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Mixed Ligand Complexation of Zinc by Some Chelating Organic Acids and Acidic Azo Dyes.

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ABSTRACT

Mixed ligand complexes of zinc(II) involving some chelating organic acids viz., salicylaldehyde, salicylic acid, anthranilic acid or 8-hydroxyquinoline and some acidic azo dyes viz., 5-(phenylazo)salicylic acid or 5-(phenylazo)-8-hydroxyquinoline, have been synthesised and characterised. Analytical results suggest the complexes to be of general formula, $[Zn L.L']$, where, L = deprotonated chelating organic acid and L' = unideprotonated acidic azo dye. Molar conductance values indicate the compounds to be non-electrolytic in nature. Infrared spectra of the compounds suggest that the $-N=N-$ of the azo dyes did not coordinate to the metal. This may probably due to non-availability of a donor group at ortho position to the azo group, for chelation. Infrared spectra further evidenced the bonding of 5-(phenylazo)salicylic acid to the metal by deprotonation of COOH and coordination of OH group. 5-(phenylazo)-8-hydroxyquinoline was evidenced to bind to the metal by the deprotonation of OH and coordination of ring-N. The chelating organic acid ligands too have been evidenced to bind to the metal by deprotonation of COOH/OH and coordination of suitably oriented donor groups to form the chelate rings. 1H NMR spectra of the compounds also suggested the above mode of bonding of the ligands to the metal.

Keywords: Zinc, Azo dyes, Acidic azo dyes, Metal-complexed dyes, Mixed ligand complexes, Zinc chelates.

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INTRODUCTION

Zinc is a biologically as well as industrially important metal. It is essential for plants as well as animals. Zinc is an essential component of a number of enzyme systems. Excessive quantities of zinc, however, are toxic for both plants and animals [1]. Azo dyes are used in dyeing textile fibres. They are cost effective and have good fixative properties. Azo dyes also find application in complexometric titrations [2,3] and as corrosion inhibitors [4,5]; they also possess good pharmacological activity [6]. Pre-metallised/metal-complexed dyes have recently been receiving more attention owing to their better washing and light fastness properties. However, azo dyes have also been found to be toxic to fauna and flora, when released into the environment through untreated effluents of dye and textile industries. They are resistant to natural degradation and have toxic potential such as genotoxic, mutagenic and carcinogenic effects [7,8]. Metallised azo dyes containing chromium, cobalt or copper would be additionally polluting due to the release of toxic metals to the environment. Hence, eco-friendly metal-complexed dyes eg. dyes complexed with less toxic metals like iron, aluminium, zinc etc. have recently been receiving attention [9-12].

Coordination chemistry of zinc involving azo dyes as ligands, particularly in the mixed ligand environment, would be of academic as well as applied interest. As such, we have presently studied the mixed ligand complexation of zinc (II) by some chelating organic acids and some acidic azo dyes. The azo dyes that we have studied with are acidic dyes of multidentate nature. They have chelating as well as non-chelating coordination sites within the molecule. Study of the mode of coordination of these dyes with the metal would be rather interesting. Zinc, being a non-transition metal, is also less likely to alter much the original shade of the dye upon complexation. Mixed ligand complexes of general formula, $[Zn L L']$, where, L= deprotonated salicylaldehyde (sald), salicylic acid (sal), anthranilic acid (anth) or 8-hydroxyquinoline (8hq) and L'= unideprotonated azo dye, viz., 5-(phenylazo)salicylate (PASA) or 5-(phenylazo)-8-hydroxyquinolate (PAHQ), have been synthesised. The compounds were characterised by elemental analysis and spectral (infrared and 1H NMR) studies.

MATERIALS AND METHODS

All chemicals used were of A.R. (Analytical Reagent) quality.

Preparation of azo dyes: The azo dyes, 5-(phenylazo)salicylic acid and 5-(phenylazo)-8-hydroxyquinoline were prepared by diazotising aniline (9.8ml) in 32ml conc. HCl and 32ml water with an aqueous solution of sodium nitrite (8.0g) at 0-5°C by usual method and coupling the diazotised solution with an alkaline solution of salicylic acid (14.9g) or 8-hydroxyquinoline (15.6g) as the case may be. The dyes were filtered, washed with water and dried.

