

Final Report
On Minor Research Project

Spectroscopic properties of azo metal chelate

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By

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Introduction

In recent years considerable research efforts have been focused on the synthesis and properties of metal complexes of hybrid ligand because they can provide new materials with useful properties such as magnetic exchange [1-2], electrical conductivity [3], nonlinear optical activity [4] and antimicrobial activity. Azo compounds have attracted much attention as they are sensitive chromogenic reagent in addition to being important complexing agents. Azo compounds are very important class of chemical compounds receiving attention in scientific research. Due to presence of one or more azo ($-N=N-$) groups, these dyes possess several distinctive properties including aggregation, optical data storage and tautomerization, which define as distinct class of dyestuff [5-7]. The wide spread application of azo compound and their metal complexes as dyes, acids-base indicators and histological stain has attracted the interest of many investigators [8-11]. Azo compounds can also exhibit strong pharmacological activities [12]. Recently metal complex dye have been introduced into many high technological frontier applications as key role functional materials for example in high density memory storage (CD-R) and (DVD-R) nonlinear optical elements and printing system.[13-14].

Copper(II) complexes have been widely explored for the versatility of their coordination geometries, exquisite colours, technical applications, spectroscopic properties and their biochemical significance [15]. Cadmium and Zinc is well studied[16-18] to this study as its d^{10} configuration permits a wide range of symmetries and coordination numbers. The pseudohalide, especially azide [19-20] and ambidentate thiocyanate are interesting bridging agents which form a variety of networks with transition and nontransition metals. In transition metal complexes the structure and electronic versatility of these bridges have been used to explore magnetic materials photo devices, liquid crystals, catalysts and other functional materials [21-24].

In the present article, we report the synthesis, properties and molecular structure of the M(II) complexes of thiazolylazo ligand with Triphenylphosphine and N_3 (1a-6a) or NCS(1b-6b) as coligands. The complexes were characterized on the basis of microanalysis, spectroscopic, magnetic, and electrochemical and photophysical properties.

2. Experimental

Chemicals and Reagents

Solvents

The solvents used in the present investigation are acetone, dichloromethane, chloroform, petroleum ether, ethanol, DMF and DMSO were obtained from sd-fine and were purified and dried by conventional methods [1].

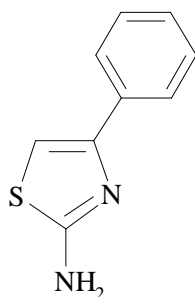
Other reagents

- 2-aminothiazole, $n\text{-Bu}_4\text{NClO}_4$ from Alfa Aesar.
- Sodium azide, ammonium thiocyanate from Merck.
- Sodium hydroxide, sodium acetate, acetophenone, iodine, thiourea, sodium thiosulphate, ammonia, hydrochloric acid, sulphuric acid, nitric acid chlorobenzene, bromobenzene, iodobenzene from sd-fine.
- Triphenylphosphine, *cis*-1,2-bis(diphenylphosphino)ethane from Aldrich.
- $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ from E-Merck, India

Synthesis

Synthesis of 4-phenyl-2-aminothiazole

4-phenyl-2-aminothiazole was synthesized by the method of Dash and Raut [2]. A mixture of acetophenone (0.1 mole, 6.8 g), iodine (0.1 mole, 12.7 g) and thiourea (0.1 mole, 7.6 g) was refluxed for 8 hours on a water bath and again 12 to 16 hours with air condenser. The period of heating influences yield of final product. The crude reaction product was kept in contact with ether with occasional shaking for 48 hours (to remove unreacted ketone which otherwise lead to a gummy product). Final removal of excess of iodine was achieved by treatment with thiosulphate solution. The resulting solution was filtered and treated with concentrated ammonia to liberate the base. The product obtained was recrystallized from ethanol.



