Synthesis and EPR Studies of Copper Metal Complexes of Dyes Derived from Remazol Red B, Procino Yellow, Fast Green FCF, Brilliant Cresyl Blue with Copper Acetate Monohydrate

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Abstract: The synthesis and characterization of four new solid dye complexes, CuL_2 (L= 2-[2-methoxy-5-(propane-1-sulfonyl)-phenyl azo]-naphthalen-1-ol, 5-[[3-(4,6-dihydroxy-[1,3,5]triazine-2-ylamino)-phenyl]-hydrazones}-1-ethyl-4-methyl-2,6-dioxo-1,2,5,6-tetrahydro-pyridine-3-carboxylic acid diethylamide, 4-{bis-[4-(benzyl-ethyl-amino)-phenyl]-methyl}-phenol and 7-imino-4-methyl-7H-phenoxazine-1,3-diamine) is reported. The mode for ligand coordination has been determined by IR and EPR spectra. The carboxyl and amino group of dyes coordinates to the Cu(II) atom as a unidentate or as a chelating ligand.

Keywords: Dyes, Copper complexes, EPR, Spectroscopy

Introduction

Reactive dye compounds are highly colored and have been used as dyes and pigments for a longtime. They have been receiving extensive attention due to many practical applications such as coloring the fibers^{1,2}, photo electronic applications³, printing systems^{4,5}, optical storage technology^{6,7}, textile dyes⁸⁻¹⁰ as well as in many biological reactions¹¹⁻¹³ and also in analytical chemistry^{14,15}. Recently metal complex dyes have also attracted increasing attention due to their increasing electronic and geometrical features in connection with their application for molecular memory storages, non linear optical elements and printing system, *etc*¹⁶. Therefore, several studies have been published on the synthesis and spectral properties of several dyes and metal complexes, so far¹⁷⁻²⁵.

In this work, we synthesized four new solid dye-copper metal complexes by using four reactive dyes appropriate simple ligand and metal ions. The chemical structures of both dyes and metal complexes were studied.

Experimental

All the reagents and solvent-grade quality and were used further purification.

Preparation of dye solution

The dyes used in this study are listed in Table 1. The dyes are commercial grade and used as such without any further purification. The dyes stock solutions were prepared by dissolving accurately weighed dyes in distilled water to the concentration of (40 g/L, 20 g/L, 30 g/L and 30 g/L) respectively. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to needed initial concentration.

Preparation of copper acetate solution

The cupric acetate mono hydrate used in this study was obtained from Ponmani & Co Scientific, India. The commercial purity of copper acetate mono hydrate used without further purification. The copper acetate mono hydrate stock solution was prepared by dissolving accurately weighted copper acetate mono hydrate in distilled water to the concentration of 20 g/L. The experimental solutions were obtained by diluting the copper acetate mono hydrate stock solution in accurate proportions to needed initial concentration.

Preparation of stock solution

The stock solution of dyes and copper acetate monohydrate are listed in Table 1.

Table 1. Stock solution of dyes and copper acetate

Trade name	g/L	Stock solution, M	Dilution, M
Remazol red B	40	0.0555	10^{-3}
Procion yellow	20	0.0572	10^{-3}
Fast green FCF	30	0.0576	10^{-3}
Brilliant Cresyl Blue	30	0.0640	10^{-3}
Copper acetate Monohydrate	20	0.1001	10^{-3}

Table 2. The IR spectral data of dyes and their complexes (KBr, cm^{-1})

Dyes	(N=N)	Others
Remazol red B	1342, 1418, 1485	3417(NH), 1576(C=N), 1085(N-N), 1202(C-N)
Procion yellow	1415,	1564(C=N), 1031(N=N), 1206 (C-N=), 2143(C-N=), 3355(NH)
Fast green FCF	1328, 1410.	1031(N-N=), 1565(C=N), 2154(C-N=), 3428(NH).
Brilliant cresyl blue	1414	1036(N-N=), 1205(C-N=) 3354(NH)

Table 3. Absorption spectral data of dyes and their complexes

Dyes	λ_{max}	Δmax
Remazol red B	207.94, 323.96, 379.31, 560.0, 635.40	0.99, 0.75
Procion yellow	228.39, 349.97, 365.00, 375.98, 379.96.	1.68, 3.69
Fast green FCF	228.01, 339.34, 348.08, 605.42, 619.68, 661.96, 670.05	1.87, 3.20
Brilliant Cresyl Blue	234.56, 288.24, 326.96, 543.88, 559.5, 993.93	1.15, 0.26

Table 4. EPR spectral data of the dye-copper complexes at RT

$g_{\parallel}$	$g_{\perp}$	g_{iso}	G
2.30	2.135	2.277	2.16
2.704	2.280	2.412	2.03
2.261	2.162	2.141	2.02
5.861	3.577	4.002	2.04

Figure 1. Chemical structure of the four dyes used in this study

Synthesis of dye-copper complexes

Preparation of copper-remazol red B complex

A solution of remazole red B (1 mmol, 0.030 g) in distilled water (40 mL) was added and solution of copper acetate monohydrate (1 mmol, 0.032 g) in distilled water (160 mL) was added to above remazole red B solution, the mixture was refluxed for 3 h and then 50 mL of water was added. The navy blue colored precipitate was filtered off, washed several times with water, dried in vacuum.

