

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Mixed Ligand Complexation Of Zinc By Some Chelating Organic Acids And Polydentate Azo Dyes.

TVRK Rao* and Chanchal Kumari

Department of Chemistry, Purnea College, Purnia- 854301, Bihar, India

*Corresponding author email: tvrk_rao@rediffmail.com

ABSTRACT

Mixed ligand complexes of Zinc(II) involving some chelating organic acids viz., salicylaldehyde, salicylic acid, anthranilic acid or 8-hydroxyquinoline and some polydentate azo dyes viz., 1-(2^A-carboxyphenylazo)-2-naphthol or 4-(2^A-carboxyphenylazo)resorcinol have been synthesised and characterised. Analytical results suggest the complexes to be of general formula, [Zn L.L^A], where, L = deprotonated chelating organic acid and L^A = unideprotonated polydentate azo dye. Molar conductance values indicate the compounds to be non-electrolytic in nature. Infrared spectra of the compounds suggest coordination of -N=N- of azo dye along with deprotonation of COOH group to bind to metal. The phenolic OH group of the dyes (oriented ortho to the azo group) has also been evidenced to be coordinated to the metal. 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, Polydentate azo dyes, Metal-complexed dyes, Mixed ligand complexes, Zinc chelates.

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], 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 polydentate azo dyes. Mixed ligand complexes of general formula, $[Zn L.L^A]$, where, L= deprotonated salicylaldehyde (sald), salicylic acid (sal), anthranilic acid (anth) or 8-hydroxyquinoline (8hq) and L^A = Unideprotonated azo dye, viz., 1-(2^A-carboxyphenylazo)-2-naphthol (CPAN), or 4-(2^A-carboxyphenylazo)resorcinol (CPAR), have been synthesised. The compounds were characterised by elemental analysis and spectral (infrared and ¹H NMR) studies.

EXPERIMENTAL

Preparation of Azo dyes:

The azo dyes, 1-(2^A-carboxyphenylazo)-2-naphthol and 4-(2^A-carboxyphenylazo) resorcinol were prepared by diazotising anthranilic acid (6.5g) in 5ml conc. HCl and 15ml water with an aqueous solution of sodium nitrite (3.6g) at 0-5°C by usual method and coupling the diazotised solution with an alkaline solution of β-naphthol (7.2g) or resorcinol (5.5g) 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.CPAN or H.CPAR) 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. 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 $DMSO-d_6$.

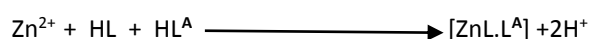
RESULTS AND DISCUSSION

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.

Table 1: Physical and Analytical Data of compounds

Compound/Colour	Melt(m)/ Decomp.(d) temp. (°C)	Analysis % Found(Calculated)				λ_m (mho $\text{cm}^2\text{mol}^{-1}$)
		Zn	C	H	N	
H.CPAN Deep Red	260(m&d)	- -	69.86 (69.44)	4.10 (4.23)	9.59 (10.12)	-
[Zn(sald)(CPAN)] Red	285(d)	12.58 (12.71)	61.24 (61.02)	3.46 (3.39)	5.78 (5.93)	6.8
[Zn(sal)(CPAN)] Red	280(d)	12.26 (12.30)	59.18 (59.02)	3.36 (3.28)	5.63 (5.74)	8.2
[Zn(anth)(CPAN)] Deep Red	290(d)	12.14 (12.32)	59.26 (59.12)	3.64 (3.49)	8.53 (8.62)	7.3
[Zn(8hq)(CPAN)] Brick Red	285(d)	12.24 (12.12)	63.21 (63.03)	3.39 (3.43)	8.36 (8.48)	7.8
H.CPAR Deep Violet	265(d)	- -	61.32 (60.70)	3.86 (3.50)	10.15 (10.89)	-
[Zn(sald)(CPAR)] Brown	300(d)	13.46 (13.70)	54.92 (54.79)	3.64 (3.20)	6.12 (6.39)	5.6
[Zn(sal)(CPAR)] Brown	295(d)	12.86 (13.22)	53.43 (52.86)	3.16 (3.08)	6.06 (6.17)	6.4
[Zn(anth)(CPAR)] Brown	295(d)	13.16 (13.25)	52.64 (52.98)	3.37 (3.31)	8.92 (9.27)	6.9
[Zn(8hq)(CPAR)] Brown	290(d)	12.88 (13.02)	57.43 (57.27)	3.41 (3.25)	9.18 (9.11)	6.2

Molar conductance of the complexes, recorded in DMF at 10^{-3} M concentration, lie in the range 5.6 to 8.2 $\text{mho cm}^2 \text{mol}^{-1}$ 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^{A} = CPAN or CPAR.