4-phenyl-2-aminothiazole

Preparation of copper (II) complexes:

Metal (II) complexes **1a-6a** were prepared from the metal (II) nitrate using the mole ratio (1:1:2:2) of metal, L_1/L_2 , PPh_3 and azide. Complexes **1b-6b** was prepared from metal (II) nitrate using mole ratio of 1:1:2:2 with L_1/L_2 , PPh_3 and thiocyanate. Typical synthesis is described below.

Copper (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 drop wise to a solution (5 ml) of $Cu(NO_3)_2 \cdot 4H_2O$ (1 mmol, 0.241 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 61%; M.P. 144⁰C; Anal. calc. for $C_{51}H_{40}N_{10}SO_2P_2Cu$; C, 62.31; H, 4.10; N, 14.30; found: C, 62.42; H, 4.19; N, 14.18; IR (KBr, cm^{-1}) $\nu(C=N)$ 1601; $\nu(N=N)$ 1435; $\nu(PPh_3)$ 1478, 748, 695; $\nu(N_3)$ 2172; Λ_m (DCM, $\Omega^{-1} cm^2 mol^{-1}$): 22.31; UV-Vis (DCM, λ_{max} nm): 596, 435, 344; Magnetic moment: μ , 1.88 B.M.

2a Yield 70%; M.P. 148⁰C; Anal. calc. for $C_{52}H_{43}N_9P_2SOCu$; C, 64.51; H, 4.47; N, 13.07; found: C, 64.45; H, 4.53; N, 13.12; IR (KBr, cm^{-1}) $\nu(C=N)$ 1589; $\nu(N=N)$ 1434; $\nu(PPh_3)$ 1478, 748, 694; $\nu(N_3)$ 2172; Λ_m (DCM, $\Omega^{-1} cm^2 mol^{-1}$): 21.51; UV-Vis (DCM, λ_{max} nm): 608, 454, 350; Magnetic moment: μ , 1.84 B.M.

Copper (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 $Cu(NO_3)_2 \cdot 4H_2O$ (1 mmol, 0.241 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 61%; M.P. 152°C ; Anal. calc. for $\text{C}_{53}\text{H}_{40}\text{N}_6\text{O}_2\text{P}_2\text{S}_3\text{Cu}$; C, 62.76; H, 3.97; N, 8.32; found: C, 60.62; H, 3.87; N, 8.41; IR (KBr, cm^{-1}): $\nu(\text{C}=\text{N})$, 1589; $\nu(\text{N}=\text{N})$, 1437; $\nu(\text{PPh}_3)$ 1478, 748, 694; $\nu(\text{NCS})$, 2095; Λ_m (DCM, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 19.92; UV-Vis (DCM, λ_{max} nm): 590, 440, 348; Magnetic moment: μ , 1.75 B.M.

2b Yield 67%; M.P. 162°C ; Anal. calc. for $\text{C}_{54}\text{H}_{43}\text{N}_5\text{P}_2\text{S}_3\text{OCu}$; C, 64.88; H, 4.33; N, 7.03; found: C, 64.84; H, 4.27; N, 7.11; IR (KBr, cm^{-1}) $\nu(\text{C}=\text{N})$, 1595; $\nu(\text{N}=\text{N})$ 1440; $\nu(\text{PPh}_3)$ 1478, 744, 693; $\nu(\text{NCS})$, 2095; Λ_m (DCM, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 31.10; UV-Vis (DCM, λ_{max} nm): 588, 435, 344; Magnetic moment: μ , 1.74 B.M.