Preparation of mixed ligand complexes: The mixed ligand complexes were prepared by the general method of interaction of a mixture of azo dye (H.PASA or H.PAHQ) and chelating organic acid (H.sald, H.sal, H.anth or H.8hq) in acetone with zinc sulphate ($ZnSO_4 \cdot 7H_2O$) in 2:2:1 mole ratio respectively. The reaction mixtures were refluxed with constant stirring on a hot plate magnetic stirrer for 2h and then allowed to settle at room temperature for another 2h. The compounds formed were then filtered, washed with a little quantity of solvent and dried in a desiccator over fused calcium chloride.

Analysis of complexes: A known weight of the complex was decomposed by a mixture of conc. HNO_3 and conc. H_2SO_4 and evaporated by dryness. The dry residue was extracted with distilled water to a known volume into a volumetric flask. Zn^{++} in the solution was estimated adopting standard method [13]. C, H and N were estimated microanalytically.

Infrared spectra (FTIR) of the compounds were recorded in KBr phase in the range, 4000-500 cm^{-1} . The 1H NMR spectra of the compounds were recorded in $DMSO-d_6$.

RESULTS AND DISCUSSION

The physical and analytical data of complexes are recorded in Table-1. Melting/decomposition temperature of the complexes were found to be higher than those of the corresponding ligands.

Molar conductance of the complexes, recorded in DMF at 10^{-3} M concentration, lie in the range 5.8 to 7.1 mho $\text{cm}^2 \text{mol}^{-1}$ suggesting non-electrolytic nature of the compounds [14]. Analytical results suggest a 1:1:1 mole ratio among the metal, 1st ligand (organic acid) and 2nd ligand (azo dye) indicating following scheme of reaction:



Where, L = sald, sal, anth or 8hq and L' = PASA or PAHQ.

Infrared studies: FTIR spectra of ligands and complexes were recorded in KBr phase in the range 4000-500 cm^{-1} . Selected infrared bands of ligands and complexes are recorded in Table-2. In the spectra of H.PASA a band spotted at 1611 cm^{-1} may be assigned to $-\text{N}=\text{N}-$ stretching vibration. This band did not get disturbed in the spectra of mixed complexes with this ligand and mostly appear again in the range 1605-1614 cm^{-1} . This suggest that the $\text{N}=\text{N}$ group of the dye did not coordinate to the metal in the complexes. This non-coordination of azo group might be due to non-availability of additional donor at a suitable position for chelate ring formation; and also, perhaps, due to the availability of other donor sites in the dye molecule for the formation of chelate ring of suitable size. The ν_{OH} of H.PASA shows as a weak band at rather low position at 3233 cm^{-1} . This suggests its involvement in hydrogen-bonding. In the spectra of complexes, the ν_{OH} again shows at 3350 - 3428 region suggesting that the OH (phenolic) does not get deprotonated during complexation; rather it probably coordinates to the metal, presumably, after the break of H-bonding. Thus, it seems, that the carboxylic OH of the dye gets deprotonated during complexation to bind the metal and account for one of the primary valencies of the later. The $\nu_{\text{C}=\text{O}}$ of carboxylic group of H.PASA shows at 1660 cm^{-1} . This band mostly remained undisturbed in the complexes suggesting non-coordination of COOH through $\text{C}=\text{O}$. The donor groups of the 1st ligands (chelating organic acids) such as CHO of sald, OH of sal, NH_2 of anth or ring-N of 8hq also seem to be coordinated to the metal, as they did not show at their usual positions in the spectra of mixed complexes and undergo shifts or get mixed-up with corresponding 2nd ligand (H.PASA) bands.

In the spectra of H.PAHQ the $\nu_{\text{N}=\text{N}}$ band shows at 1603 cm^{-1} . In the spectra of mixed complexes, this band remains undisturbed (1600-1604) suggesting that the $\text{N}=\text{N}$ group of the dye is not coordinated to the metal. Non-availability of chelation site in suitable orientation to the azo group might be the reason behind this. The ν_{OH} of H.PAHQ, once again, shows at rather low position as two bands at 3265 and 3215 cm^{-1} , indicating the OH to be hydrogen-bonded. In the spectra of mixed complexes with this ligand, the ν_{OH} disappeared indicating deprotonation of OH of H.PAHQ during complexation. The $\nu_{\text{C}=\text{N}}$ of the dye (H.PAHQ) showed at 1365 cm^{-1} . In the mixed complexes this band shifted down by 15 to 40 wave numbers suggesting coordination of ring-N of the dye to the metal. The bands due to the donor groups of the 1st ligands (sald, sal, anth etc.), once again, did not show up at their usual positions in the spectra of mixed complexes and were found shifted or mixed-up with the 2nd ligand bands, suggesting coordination of these donor groups to the metal. Thus, chelate rings seem to be formed by all the ligands in the mixed complexes, this might be the driving force behind formation and stabilisation of the mixed complexes.

