

## NOTE

## Spectral Investigation of Ligand-Metal Composition Using Dye Indicators

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The reagents  $\beta$ -arylamino crotono anilides were prepared and the dye indicator method was used to investigate the composition of number of complexes between ligand and metal ions and hence  $ML$  and  $ML_2$  type complexes of zinc and cadmium were prepared and characterised.

Chelate formation of coloured ions with ligands is generally investigated by spectrophotometric methods viz. job, slope ratio and mole ratio, which however can be only used for metal ions of many coloured complexes. However, this indicator method can be used for investigation of ions not forming coloured complexes.<sup>1</sup> In the present work, three ligands  $\beta$ -*o*-, *m*- and *p*-chloroanilino-crotono-*o*-, *m*- and *p*-chloroanilide were prepared and their  $ML$  and  $ML_2$  complexes of  $Zn(II)$  and  $Cd(II)$  were prepared and characterised. Spectral studies were done by dye indicator method.

Keeping the ligand conc. ( $M/20$ ) constant and dye concentration also constant, while the zinc or cadmium chloride conc. ( $M/20$ ) is variable, when the light absorbance measured against  $mL$  of the variant  $M/20$  was plotted, the graphs show peaks as shown in Fig. 1.

These peaks correspond to metal and ligand in stoichiometric proportions 1:1 and 1:2, according to the complexes prepared and isolated from respective solutions, purified and characterised.

Ethyl- $\beta$ -arylamino crotonates were prepared by condensing *o*-, *m*- and *p*-chloroaniline respectively with methyl acetoacetate by known method.<sup>1</sup> Arylamino crotonoanilides were prepared by refluxing equimolar mixtures of the respective crotonates with the corresponding arylamine in toluene for 3–4 h and the reaction mass was treated with dilute hydrochloric acid, saturated sodium chloride, water and then extracted with ether. Evaporation of ether gave pure products. Thus the following ligands were prepared:

1.  $\beta$ -*p*-chloroanilino crotono *p*-chloroanilide (*p*-CCD)
2.  $\beta$ -*m*-chloroanilino crotono *m*-chloroanilide (*m*-CCD)
3.  $\beta$ -*o*-chloroanilino crotono *o*-chloroanilide (*o*-CCD)

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These ligands were studied by Farasram and Desai for Cu(II) and Hg(II) metal ions by Job, slope ratio and mole ratio method.<sup>2</sup>

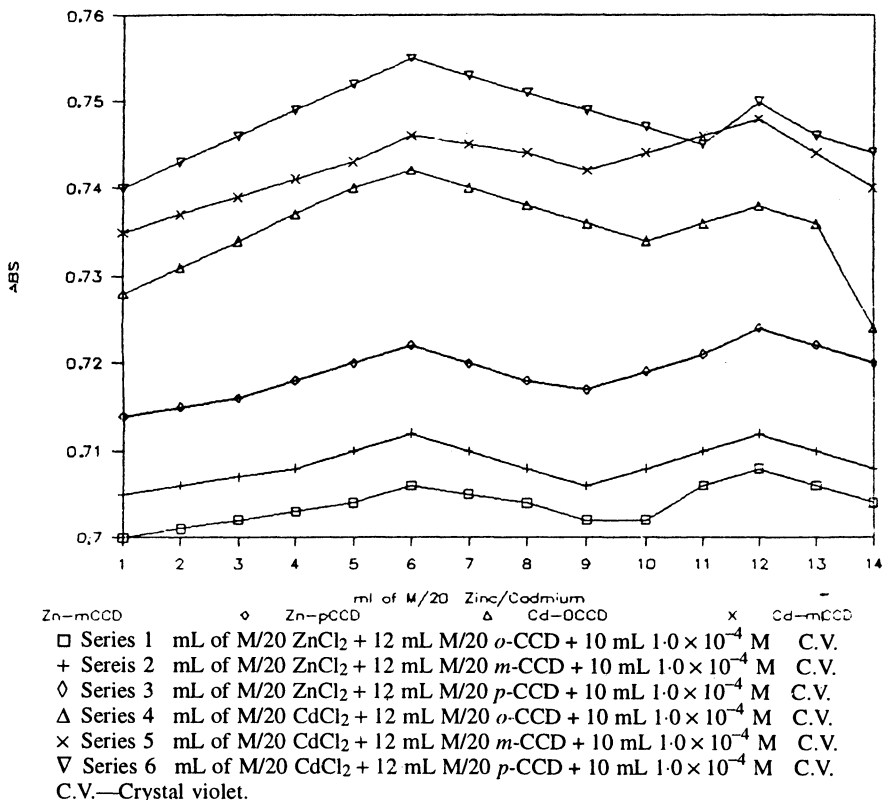
ML and ML<sub>2</sub> type complexes of zinc(II) and cadmium(II) were prepared by stirring for 1 h at room temperature mixture of methanolic solution of metal chloride (0.04 M, 25 mL) and methanolic solution reagent (0.04 M, 15 mL) for ML type addition complexes and methanolic solution of metal chloride (0.04 M, 10 mL) and methanolic solution of reagent (0.04 M, 40 mL) at pH 7.0 to 7.5 for ML<sub>2</sub> type covalent-complexes when fine crystals of complexes separated out. ML type complexes were washed with methanol and anhydrous ether. ML<sub>2</sub> type complexes were washed with methanol for purification.