Infrared studies:

FTIR spectra of ligands and complexes were recorded in KBr phase in the range $4000\text{-}500\text{cm}^{-1}$. Selected infrared bands of ligands and complexes are recorded in Table-2. In the spectra of H.CPAN a band spotted at 1590 cm^{-1} may be assigned to -N=N- stretching vibration. This band was found to appear as a double headed peak at $1590\text{ to }1597\text{ cm}^{-1}$, with a shoulder at 1525 cm^{-1} in the complexes. This split of N=N band suggest coordination of the azo group (through one of its nitrogen atoms) to the metal. The OH of H.CPAN shows as a weak band at rather low position at 3400cm^{-1} . This suggests its involvement in hydrogen bonding. In the spectra of complexes the OH again shows at $3320\text{ to }3422$ 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, the carboxylic OH of the dye seems to deprotonate (in preference to phenolic OH) to bind the metal. The bands due donor groups oriented suitably for chelation, on the 1st ligand such as CHO of sald, OH of sal, NH_2 of anth or ring N of 8hq, showed shifted from their usual position in the spectra of complexes, suggesting coordination of these donor groups to the metal.

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

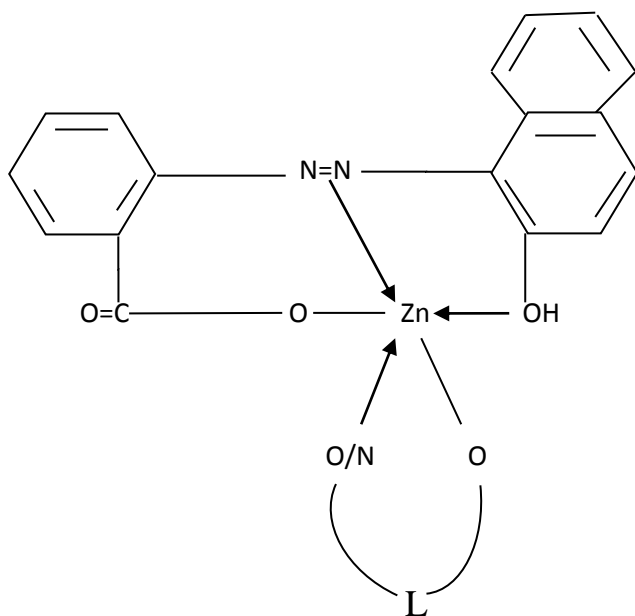
Compound	Bands due to azo dye ligand		Bands due to organic acid ligand			
	$\nu_{\text{N=N}}$	ν_{OH}	ν_{CHO}	ν_{OH}	ν_{NH}	$\nu_{\text{C}\cdots\text{N}}$
H.CPAN	1590	3400	-	-	-	-
[Zn(sald)(CPAN)]	1598 1525	3430	obscured	-	-	-
[Zn(sal)(CPAN)]	1589 1530	3360	-	3056	-	-
[Zn(anth)(CPAN)]	1593 1525	3320			obscured	-
[Zn(8hq)(CPAN)]	1595 1525	3340				1327
H.CPAR	1593	3400	-	-	-	-
[Zn(sald)(CPAR)]	1594 1535	3440	obscured	-	-	-
[Zn(sal)(CPAR)]	1592 1540	3376	-	3050	-	-
[Zn(anth)(CPAR)]	1593 1536	3437	-	-	3250	-
[Zn(8hq)(CPAR)]	1592 1535	3350	-	-	-	1322

In the spectra of H.CPAR the $\nu_{\text{N=N}}$ band shows at 1593 cm⁻¹. This band was found to split into two, appearing at 1590-1594 and 1535-1540 in the complexes, suggesting coordination of azo (N=N) group to the metal. The ν_{OH} of H.CPAR, once again, shows at rather low position at 3400 cm⁻¹, indicating the OH to be hydrogen-bonded. In the mixed complexes the ν_{OH} shows at 3370 to 3445, suggesting that neither of the two OH(Phenolic) groups deprotonate during complexation. The shift of ν_{OH} in the complexes suggest that during complexation, the hydrogen-bonding in the azo ligand breaks and one of the OH (oriented ortho to -N=N-) coordinates to the metal. The bands due to donor groups on the 1st ligand (sald, sal, anth or 8hq), once again, did not show up at their usual positions in the spectra of mixed complexes and were found shifted, 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:

