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Synthesis, structural, characterization, spectral studies and antimicrobial activities of Cobalt(II) and Nickel(II) complexes with azo dye ligand

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ABSTRACT

The solid complexes of Co(II) and Ni(II) with azo dye ligand derived by coupling of diazonium salt of sulfamethoxazole with 2-Ethyl-4-methyl phenol, have been synthesized and characterized by elemental analysis, conductometry, magnetic, IR, NMR, UV-Vis spectral studies and stepwise stability constants by P^H metric method. From the analytical data the stoichiometry of the complexes has been found to be 1:2 (metal: ligand). The low conductance values suggest that the complexes are non-electrolytes. The physic-chemical data indicates tetragonal geometry for all the complexes. Complexes have been screened for antimicrobial activity against *B.megaterium*, *B. subtilis*, *E.coli*, *P.fluorescens*, *A.awamori* and *A.niger*.

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KEYWORDS

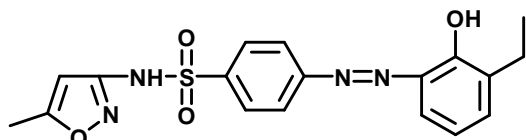
Synthesis;
Azo dye ligand;
Transition metal complexes;
Characterization;
Antimicrobial activity.

INTRODUCTION

Metal complexes of biologically important ligands are sometimes more effective than the free ligands^[1]. Azodyes have been widely used in various fields and technologies like textiles, leather, plastics, paper, laser liquid crystalline displays and ink Jet printers^[2-4]. They are also used in food^[5], drug, cosmetic and photochemical production^[6]. The pharmacological and chemotherapeutic activity of azo dyes are well recognized as they possess antibacterial, antifungal, antiseptic, herbicidal, pesticidal and anticancerial properties^[7]. Azodyes are also used as indicators in chemistry. Keeping all these important properties of azo dyes in mind the synthetic organic chemists have been inspired to prepare broad spectrum drugs from the azodyes obtained from aro-

matic and heterocyclic amines. We now focus our attention to the preparation of completely new azodyes ligands and to study their complexation behavior with divalent transition metal ions. The present paper reports the synthesis of new azo dye ligand (Figure 1) and metal complexes.

The products have been evaluated for antimicrobial activity. Some compounds are found to have antimicrobial activity comparable to that of standard drugs, viz. sulfamethoxazole, and sulfadiazine. The product has also been characterized by elemental analysis, absorption spectra, conductivity measurements, molecular weight determination, magnetic moment measurements and stepwise stability constants by P^H metric method. By using the results of above study, structure of metal complex is proposed.



3-Ethyl-2-hydroxy-5-methyl-4'-(5''-methyl-oxazol-3''-yl) Aminosulphonyl azobenzene

Figure 1 : Azo dye ligand

EXPERIMENTAL

All the chemicals were of B.D.H. or EMerk grade. Metal, carbon, hydrogen, nitrogen and sulphur were estimated by standard methods. Conductivity measurements in DMF was made using Toshniwal conductivity bridge using a dip type cell at room temperature. Magnetic moment was measured at room temperature on a Gouy balance using mercury (II) tetrathiocyanate cobalt(II) as the calibrant. IR spectra were recorded using KBr disc on NICOLET MEGNA-IR550 SERIES II. Electronic spectra were recorded on Beckman spectrometer using matched silica cells. NMR spectra were recorded on BRUKER spectrometer (300 MHz) in CDCl_3 . Mass spectra were recorded on a Jeol D-300 spectrometer at room temperature.

Preparation of the ligand

Preparation of 3-ethyl-2-hydroxy-5-methyl-4'-(5''-methyl-oxazol-3''-yl)-amino-sulphonyl azobenzene (Azo dye ligand). Sulfamethoxazole (0.025M) was taken in 10 ml HCl (0.055M) solution, and it was added to sodium nitrite solution 20ml (0.025M) and the mixture was cooled in icebath. (yields diazonium salt of sulfamethoxazole). In another flask 2-ethyl-4-methyl phenol (0.025M) dissolved in 10ml (0.025M) NaOH and cooled at 0°C . In situ diazonium salt of sulfamethoxazole was coupled with 2-ethyl-4-methyl phenol (in above solution) by adding dropwise at 0°C with constant stirring and keeping the pH of the solution neutral.