3. Results and discussion

The reaction of thiazolylazo ligands L_1 and L_2 with $\text{M}(\text{II})$ salts in presence of PPh_3 and NaN_3 or NH_4NCS in 1:1:2:2 molar ratio yields mononuclear hexacoordinated complexes (Fig. 1). The hexacoordinated mononuclear complexes $[\text{M}(\text{L}_1/\text{L}_2)(\text{PPh}_3)_2(\text{N}_3)_2]$ (1a-6a) and $[\text{M}(\text{L}_1/\text{L}_2)(\text{PPh}_3)_2(\text{NCS})_2]$ (1b-6b) are formed in an MeOH solution containing 1:1:2:2 mixture of ligands, metal salt, PPh_3 and NaN_3 or NH_4NCS . The ligands act as bidentate N, N' donor. The air stable, moisture insensitive complexes are soluble in dichloromethane, acetonitrile, chloroform. All complexes were characterized by elemental analysis, electrical conductivity, IR, UV-vis, magnetic susceptibility, E.P.R, luminescence spectra and electrochemistry of complexes 1a-2b. The results are in consistent with proposed mononuclear formulation. In DCM solution 1a-6b behaves as is evident from their low conductivities values (Ca. $15\text{--}30\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$) indicate nonelectrolyte nature. Room temperature solid-phase magnetic susceptibility measurement show that the copper complexes have magnetic moment close to the spin only value ($s=1/2$), 1.73 B.M. excepted from discrete and magnetically noncoupled mononuclear $3d^9$ ions.

IR SPECTRA

Comparison of IR spectra of the azo dye with isolated metal complexes indicates the mode of bonding. Moderately intense stretching at $1590\text{--}1605\text{ cm}^{-1}$ and $1434\text{--}1440\text{ cm}^{-1}$ are due to $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{N})$ respectively. A significant vibration is the blue shifting of the $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{N})$ stretch by $20\text{--}25\text{ cm}^{-1}$ in the complexes relative to free ligand values (19-20). In the IR spectra, the point of interest is the band due to the azide and thiocyanate in the complexes. The spectra exhibit a very strong and sharp absorption band at $2172\text{--}2173\text{ cm}^{-1}$ due to the asymmetric stretching vibration of the azide (1a-2a). In the thiocyanato complexes

(1b-2b) a sharp band at 2095-2096 cm^{-1} is indicative of N coordinated thiocynate ion. These spectral observations along with the conductance data indicate that all the thiocynate and azide are coordinated to the metal ion (21). All the other characteristics ligand vibrations are seen in the 1600-400 cm^{-1} . The spectra of all M(II) complexes show the strong Triphenylphosphine bands at around 1478, 746, 692 cm^{-1} as expected.

UV spectra

Electronic transition for all the complexes (1a-2b) were recorded in CH_2Cl_2 at 200-1100nm. Electronic spectra of 1a-2b exhibit d-d bands in the range of 580-620 nm which is assigned to the $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$ transitions. The d-d bands are shifted to longer wavelength on going from thiocynate to azido complexes with enhanced intensity of thiocynate derivative may be suggestive stronger distortion as compared to azido complexes (22-23). 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.

Photoluminescence properties

The photoluminescence properties of L_1 and L_2 and their metal complexes studied at room temperature in CH_2Cl_2 . The excitation spectra of L_1 and L_2 shows maximum at 340-350 nm gives the emission peak at 409-415 nm. The emission observed in the complexes is assigned to the $(\pi-\pi^*)$ intraligand fluorescence and these are shifted by $> 60\text{nm}$. The intensity of the emission is found to be higher than that of the free ligand. The intensity may be greatly enhanced by the coordination to metal which is defined as chelation enhanced fluorescence intensity. The chelation of ligand increases the rigidity and reduces the loss of thermal vibration decay (27-28).

The quantum yields are estimated with references to quinine sulfate as references with known Φ_R of 0.52 and appear at 0.01-0.05. The area of emission spectrum was integrated using the software available in the instrument and quantum yield was calculated according to the following equation.

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

Here Φ_S and Φ_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. $(\text{Abs})_S$ and $(\text{Abs})_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation.