Preparation of copper-procion yellow complex

A solution of procion yellow (1 mmol, 0.014 g) in distilled water (40 mL) was added and a solution of copper acetate monohydrated (1 mmol, 0.016 g) in distilled water (80 mL) was added

to above procion yellow, the mixture was refluxed for 3 h and then 60 mL of water was added. The brown colored precipitated was filtered off, washed several times with water, and dried in vacuum.

Preparation of copper- fast green FCF complex

A solution of fast green FCF (1 mmol, 0.021 g) in distilled water (40 mL) was added and a solution of copper acetate monohydrated (1 mmol, 0.20 g) in distilled water (120 mL) was added to above fast green FCF, the mixture was refluxed for 3 h and then 80 mL of water was added. The light brown colored precipitated was filtered off, washed several times with water and dried in vacuum.

Preparation of copper-brilliant cresyl blue complex

A solution of brilliant cresyl blue (1 mmol, 0.021 g) in distilled water (40 mL) was added, and a solution of copper acetate monohydrated (1 mmol, 0.20 g) in distilled water (120 mL) was added to above brilliant cresyl blue, the mixture was refluxed for 3 h and then 80 mL of water was added. The purple colored precipitated was filtered off, washed several times with water and dried in vacuum.

Results and Discussion

Structural identification of dye- metal complexes

A four new mono nuclear macro cyclic complex of dye- copper metal complexes were synthesized. FT-IR, UV-Visible and EPR spectroscopy were used to characterized the dye-metal complexes. The complexes were stable in atmosphere and polycrystalline.

IR-spectra

The IR spectra of the dyes and dye-metal complexes were recorded, the corresponding absorption intensity are present in Table 2. The dye-metal complexes and ligand exhibits the medium intensity absorption at 1576 cm^{-1} which is attributable to the imines $\nu(\text{C}=\text{N})$ ¹⁴ and that absorption support the macro cyclic structure. A shift in absorption of the $\nu(\text{C}=\text{N})$ frequency in case of the complexes suggests the coordination through the nitrogen of $(\text{C}=\text{N})$ group. Moreover, another new band around 1415 cm^{-1} which is observed in the spectra of metal free ligands is assigned as $\nu(\text{N}=\text{N})$. The appearance of this peak at relatively lower field may indicate coordination via the $\text{N}=\text{N}$ group²⁵⁻²⁷.

Absorption spectral data

The electronic absorption spectra of the dyes and dye-metal complexes were recorded; the corresponding absorption intensity is present in Table.3. The chemical shift values ($\Delta\lambda_{\text{max}}$) were determined by taking the difference between the absorption maximum of the azo metal complexes with corresponding ligand. The band of shortest wavelength appearing at 228.0 nm may be attributed $\pi \rightarrow \pi^*$ transition of hetero cyclic moiety of dye compounds. The second band observed at (323.9-349.9) is attributed to $n \rightarrow \pi^*$ electronic transition of $-\text{N}=\text{N}-$ group.

In the spectra of dye-metal complexes the absorption bands in the visible region of complexes are shifted to higher wave length relative to their corresponding metal free ligands. These strong absorptions of the complexes in the near lost in the low- energy tail of the intense charge transfer transition.

EPR spectra

The EPR spectra of dye-metal complexes were recorded, the observed g -values are present in the Table 4. The complexes exhibit anisotropic EPR spectra, recorded as polycrystalline sample at RT, which is characteristic for tetragonal Cu(II) complexes²⁰⁻²⁵. The anisotropic g -values have been calculated by kneubuhl's method²⁶⁻³² and by method reported earlier³³. The $G = (g_{\parallel} - 2) / (g_{\perp} - 2)$, which measure the exchange interaction between the copper centers in polycrystalline samples, have been calculated. According to Hathaway³³⁻³⁶, if $G > 4$, the exchange interaction is negligible. A value of $G < 4$, indicates considerable exchange interaction in the solid complexes. The calculated G values are larger than four suggesting that there is no exchange interaction between the copper centers. The structures of azo-copper metal complexes are shown in Figure 2.

Green HE4BD-copper complex

R=CH₃, C₂H₅ ..

Golden yellow HER-Copper complex

T.Blue HE5G-copper complex

Red HE7B-copper complex

Figure 2. Structure of copper-azo dyes complexes

Figure 3. IR spectral data of azo dyes and azo-copper metal complexes

Figure 4. Absorption spectra of azo dyes and azo-copper metal complexes

Figure 5. EPR spectra of azo-copper metal complexes

Conclusion

In conclusion, we described the synthesis and EPR studies of the four new azo-metal complexes bearing green HE4BD, golden yellow HER, T.blueHE5G, red HE7B and copper acetate monohydrate. These azo dyes exist in the form of solid state. The interaction between ligand and metal was conformed from EPR spectral values through amine and imines.

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