SYNTHESIS AND ANALYTICAL STUDIES OF SOME AZO DYES AS LIGANDS AND THEIR METAL CHELATES

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ABSTRACT

Ortho-, meta- and para-chlorophenyl azo substituted quinolone compounds have been synthesised. The structure of these products have been established by IR and ^{1}H NMR data. Metal chelates of these ligands have been synthesised with Cu (II), Co (II), Ni (II) and Fe (II) metal ions. All metal chelates have been characterised by elemental analysis, IR spectroscopy, UV-visible absorption spectroscopy, ^{1}H NMR spectral data and supported by ESR, Mossbauer and Mass spectrometry.

Key words: Chelates, Azo dyes, Cu (II), Co (II), Ni (II), Fe (II).

INTRODUCTION

The literature survey reveals that large number of azo dyes have been investigated by many workers[1-3] as chelating agent and their metal chelates have been extensively used in dyeing industries. The azo dyes have the general structure R-N = N-R', where R and R' are aryl, alkly or heterocyclic groups. Most of them are prepared by condensation of azo compounds with hydroxy aldehydes or ketones.

Keeping in view the importance of metal complexes of azo dyes in the dyeing industries, we have proposed to synthesise some metal complexes of 4-Hydroxy-N-methyl-3-o-chlorophenylazo-2-quinolone i.e. [HNMOCPAQ]; 4-hydroxy-N-methyl-3-m-chloro-phenylazo-2-quinolone i.e. [HNMMCPAQ] and 4-hydroxy-N-methyl-3-p-chlorophenylazo-2-quinolone i.e. [HNMPCPAQ]. The selected metal ions to study the charcteristic properities of chelates are Cu (II), Co (II), Ni (II) and Fe (II)

EXPERIMENTAL

Synthesis of ligands involves three steps : (i) Synthesis of N-methyl anthranilic acid[4]

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(ii) Acetylation of N-methyl anthranilic acid and cyclisation of this acetyl derivative[5] and (iii) Synthesis of ligands i.e. [HNMOCPAQ], [HNMMCPAQ] & [HNMPCPAQ].

Synthesis of ligands

An ice-cold mixture of o-chloroaniline (3.82 g) and 10 mL 50% HCl was added dropwise to the ice-cold solution of 20 mL $NaNO_2$ (1.25 M). This mixture was kept at 0^oC and then added dropwise to the solution of 4-hydroxy-N-methyl-2-quinolone (4.4 g, 0.025 M) prepared in 50 mL (1.25 M) NaOH. All reactions were carried out in ice bath with constant stirring. The product [HNMOCPAQ] so obtained was washed with chilled water, dried and recrystallised using glacial acetic acid. The same procedure was followed with m-chloroaniline and p-chloroaniline to synthesise [HNMMCPAQ] and [HNMPCPAQ], respectively.

Table 1: Physical constants of synthesised ligands

Name	Molecular formula	M.P. (^{o}C)	Yield (%)	Found (%) (Calc.)		
				C	H	N
HNMOCPAQ	$C_{16}H_{12}N_3O_2Cl$	249	70.50	61.18 (61.24)	3.75 (3.82)	13.36 (13.39)
HNMMCPAQ	$C_{16}H_{12}N_3O_2Cl$	169	69.04	61.15 (61.24)	3.72 (3.82)	13.33 (13.39)
HNMPCPAQ	$C_{16}H_{12}N_3O_2Cl$	178	73.22	61.15 (61.24)	3.8 (3.82)	13.32 (13.39)

Synthesised ligands have been characterised by different spectroscopies.