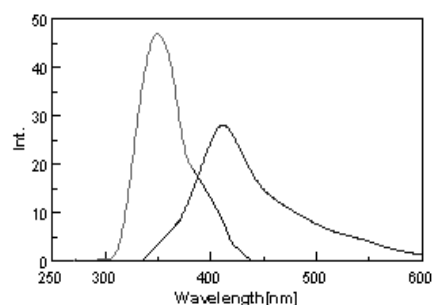


Table: Photophysical data of copper complexes

complex	Excitation(nm)	Emission(nm)	Quantum yield. Φ
1a	344	406	0.013
2a	355	408	0.039
1b	337	409	0.050
2b	339	410	0.042

ESR SPECTRA

The epr spectrum of the polycrystalline Cu(II) complex at room temperature exhibited a strong signal and its g_{\parallel} , g_{\perp} and G values were calculated. The spectrum did not show hyperfine structure at room temperature which may be attributed to strong dipolar and exchange interactions between the Cu(II) ions in the unit cell. The g tensor value of the copper complex can be derived to drive ground state. The g_{\parallel} and g_{\perp} values suggest that dx^2-y^2 may be ground state as $g_{\parallel} > g_{\perp} > 2.0023$. The epr parameter of the complex coincides well with related system which suggests that the complex have distorted octahedral geometry and the systems are axially symmetric. In the axial spectra, the g values are related with exchange interaction coupling constant G by the expression

$$G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023)$$

According to the hathway (24-25), if the G value is larger than four, the exchange interaction in negligible because the local tetragonal axes are alined parallel, if its value is less than four, the exchange interaction is considerable and the local tetragonal axes are misligand. The axial symmetry parameter G is with range indicates there is no exchange interaction between

copper centers. This is in support of axially elongated octahedral geometry (26). It is usual to determine the covalent bonding parameter for the copper ion in various ligand filed environments. We adopted the simplified molecular orbital theory to calculate the bonding coefficients such as in plane π bonding (β^2) and in plane σ bonding (α^2).

The in plane σ bonding parameters α^2 are related to g_{\parallel} and g_{\perp} according to following equation

$$\alpha^2 = - (A_{\parallel}/0.036) + (g_{\parallel}-2.0023) + 3/7 (g_{\perp}-2.0023) + 0.04$$

If the α^2 value = 0.5 it indicates a complete covalent bonding while the value of $\alpha^2 = 1.0$ suggests a complete ionic bonding. The observed value indicates that the complexes have some covalent character. The in plane π bonding (β^2) parameters are calculated from the following expression.

$$\beta^2 = (g_{\parallel}-2.0023) E / -8\lambda\alpha^2$$

Where $\lambda = -828 \text{ cm}^{-1}$ for copper ion and E the electronic transition energy. The lower value of α^2 compared to β^2 indicates that the in plane σ bonding is more covalent than the in plane π bonding.

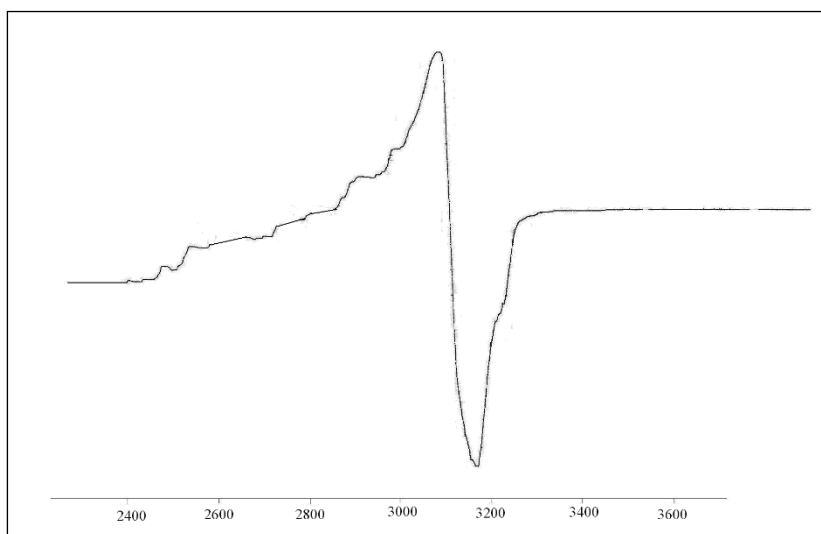


Fig. ESR spectrum of **1a** in DMF solution at 77 K.