Earlier 2-ethyl-4-methyl phenol was prepared by Clemmensen's reduction^[8,9] of 2-acetyl-4-methyl phenol. 2-acetyl-4-methyl phenol was prepared by Fries migration^[10] of p-cresyl acetate. p-cresyl acetate was prepared by acetylation^[11] of p-cresol.

Preparation of the complexes

The complexes of cobalt(II) and Nickel(II) pre-

pared by refluxing the mixture of alcoholic solution of azo dye ligand (2M) i.e. 3-ethyl-2-hydroxy-5-methyl-4'-(5''-methyl-oxazol-3''-yl)-amino-sulphonyl azobenzene and metal salt solution (1M) for two hours in presence of excess of ammonium hydroxide ($\text{pH} = 10.0$). The complexes were recrystallised from alcohol.

RESULTS AND DISCUSSION

IR spectral data of the ligand

IR (KBr) cm^{-1} : 3432 (N-H str. Sym. & O-H str.), 3080 (= C-H str.), 2969 (C-H str.- CH_3), 2915 (C-H str.- CH_2), 2860 (C-H str.sym.), 1614(-N=N- str.& N-H def.), 1580 (-C=C str.), 1467 (oxazole ring str.), 1417 (C-H def.asym.,-N=N- Str.), 1398 (O-H def.& C-H def.sym.), 1341 (S=O str.asym.), 1264 (C-H i.p. def.disub.benzene), 1177 (S=O str.sym.), 1140 (C-H i.p. oxazol), 1034 (ring skeletal oxazol), 900 (C-H o.o.p. oxazol), 755 (N-H wag.).

NMR spectral data of the ligand

^1H NMR (CDCl_3): 1.21-1.25 δ (3H, t, $-\text{CH}_2 - \text{CH}_3$), 2.34-2.38 δ (6H, 2 x s, 2 X - CH_3), 2.64-2.71 δ (2H, q, $-\text{CH}_2 - \text{CH}_3$), 6.28 δ (1H, s, = CH oxazole ring), 7.11 δ (1H, s, Ar-H), 7.54 δ (1H, s, Ar-H), 7.86-7.89 δ (2H, d, Ar-H), 7.96-7.98 δ (2H, d, Ar-H), 12.86 (1H, s, Ar-OH).

Mass spectra

(m/z): 401 (M^+), 309, 287, 266, 239, 207, 154, 135, 120, 105, 91, 77, 69, 55, 41.

Absorption spectra

λ max (nm): 232, 323, 362, 412; log ϵ : 4.3456, 4.2735, 4.3237, 4.1455.

Antimicrobial activity

The testing were carried out by cup-plate method at a concentration of 50 μg using gram positive bacteria as *B. megaterium* and *B. subtilis* and gram negative bacteria as *E. coli*. And *P. fluorescens* and fungi as *A. awamori* and *A. niger*. Most of the compounds were moderately active against different strains of bacteria and fungi. However, comparatively significant was observed in compounds (along with zone of inhibition in mm) having azodye ligand -(18), Co(II) complex -(20), Ni(II) complex -(18) against *B. mega*, azodye ligand -

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(14), Co(II) complex -(19), Ni(II) complex -(16) against *B. subtilis*, azodye ligand -(16), Co(II) complex -(16), Ni(II) complex -(22) against *E. coli.*, azodye ligand -(18), Co(II) complex -(19), Ni(II) complex -

(15) against *A. arogers*, azodye ligand -(17), Co(II) complex -(17), Ni(II) complex -(17) against *A. awamori*, azodye ligand -(19), Co(II) complex -(15), Ni(II) complex -(16) against *A. niger*

TABLE 1 : Some physical properties of metal complexes.

Compound	Molecular weight Found/ (Req.)	Elemental analysis % found/(calculated)				Conductivity (Mohs.cm ² mole ⁻¹)	μ_{eff} B.M.
		M	C	H	N		
Co(C ₁₉ H ₁₉ O ₄ N ₄ S) ₂	856.93	6.88	53.21	4.43	13.07	11.4	2.08
	(845.85)	(6.89)	(53.22)	(4.45)	(13.11)		
Ni(C ₁₉ H ₁₉ O ₄ N ₄ S) ₂ Diamag.	856.71	6.85	53.23	4.43	13.07	9.5	
	(845.90)	(6.87)	(53.25)	(4.47)	(13.11)		

P^H-metric measurements

For the determination of stepwise stability constants an expanded scale systronic P^H meter with accuracy ± 0.02 units was employed. All experiments were carried out at 30 ± 0.2 °C and temperature was mentioned constant using thermostat. The three sets acid, acid + ligand, acid + ligand + metal were prepared.