Synthesis of metal chelates

One percent ethanolic solution of the ligand was added dropwise to 2 mL of metal chloride at different pH adjusted by using different buffers to determine the pH range, where the complex was being formed. All metal ion solutions were standardized using proper method[6]. Copper complexes were synthesised at 10.7 pH. $CuCl_2$ (0.IM, 0.0063 g/mL, 10 mL) was treated with NH_4OH to get required pH 10.7 and then at 60^oC, 1% ethanolic solution of ligand was added dropwise to get the product. Cobalt complexes were obtained, when a mixture of cobalt chloride (10.0 mL, 0.1M) and ligand solution (1%, 10 mL) containing excess NH_4OH (pH = 10.0 to 11.0) was refluxed for 15 to 20 minutes. Nickel complexes were prepared at 9.0 pH, adjusted with NH_4OH and CH_3COONH_4. The mixture of nickel chloride (10 mL, 0.1M) and buffer (3 g in 10 mL D.W.) was heated on a water bath. On addition of ligand solution, brown precipitates of metal complex were separated. Complexes of Fe^{2+} were prepared at pH between 5.0 to 6.0; adjusted using NH_4OH followed by drops of CH_3COOH. Mixture of ferrous ammonium sulphate (10.0 mL, 9.1M), buffer and ethanolic

solution of ligand was refluxed on a waterbath for half an hour to get precipitates of metal complex. All these complexes were dried and recrystallised using chloroform, ether or benzene. Analytical data of metal complexes[7,8] are given in Table 2.

Table 2: Analytical data of metal complexes

Name of complex	Molecular formula	M.W.	Analytical (%) Found/(Calc.)				Conductivity (Ω^{-1} cm^2 mol^{-1})
			C	H	N	Metal	
Cu (HNMOCPAQ)$_2$	Cu (C$_{16}$H$_{11}$N$_3$O$_2$CI)$_2$		55.72 (55.77)	3.17 (3.19)	12.15 (12.19)	9.19 (9.228)	9.4
Cu (HNMMCPAQ)$_2$	Cu (C$_{16}$H$_{11}$N$_3$O$_2$CI)$_2$	688.54	55.69 (55.77)	3.13 (3.19)	12.11 (12.19)	9.17 (9.228)	8.9
Cu (HNMPCPAQ)$_2$	Cu (C$_{16}$H$_{11}$N$_3$O$_2$CI)$_2$		55.71 (55.77)	3.09 (3.19)	12.16 (12.19)	9.20 (9.228)	9.2
Ni (HNMOCPAQ)$_2$	Ni (C$_{16}$H$_{11}$N$_3$O$_2$CI)$_2$		56.14 (56.16)	3.18 (3.21)	12.24 (12.28)	8.50 (8.586)	9.9
Ni (HNMMCPAQ)$_2$	Ni (C$_{16}$H$_{11}$N$_3$O$_2$CI)$_2$	683.71	56.11 (56.16)	3.15 (3.21)	12.21 (12.28)	8.53 (8.586)	10.1
Ni (HNMPCPAQ)$_2$	Ni (C$_{16}$H$_{11}$N$_3$O$_2$CI)$_2$		56.09 (56.16)	3.14 (3.24)	12.23 (12.28)	8.55 (8.586)	9.8
Co (HNMOCPAQ)$_2$	Co (C$_{16}$H$_{11}$N$_3$O$_2$CI)$_2$		56.07 (56.14)	3.15 (3.21)	12.22 (12.28)	8.58 (8.616)	10.9
Co (HNMMCPAQ)$_2$	Co (C$_{16}$H$_{11}$N$_3$O$_2$CI)$_2$	683.93	56.09 (56.14)	3.17 (3.21)	12.16 (12.28)	8.54 (8.616)	11.2
Co (HNMPCPAQ)$_2$	Co (C$_{16}$H$_{11}$N$_3$O$_2$CI)$_2$		56.11 (56.14)	3.12 (3.21)	12.18 (12.28)	8.56 (8.616)	11.5
Fe (HNMOCPAQ)$_2$ (H$_2$O)$_2$	Fe (C$_{16}$H$_{11}$N$_3$O$_2$CI)$_2$.(H$_2$O)$_2$		53.50 (53.56)	3.60 (3.628)	11.69 (11.71)	7.69 (7.791)	12.0
Fe (HNMMCPAQ)$_2$ (H$_2$O)$_2$	Fe (C$_{16}$H$_{11}$N$_3$O$_2$CI)$_2$.(H$_2$O)$_2$	716.85	53.47 (53.56)	3.58 (3.628)	11.62 (11.71)	7.72 (7.791)	12.6
Fe (HNMPCPAQ)$_2$ (H$_2$O)$_2$	Fe (C$_{16}$H$_{11}$N$_3$O$_2$CI)$_2$.(H$_2$O)$_2$		53.49 (53.56)	3.53 (3.628)	11.64 (11.71)	7.76 (7.791)	11.4

Metal complexes were characterised by absorption spectroscopy, ESR spectra, Moss-bauer spectra and magnetic susceptibility measurements.