Table: Spin Hamiltonian parameter and bonding coefficient for Copper(II) Complex

complex	g_{\parallel}	g_{\perp}	G	$A_{\parallel} \times 10^{-4}$	$A_{\perp} \times 10^{-4}$	α^2	β^2
1a	2.30	2.11	2.72	149	56	0.79	0.95
2a	2.32	2.10	3.20	140	37	0.78	0.97
1b	2.24	2.09	2.66	149	56	0.73	0.86

2b	2.27	2.07	3.85	158	65	0.76	0.90
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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.

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. $186^{\circ}C$; 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; Λ_m (DCM, $\Omega^{-1} cm^2 mol^{-1}$): 16.73; UV-Vis (DCM, λ_{max} nm): 442, 345;

2a Yield 67%; M.P. $141^{\circ}C$; 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; Λ_m (DCM, $\Omega^{-1} cm^2 mol^{-1}$): 16.42; UV-Vis (DCM, λ_{max} nm): 448, 345;

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. $135^{\circ}C$; 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; Λ_m (DCM, $\Omega^{-1} cm^2 mol^{-1}$): 19.10; UV-Vis (DCM, λ_{max} nm) 438, 350;

2b Yield 64%; M.P. 132⁰C; Anal. calc. for C₅₄H₄₃N₆P₂S₃OZn; C, 64.80; H, 4.33; N, 7.02; found: C, 64.91; H, 4.26; N, 7.11; IR (KBr, cm⁻¹) ν (C=N), 1589; ν (N=N) 1437; ν (PPh₃) 1480, 744, 695; ν (NCS), 2096; Λ_m (DCM, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 31.10; UV-Vis (DCM, λ_{max} nm): 436, 342;

Results and discussion

The reaction of thiazolylazo ligands **L**₁₋₂ with Zn(II) salts in presence of PPh₃ and NaN₃ or NH₄NCS in 1:1:1:2 molar ratio yields mononuclear complexes of the type [M(**L**)(PPh₃)₂(N₃)₂] (**1a-2a**) and [M(**L**)(PPh₃)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 ν (C=N) of thiazole nitrogen. This band shifted to lower frequencies (1584-1594cm⁻¹) in the complexes indicates involvement of thiazole nitrogen in coordination [29]. 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 (1430-1444cm⁻¹) in the complexes indicates involvement of azo nitrogen in coordination with metal ion [30]. This is also supported by the appearance of ν (M-N) band at 435-448 cm⁻¹ in the complexes. The azido complexes **1a-2a** show sharp band at ~ 2115 cm⁻¹ and strong band at ~ 1340 cm⁻¹. The thiocyanato complexes **1b-2b** exhibit a strong and sharp band at ~ 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- π^* , π - π^* 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[31]

Photoluminescence properties

The photoluminescence properties of ligands L₁₋₂ and their Zn(II) complexes were studied at room temperature in DMF. The ligand L₁₋₂ 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 [32, 33].

The quantum yields are estimated with references to quinine sulfate with known Φ_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 Φ_S and Φ_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.

Table: Photophysical data of complexes

complex	Excitation(nm)	Emission(nm)	Quantum yield. Φ
1a	354	412	0.020
2a	340	409	0.033
1b	353	408	0.031
2b	343	407	0.039

Conclusion

In the present study, the synthesis and spectroscopic characterization of copper, 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.

Reference

1. R. C. Maurya, P. Sharma, D. Sutradhar, (2003) Synth. React. Inorg, Met.-Org. Chem., 33 (4): 230-238.
2. Y. T. Li, C. W. Yan, C. Y. Zhu, H. S. Guan, (2004) Synth. React. Inorg, Met.-Org. Chem., 34 (7):1165.
3. Y. Aydogdu, F. Yakuphanoglu, A. Aydogdu, E. Tas, A. Cukurovali, (2003) Mater. Lett. 57:3755
4. S. H. Ramadan, H. K. Fun, B. K. Ghosh, (2005) Polyhedron, 24(18): 3074.
5. H. Y. Bie, J. H. Yu, J. Q. Xu, J. Lu, Y. Li, X. B. Cui, X. Zhang, Y. H. Sun, L. Y. Pan, (2003) J. Mol. Str., 660:107.
6. W. M. Fabian, L. Antonov, D. Nedeltcheva, F. S. Kamounad, P. J. Taylor, (1997) J. Phys. Chem., 108:7603.
7. X. Chen, J. Zhang, H. Zhang, Z. Jiang, G. Shi, Y. Li, Y. Song, (2008) Dyes Pigments, 77: 223.
8. Regen N.M. (1997) Can J Sci spectrosc 42:6