In each case total volume was made up to 40 ml by adding required amount of double distilled water or purified dioxane as the case may be. The ionic strength was maintained by adding appropriate amount of sodium nitrate (0.01M) and mixtures were titrated with standard NaOH solution. A modified form of Irving-Rosstti^[12] titration technique was used for calculating the stability constants. The P^H meter was calibrated with aqueous buffers. In the calculations for pL the pH meter reading 'B' was used instead of converting it to true pH value (Corresponding to aqueous medium). The use of pH meter reading 'B' instead of true pH values did not make any differences^[13,14] in the calculation of free ligand concentration and was usually valid for water dioxane media.

TABLE 2 : Stepwise stability constants of metal complexes of 3-ethyl-2-hydroxy-5-methyl-4'-(5''-methyl-oxazol-3''-yl)-amino-sulphonyl azobenzene in (60: 40) Dioxane: Water, $\mu = 0.1\text{M}$, Temp 30 ± 0.2 °C.

Ligand	logK ₁ ^H	logK ₂ ^H	logB ₂ ^H
C ₁₉ H ₂₀ O ₄ N ₄ S	10.622	3.703	14.365
Complex	logK ₁	logK ₂	logB ₂
Co (C ₁₉ H ₁₉ O ₄ N ₄ S) ₂	6.7019	4.0221	10.7240
Ni (C ₁₉ H ₁₉ O ₄ N ₄ S) ₂	7.6232	4.4043	12.0275

Conductance measurements

Molar conductance values of all the complex in

10⁻³ M DMF solutions are given in TABLE 1. These values are consistent with the non-electrolytic^[15] nature of this complex.

Magnetic measurements

The observed magnetic moments of the resulting complex are given in TABLE 1. This value shows that Co(II) complex is paramagnetic nature with one unpaired^[16,17] electron and. Ni(II) complex is diamagnetic.

UV and visible spectra

The spectra of Cobalt(II) complex (D₄h) show a band at 768 nm along with ligand bands. The transition corresponding to ²A_{1g} → ²B_{1g} and ²A_{1g} → ²E_g are expected. Here only one absorption maxima is observed at 768 nm which can be attributed to ²A_{1g} → ²B_{1g}. The spectra of Nickel(II) complex two Absorption bands are expected corresponding to ³B_{1g} → ¹A_{1g} at 685 nm and ¹A_{1g} → ¹E_g at 360 nm. Hence it is concluded that the nickel complex is having tetragonal symmetry.

Potentiometric study

The P^H metric studies of the metal complex show the n values as 1.78 and 1.70 for Co(II) and Ni(II) respectively, indicating two ligands per metal ion, the stepwise stability constants (TABLE 2) follow the Irving-Williams order.

CONCLUSION

Basing upon the above observation, the Co(II) and Ni(II) complexes structure have been proposed as under (Figure 2). The cokplexes are biologically active since they exhibit enhanced antibacterial activities com-

pared to their parent ligands.

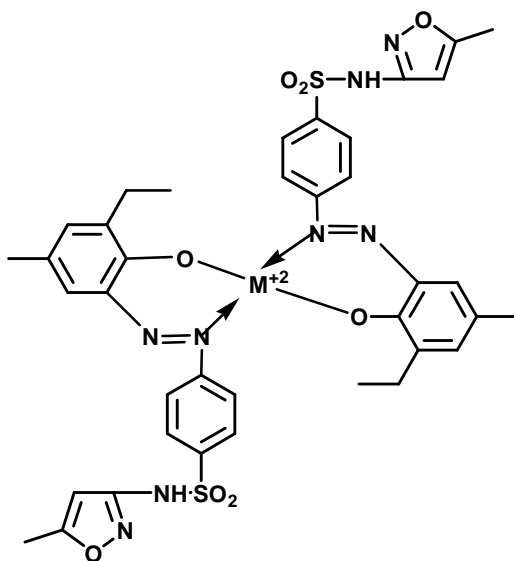


Figure 2 : M = Co(II) & Ni(II)

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