RESULTS AND DISCUSSION

The ligands have nitrogen and oxygen as hetero atom, which form heterocyclic ring with the metal ion in complex. The elemental analysis are given in Table 1, which agrees with theoretically expected value, supporting their molecular composition.

Molecular structure of ligand
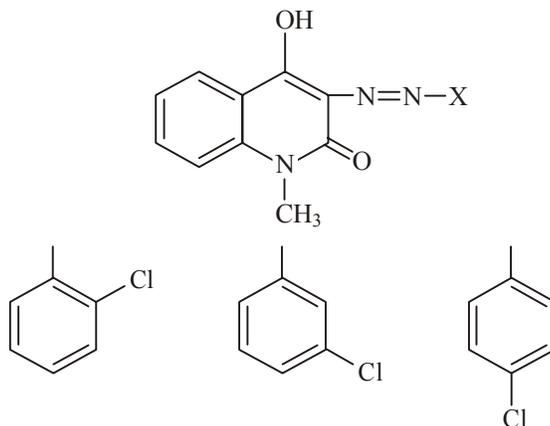
Where X = o-Chlorophenyl   m-Chlorophenyl   p-Chlorophenyl

Table 3: UV-Visible absorption spectral data of ligands

Ligand	HNMOCPAQ			HNMMCPAQ			HNMPCPAQ		
λ_{max} (nm)	235	260	350	245	265	360	224	280	345
log ε	4.7018	4.6723	4.2310	4.3796	4.3601	4.0326	4.7919	4.4102	4.0610

The absorption spectra of the ligands in UV-Visible region show three bands at 224-235 nm, 260-280 nm and 335-352 nm. These are attributed to $n \rightarrow \pi$ and $\pi \rightarrow \pi*$ transitions (Table 3).

The IR spectral data of all ligands are identical with slight variation in group frequency, which are according to the suggested structure of the ligand molecules (Table 4).

NMR spectrum of ligands were recorded in TFA solution on EM-360-280 MHz spectrometer.

¹H NMR (TFA) [HNMOCPAQ] : δ 0.49 (s, ortho-substitution); 3.94 (S, 3H of > N-CH₃); 7.60-8.6 (m, Ar-H).

[HNMMCPAQ]: δ 0.462 (s, meta-substitution); 3.871 (s, 3H of > N-CH₃); 7.546-8.1 (m, Ar-H)

[HNMPCPAQ]: δ 0.5 (S, para-substitution); 3.93 (s, 3H of > N-CH₃); 7.69-8.52 (m,Ar-H)

The mass spectrum of ligands were taken on Jeol D-300 spectrometer at room temperature. The mass fragmentation data also support the stucture of the ligand molecules.

Table 4: IR Spectral data of ligand molecules (cm⁻¹)

Ligand → Groups ↓	HNMOCPAQ	HNMMCPAQ	HNMPCPAQ
– OH	3450	3500	3500
C-N	1300	1295	1300
C = O	1600	1639	1620
N = N	1570	1575	1575
-CH str. in-plane/ out of plane	1100/700	1110/690	1110/650

All the prepared metal complexes were stable at room temperature. They are water insoluble, sparingly soluble in ethanol and considerably soluble in benzene, ether, chloroform or carbon tetrachloride. Molecular weight determination and elemental analysis indicate that the structure of complexes of Cu^{2+}, Co^{2+} and Ni^{2+} are ML_2 type, while that of Fe^{2+} is $ML_2 (H_2O)_2$.

In metal chelates, the light absorption occurs in UV-Visible region due to the absorption arising from electronic transition in a conjugated system, where a metal may or may not participate. These are known as 'K' type of absorptions and has been investigated in several cases[9]. Calvin et al.[10] observed absorption bands in the visible region due to the forbidden transitions and also K type band characteristic of the ligands in UV region. They concluded from the experimental data that the influence of a metal ion on the characteristic

absorption is much weaker than the ligand with a large conjugated system.