ML complexes were microcrystalline solids, soluble in alcohol and insoluble in ether. They were soluble with decomposition in hydrochloric acid. They have high melting points. ML<sub>2</sub> complexes were also microcrystalline solids. They were insoluble in water, alcohol and chloroform and soluble in dimethyl formamide.

The molecular formulae of  $\beta$ -chloroanilino crotono chloroanilides for zinc(II) and cadmium(II) are as below.



A Shimadzu double beam spectrophotometer UV 160A was used for spectral study and the study was carried out by monovariation method using dye crystal violet as indicator. The absorbance of pure dye in methanolic solution was



measured and absorbance at  $\lambda_{\max}$  of the dye taken as standard. The absorbance at  $\lambda_{\max}$  in each case of dye reagent metal chloride system in methanol was measured with increase in concentration of metal chloride, while keeping the concentration of reagent constant using monovariation method, dye concentration being constant.<sup>1</sup> When such absorbance is plotted against increasing metal chloride concentration the graphs indicate peaks corresponding to complex formation in the ratio of metal and ligand in stoichiometric proportion for the system in 1 : 2 and 1 : 1 (Fig. 1).

### IR spectra

(i) N—H stretching frequencies (*ca.* 3195  $\text{cm}^{-1}$ ) of ligands shift to higher frequency (3440 to 3285  $\text{cm}^{-1}$ ) with decrease in intensity in the complexes. The increase in the frequency can be accounted for hydrogen bonding of NH group due to complexation.

(ii) The strong band *ca.* 1700  $\text{cm}^{-1}$  in the spectra of the ligands can be attributed to C=O stretching frequency (amide-I band) which on complexation disappears and appears at lower frequency (1585 to 1555  $\text{cm}^{-1}$ ) as C—O stretch merges with C=C vibration band.

(iii) The band due to CH<sub>2</sub> wagging vibrations located at *ca.* 1154  $\text{cm}^{-1}$  in spectra of ligands is absent in the spectra of complexes in which new bands appear at 1198 and 1183  $\text{cm}^{-1}$  and 826 to 738  $\text{cm}^{-1}$  corresponding to CH in-plane bending and CH out-of-plane bending vibrations. This supports the enolisation of the ligands when complexation takes place.

(iv) In all the ligands and complexes bands appear at 3200 to 3045  $\text{cm}^{-1}$  corresponding to symmetric and antisymmetric aromatic CH stretching vibrations. The bands observed at 2980 to 2880  $\text{cm}^{-1}$  are due to aliphatic CH stretching vibrations.

(v) The band observed at *ca.* 1670  $\text{cm}^{-1}$  in the spectra of the ligands is attributed to C=N stretching vibrations. This band shifts to lower frequency (1615 to 1595  $\text{cm}^{-1}$ ) in the spectra of the complexes suggesting coordination through the nitrogen and formation of M—N bond.

### REFERENCES

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2. P.L. Farasram and C.M. Desai, *South Gujarat University Journal*, **8**, 70 (1979).

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