¹H NMR studies: ¹H NMR spectra of azo ligand, H.PASA shows multiplet at δ 6.938 to 6.864 ppm which may be assigned to the phenyl protons. Proton of COOH shows as a triplet at δ 7.493 - 7.448. A doublet at δ 7.790 - 7.765 may be assigned to the phenolic proton (OH). This signal at rather down field to its usual position indicates its involvement in hydrogen-bonding. In the spectra of mixed complexes involving PASA, the phenylic protons show as multiplet in the region δ 6.989 to 6.456. In fact, the mixed complexes have several phenyl protons in different environments contained in different ring systems. The signal due to COOH has been found to disappear in the spectra of complexes indicating its deprotonation during complexation. The proton of OH (of H.PASA), once again shows at δ 7.790 - 7.762, almost undisturbed. The down field position continues, indicating that OH undergoes break of hydrogen-bonding with simultaneous coordination to the metal. The signals due to the protons of additional donor group on the 1st ligand, oriented suitably for chelation (CHO of sald, OH of sal, NH_2 of anth) showed slightly down field to their usual positions indicating their coordination to the metal.

In the ligand H.PAHQ, the phenyl naphthyl protons show signals as several multiplet in the region 7.750 - 6.708. The OH proton shows at 8.120 - 7.996. Its rather down field position might be due to O-H...N hydrogen-bonding. In the spectra of mixed complexes involving this ligand, the signal due to phenolic proton disappears, indicating its deprotonation during complexation. The phenyl and naphthyl protons of PAHQ as well as other ligand (1st ligand) show signals at 8.24 to 6.72 as several multiplet in the spectra of mixed complexes. The protons on the donor groups of the 1st ligand, once again, showed signals slightly shifted from their usual positions, suggesting their involvement in coordination to the metal.

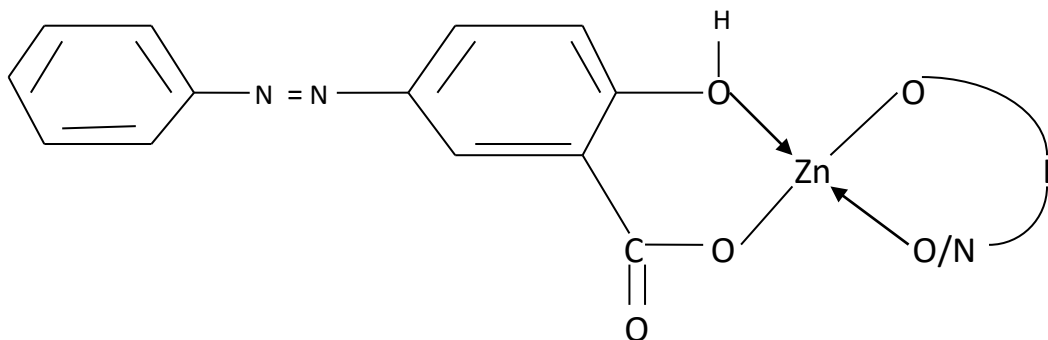
Thus, spectral studies suggest formation of chelate rings by all the ligands in the mixed complexes. This might be the driving force behind the formation and stabilisation of these mixed complexes. Structures of the complexes involving H.PASA or H.PAHQ may tentatively be proposed as shown in Fig. 1 & 2, respectively.