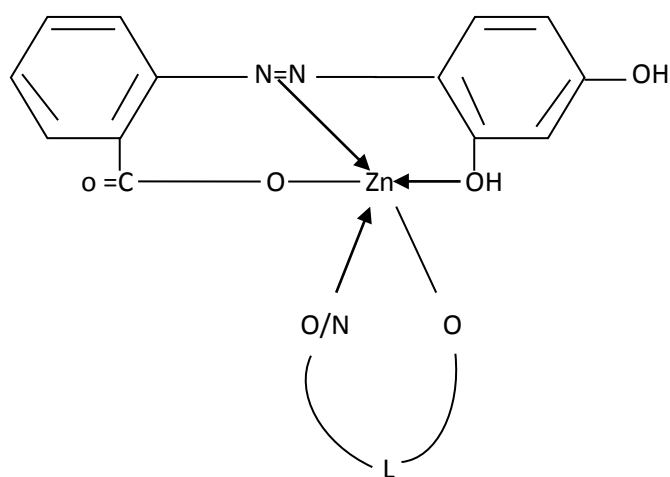
¹H NMR spectra of azo ligands and complexes shows phenylic and naphthyl protons as a complex pattern of several multiplets in the region δ 6 to 8.5 ppm. The carboxylic proton of azo ligands, showing as a singlet at δ 7.90 (for H.CPAN) or δ 7.21 (for H.CPAR), disappeared in the complexes, suggesting deprotonation of COOH during complexation. Phenolic protons of azo ligands, positioning at δ 7.87 (for H.CPAN) or δ 6.22 and 7.07 (for H.CPAR), shifted slightly downfield in complexes, indicating that the phenolic OH are not deprotonated and are rather coordinated to the metal. In case of complexes involving CPAR, the phenolic protons showed as two signals, one that is relatively downfield might be due to the OH oriented ortho to the azo group, while the other might be due to the OH oriented para to the azo group. The signal due protons of additional doner group on the 1st ligand, oriented suitably for chelation viz OH of sal, NH₂ of anth, showed slightly shifted from their usual positions in the spectra of complexes suggesting their coordination to the metal.

Structures of the complexes involving H.CPAN or H.CPAR may tentatively be proposed as shown in Fig. 1 & 2, respectively.



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

Fig.1



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

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.

ACKNOWLEDGEMENT

Authors express gratefulness to the SAIF, CDRI, Luck now for FTIR, ¹H NMR and micro analytical facilities.

REFERENCES

- [1] Singh VP Metal Toxicity and Tolerance in Plants and Animals. Sarup & Sons Publishers, New Delhi, 1st Edition, 2005, p.108.
- [2] Bhaskare CK and Desmukh SK. Acta Ciencia India, 2C, 1976, 34.
- [3] Ghose SB, Sharma OP, Kharat RB. J. Indian Chem. Soc., 1978; 55:776
- [4] Talati JP and Daragi, J.Indian Chem. Soc., 1991., 68:67.
- [5] Jeyaraj T, Paramasivam M, Raja C, Thangeppa V and Stella Shalini AS. Transactions of the SAEST, 2005; 40:139-145.
- [6] Gaiind KN and Gulati SK. Indian J. Pharm., 1966; 28:272.
- [7] Clonfero E, Vermir P, Granell N and Levis AG. La Medicina del Lavoro, 1990; 81:222-229.
- [8] Garg A, Bhat KL and Bock CW Dyes and Pigment 2002; 55:35-52.
- [9] Bardole HA, Freeman HS and Reife A. Text Res J 1998; 68: 141-149.
- [10] Freeman HS, Sokolowska-Gajda J, Reife A, et al. Text Chem Color 1995; 27(2): 13-16.
- [11] Czajkowski W and Szymczyk M. Dyes Pigments 1998; 37: 197-204.
- [12] Zarkogianni M, Argyropoulos G, Dimitriadou S, Anthemidis A, Nikolaidis N and Tsatsaroni E. Text Res J 2012; 82: 1545-1552.
- [13] Vogel AI Test Book of quantitative inorganic analysis (Fourth Edition), ELBS and Longman, London. 1978; p.325.
- [14] Geary WJ. Coord. Chem. Rev. 1971; 7: 82.