9. Jannkaudakis D, Thedoidou E, Pekekoursla A (1922) *Chemcron* 1:69
10. Zollinger H (2003) *Colour chemistry*, 3rdedn. Wiley-VCH Weinheim, 15 p.544.
11. Williams DR (1972) *Chem Rev* 72:203.
12. Abrams Mj(1995) *Platinium metal Rev* 39:14
13. Wang.S, Shen.S, Xu, H *Dyes Pigments*, 44(2000) 195-198.
14. Wu.S, Qian W, Xia.Z, Zou.Y, Wang.S, Shen.S, *Chem phys Lett* 330(2000) 535-540.
15. a) G.Wilkinson, *Comprehensive coordination chemistry*, Vol, 5, p.775.pregamon pree.Oxford, 1987
b) K.D.Karlin and J Zubieta: Eds, *copper coordination chemistry*, Biochemical and inorganic perspectives, Adenine press, Guilderland, New York 1983, 1986.
16. A.M.Golub, H.Kohler, V.V Skopenko, *Chemistry of Pseudohallide* Elsevier, Amsterdam 1986.
17. B.Das.M.K.Raut, *Ind.Chem.Soc.*32, 663(1955)
18. P. P. Hankare, S. S. Chavan, (2003) *Indian J. Chem. Sect. A*, 42:540.
19. T.Mathur, U.Ray, J.C.Liou, J.S.Wa,T-H.Lu,C.Sinha, (2005) *polyhedron* 24:739.
20. S.Pal, D.Das, C.Sinha, C.H.L.Kehhard, *Inorg.Chim. Acta.*313(2001) 21.
21. B.Chand,U.S.Ray, G.Mostafa, T-H.Lu,C.Sinha(2004) *Polyhedron* 23:1969.
22. N. Kabey, E.Erdem, R.Kilincarslan, G.Y.Sari, *Transition Met-Chem*, 32 1068(2007)
23. U.Ray, D.Banarjee, G.Mosfata, Tian-Huey Lu, C.Sinha.*New J. Chem*, 28, 1437(2004)
24. B. J. Hathaway, D. E. Billing, (1970) *Coord. Chem. Rev.* 5:143
25. B. J. Hathaway,(1984) *Struct. Bond.* 57:55.
26. U. Ray, D. Banerjee, G. Mostafa, T.-H. Lu, C. Sinha, (2004) *New J. Chem.*, 28:1437.
27. S. H. Ramadan, R. Ghosh, T. H. Lu, B. K. Ghosh, (2005) *Polyhedron*, 24:1525.
28. T. Yu, K. Zhang, Y. Zhao, C. Yang, H. Zhang, L. Qian, D. Fan, W. Dong, L. Chen, Y. Qiu, (2008) *Inorg. Chem. Acta.*, 361:233
29. Krishnankutty K, Babu, DK, *Journal of the Indian Chemical Society*, 1996;73(8):379-384
30. Kandil SS, El-Hanaway GB, Bakr EA, El-Ezz AZA, *Transition metal Chemistry*, 2003;28(2):168-175
31. Rahaman SH, Ghosh R, Lu T-H, Ghosh BK, *Polyhedron*, 2005;24(12):1525-1532
32. Datta P, Gayen P, Sinha C, *Polyhedron*, 2006;25(17):3435-3440
33. Das D, Chand BG, Sarker K.K., Dinda J, Sinha C, *Polyhedron*, 2006;25(11):2333-2340