Table-1: Physical and Analytical Data of Compounds

Compound/Colour	Melt(m)/Decomp.(d) temp.(°C)	Analysis % found (Calculated)				λ_m (mho cm ² mol ⁻¹)
		Zn	C	H	N	
H.PASA Greenish Grey	170(d)	-- --	64.82 (64.46)	4.35 (4.13)	11.26 (11.57)	--
[Zn(sald)(PASA)] Dirty White	300(d)	15.06 (15.22)	56.43 (56.21)	3.52 (3.28)	6.31 (6.56)	6.7
[Zn(sal)(PASA)] Grey	295(d)	14.52 (14.67)	54.36 (54.18)	3.48 (3.16)	6.18 (6.32)	6.9
[Zn(anth)(PASA)] Light Brown	290(d)	14.55 (14.71)	54.63 (54.30)	3.53 (3.39)	9.41 (9.50)	7.1
[Zn(8hq)(PASA)] Dirty White	295(d)	14.36 (14.44)	58.56 (58.67)	3.62 (3.33)	9.14 (9.33)	6.8
H.PAHQ Brick Red	190(d)	-- --	72.46 (72.29)	4.64 (4.42)	16.61 (16.87)	--
[Zn(sald)(PAHQ)] Brick Red	215(d)	14.67 (14.98)	61.26 (60.83)	3.60 (3.46)	9.35 (9.68)	5.8
[Zn(sal)(PAHQ)] Yellow	210(d)	14.23 (14.44)	58.72 (58.67)	3.25 (3.33)	8.97 (9.33)	6.4
[Zn(anth)(PAHQ)] Brownish Yellow	210(d)	14.16 (14.48)	58.97 (58.80)	3.61 (3.56)	12.23 (12.47)	6.2
[Zn(8hq)(PAHQ)] Brick Red	215(d)	13.96 (14.22)	63.15 (63.02)	3.66 (3.50)	12.14 (12.25)	5.9

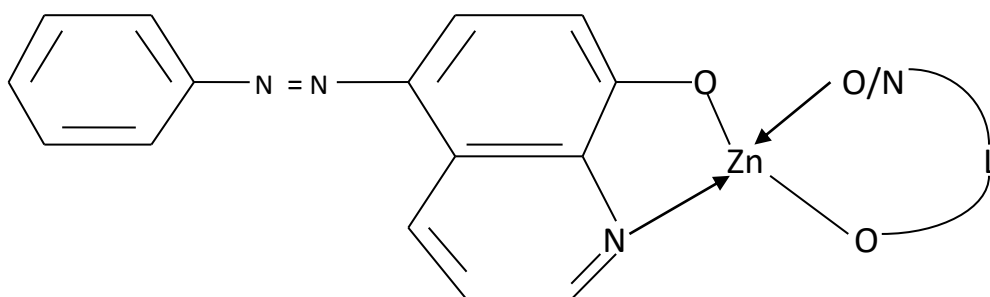
Table-2: Selected Infrared Bands (cm⁻¹) of Compounds

Compound	Bands due to azo dye ligand				Bands due to organic acid ligand			
	$\nu_{N=N}$	ν_{OH}	$\nu_{C=O}$	$\nu_{C\cdots N}$	ν_{CHO}	ν_{OH}	ν_{NH}	$\nu_{C\cdots N}$
H.PASA	1611	3233	1660	--	--	--	--	--
[Zn(sald)(PASA)]	1614	3400	1665	--	Obscured	--	--	--
[Zn(sal)(PASA)]	1610	3350	1662	--	--	3235	--	--
[Zn(anth)(PASA)]	1605	3428	1655	--	--	--	Obscured	--
[Zn(8hq)(PASA)]	1608	3400	1662	--	--	--	--	1325
H.PAHQ	1603	3265 3215	--	1365	--	--	--	--
[Zn(sald)(PAHQ)]	1600	--	--	1345	1660	--	--	--
[Zn(sal)(PAHQ)]	1604	--	--	1350	--	3365	--	--
[Zn(anth)(PAHQ)]	1602	--	--	1330	--	--	3336	--
[Zn(8hq)(PAHQ)]	1600	--	--	1325	--	--	--	Obscured



L= 1st ligand (sald, sal, anth or 8hq)

Fig.-1



L= 1st ligand (sald, sal, anth or 8hq)

Fig.-2

CONCLUSION

Zinc complexes, synthesised presently, might throw light in exploring possibilities for the application of mixed ligand zinc complexation in colour lakes in mordant dyeing with azo dyes; such lakes might have better fixability, dyeing performance as well as novel shades. When applied to the fabric, the 1st ligand (organic acid ligand) of the mixed complex might get replaced by the donor groups of the fabric to form a mixed chelate of higher stability on the fabric and, in turn, enhance fastness. Zinc being less toxic than chromium and cobalt might form more environment-friendly metal-complexed dyes. Moreover, zinc would also not effect much the original shade of the dye.

Another application of our present work would also be to trace the role of azo dyes, released into the environment, in the retention of zinc in the soil and aquatic systems, by chelation.

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