In copper complexes, two bands due to d-d transition [$^2A_{1g} \rightarrow {}^2B_{1g}$ (635-687 nm) and $^2B_{2g} \rightarrow {}^2B_{1g}$ (727-748 nm)] are observed with the shifted position of the ligand bands. The shifting in ligand bands may be due to the interaction of the ligands with metal ion. The absorption spectra of nickel complexes show two absorption bands at 415-478 nm ($^1A_{1g} \rightarrow {}^1E_g$) and 635-687 nm ($^1A_{1g} \rightarrow {}^1B_{1g}$). The extensive mixing of the metal d-orbital and ligand orbitals enlarge the extinction coefficient in nickel complexes although the transitions are Laporte forbidden. The complexes of Co^{2+} show only one band at 642-667 nm corresponding to $^2A_{1g} \rightarrow {}^2B_{1g}$ along with ligand bands. Fe^{2+} complexes also give only one weak band at 653-682 nm, which is probably due to the transition $^1A_{1g} \rightarrow {}^1T_{1g}$. ESR spctra of all metal complexes were recorded at ESR laboratory, RSIC, IIT, Madras at room temperature and at liquid nitrogen temperature. ESR spectroscopy provides a powerful tool[11] for the study of chemical species having unpaired electrons. It gives the information about the number and presence of unpaired electrons and also distribution of them in the molecule. The ESR spectral study indicates that the value $g_{II} > g_\perp$ support D_{4h} symmetry of copper complexes. They are tetragonal with unpaired electron in the $d_{x^2-y^2}$ orbital and hence, there is no Cu-Cu interaction. Cobalt complexes have one unpaired electron in d_{z^2} orbital with square planar structure. Ni^{2+} complexes are having tetragonal crystal field, while Fe^{2+} complexes are having distorted octahedral geometry. The probable structure of metal complexes are as follows -

(i) Tetragonal structure of Cu^{2+}, Co^{2+} and Ni^{2+} complexes
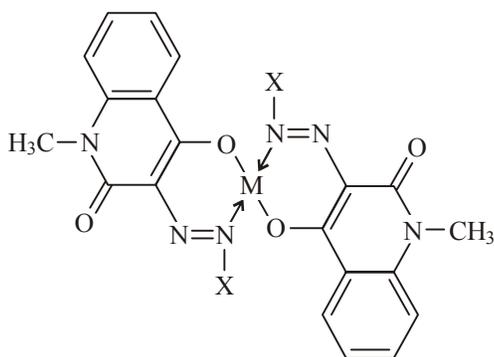
Where M = Cu^{2+}, Co^{2+}, Ni^{2+}

and (ii) Distorted octahedral structure of Fe^{2+} complexes
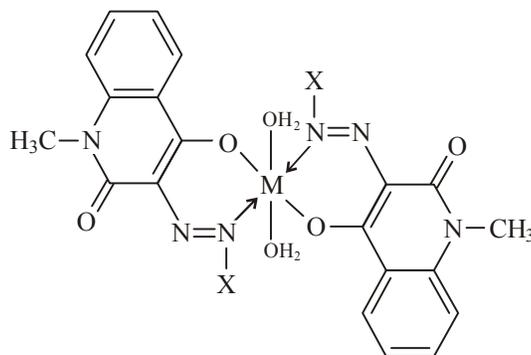
Where M = Fe^{2+}

Mossbauer spectral data[12] and the conductivity measurement also support the given structure of complexes. The molar conductance values for complexes in DMF (10^{-3} M) explained their nonelectrolytic nature[13]. The magnetic susceptibility of all the complexes was measured at room temperature by Gouy balance method and corrected for diamagnetism using Pascal's constant. The values of μ_{eff} for all copper complexes were observed in the range of 2.03 to 2.14 B.M., which is greater than the spin only magnetic moment for a system having one unpaired electron. This excess value is considered to be due to spin-orbit coupling[9]. All nickel complexes are diamagnetic, while all cobalt complexes were found to be paramagnetic with μ_{eff} between 1.92 to 2.12 B.M. The diamagnetic nature of Fe^{2+} complexes supports the presence of Fe in + 2 oxidation state.

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