 442, 345;

**2a** Yield 67%; M.P. 141<sup>o</sup>C; Anal. calc. for  $C_{52}H_{43}N_9P_2SOZn$ ; C, 64.39; H, 4.46; N, 13.05; found: C, 64.32; H, 4.38; N, 13.10; IR (KBr,  $cm^{-1}$ )  $\nu(C=N)$  1596;  $\nu(N=N)$  1437;  $\nu(PPh_3)$  1476, 748, 690;  $\nu(N_3)$  2172;  $\Lambda_m$  (DCM,  $\Omega^{-1}cm^2mol^{-1}$ ): 16.42; UV-Vis (DCM,  $\lambda_{max}$  nm): 448, 345;

### 2.3.2. Zinc(II) thiocyanato complexes

A methanolic solution of (5 ml) azo dye ligand (1 mmol, 0.310 g  $L_1$ ; 1 mmol, 0.295 g,  $L_2$ ) was added dropwise to a solution (5 ml) of  $Zn(NO_3)_2 \cdot 4H_2O$  (1 mmol, 0.297 g) in the same solvent followed by  $PPh_3$  (2 mmol, 0.524 g) and  $NH_4NCS$  (2 mmol, 0.152 g) in warm methanol. The resultant mixture was stirred for 2h where upon the solid complexes were precipitated which were collected by filtration, washed several times with 1:1 ethanol: water mixture and dried under vacuum over  $CaCl_2$ .

**1b** Yield 63%; M.P. 135<sup>o</sup>C; Anal. calc. for  $C_{53}H_{40}N_6P_2S_3O_2Zn$ ; C, 62.60; H, 3.96; N, 8.30; found: C, 62.52; H, 3.87; N, 8.37; IR (KBr,  $cm^{-1}$ ):  $\nu(C=N)$ , 1590;  $\nu(N=N)$ , 1435;  $\nu(PPh_3)$  1478, 746, 692;  $\nu(NCS)$ , 2096;  $\Lambda_m$  (DCM,  $\Omega^{-1}cm^2mol^{-1}$ ): 19.10; UV-Vis (DCM,  $\lambda_{max}$  nm) 438, 350;

**2b** Yield 64%; M.P. 132<sup>o</sup>C; Anal. calc. for  $C_{54}H_{43}N_6P_2S_3OZn$ ; C, 64.80; H, 4.33; N, 7.02; found: C, 64.91; H, 4.26; N, 7.11; IR (KBr,  $cm^{-1}$ )  $\nu(C=N)$ ,

1589;  $\nu(N=N)$  1437;  $\nu(PPh_3)$  1480, 744, 695;  $\nu(NCS)$ , 2096;  $\Lambda_m$  (DCM,  $\Omega^{-1}cm^2mol^{-1}$ ): 31.10; UV-Vis (DCM,  $\lambda_{max}$  nm): 436, 342;

## 3. Results and discussion

The reaction of thiazolylazo ligands  $L_{1-2}$  with Zn(II) salts in presence of  $PPh_3$  and  $NaN_3$  or  $NH_4NCS$  in 1:1:1:2 molar ratio yields mononuclear complexes of the type  $[M(L)(PPh_3)_2(N_3)_2]$  (**1a-2a**) and  $[M(L)(PPh_3)_2(NCS)_2]$  (**1b-2b**); where  $M = Zn(II)$ ,  $L = 4-(2'-thiazolylazo)nitrobenzene$  ( $L_1$ ), 4-(2'-thiazolylazo)anisole ( $L_2$ ). All the metal complexes are coloured, non-hygroscopic and are fairly stable at room temperature. The conductivity values of all complexes indicate that the complexes are non-electrolytes.

### IR SPECTRA

The IR spectra of ligands and their complexes are found to be quite complex as they are in general exhibit large number of bands on varying intensities. However, a strong band observed at 1610-1630  $cm^{-1}$  in the spectra of all ligands ( $L_{1-2}$ ) is due to  $\nu(C=N)$  of thiazole nitrogen. This band shifted to lower frequencies (1584-1594  $cm^{-1}$ ) in the complexes indicates involvement of thiazole nitrogen in coordination [19]. Another band appeared at the frequency range 1460-1480  $cm^{-1}$  in the spectra of ligands assigned to  $-N=N-$  group shifted to lower frequency (1430-1444  $cm^{-1}$ ) in the complexes indicates involvement of azo nitrogen in coordination with metal ion [20]. This is also supported by the appearance of  $\nu(M-N)$  band at 435-448  $cm^{-1}$  in the complexes. The azido complexes **1a-2a** show sharp band at  $\sim 2115$   $cm^{-1}$  and strong band at  $\sim 1340$   $cm^{-1}$ . The thiocyanato complexes **1b-2b** exhibit a strong and sharp band at  $\sim 2095$   $cm^{-1}$ .

### UV spectra

The electronic transition for all the complexes were recorded in dimethylformamide ( $10^{-4}$  M) at 200-1100 nm range. The transition below 400 nm observed in complexes may be attributed to usual  $n-\pi^*$ ,  $\pi-\pi^*$  transition occurring within ligand orbital. Zn (II) complexes are diamagnetic and the electronic spectra of these complexes exhibits high intense charge transfer transition in the visible region which is assigned to MLCT band. Spectroscopic studies of the complexation of the metal ion with an azo dye showed that absorption maxima of the complexes are bathochromically shifted compared with azo dye[21]



### Photoluminescence properties

The photoluminescence properties of ligands  $L_{1-2}$  and their Zn(II) complexes were studied at room temperature in DMF. The ligand  $L_{1-2}$  shows a photoluminescence with emission at 486-492 nm at 298 K upon excitation at 348-370 nm. In complexes the emission spectra excited at 352-356 nm shows an emission peak at 498-532 nm. The emission intensity of the zinc(II) complexes is assigned to ( $\pi \rightarrow \pi^*$ ) intraligand fluorescence. It is interesting that zinc(II) complexes show higher emission intensity than that of free ligand values. This is supported from their calculated quantum yield with reference to quinine sulfate. The emission intensity is greatly enhanced by the coordination to zinc(II) which increases the rigidity and reduces the loss of thermal decay [22, 23].

The quantum yields are estimated with references to quinine sulfate with known  $\Phi_R$  of 0.52 and appear at 0.02-0.03. The area of emission spectrum was integrated using the software available in the instrument and quantum yield was calculated according to the following equation.

$$\Phi_S = A_S/A_R \times (Abs)_R / (Abs)_S \times \Phi_R$$

Here  $\Phi_S$  and  $\Phi_R$  are the fluorescence quantum yield of the sample and reference, respectively.  $A_S$  and  $A_R$  are the area under the fluorescence spectra of the sample and reference, respectively.  $(Abs)_S$  and  $(Abs)_R$  are the respective optical densities of the sample and the reference solution at the wavelength of excitation.

### Conclusion

In the present study, the synthesis and spectroscopic characterization of zinc(II) complexes of thiazolylazo dye have been carried out by elemental analyses, IR, UV-Vis and photophysical studies. Electronic spectral data measurement supports an octahedral geometry of the complexes. All the complexes exhibit intraligand ( $\pi \rightarrow \pi^*$ ) fluorescence enhanced by zinc coordination.

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**Table: 1 Photophysical data of complexes**

complex	Excitation(nm)	Emission (nm)	Quantum yield. $\Phi$
<b>1a</b>	354	412	<b>0.020</b>
<b>2a</b>	340	409	<b>0.033</b>
<b>1b</b>	353	408	<b>0.031</b>
<b>2b</b>	<b>343</b>	<b>407</b>	<b>0.039</b>