

APPENDIX :

Papers published or accepted for publication :

Abstracts :

1. Some metal complexes with catechol, pyrogallol, 2,3-dihydroxynaphthalene and protocatechuic acid. Indian J.Chem., 10(12), 1190 (1972).

The formation constants of the chelates of different metal ions with the polyhydroxy aromatic ligands have been determined at 30°C. using Irving-Rossotti titration technique. The stabilities of the complexes follow the Irving-Williams order in each case and they increase in the order



The stabilities in the case of Zn(II), Ni(II), UO_2^{2+} and Al^{3+} chelates have been explained on the basis of the relative contributions of ionic and covalent forces.

2. Study of Zn(II) and Cd(II) complexes of polyhydroxy aromatic ligands., J.Inst.Chemists (India), Vol. XLIV, Part III, May, 91-92 (1972).

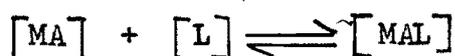
The complexes of the types $[\text{M}(\text{L})_2]\text{enH}_2$ and $[\text{M}(\text{L})\text{en}]$, where M = zinc or cadmium, L = catechol, or pyrogallol, L₁ = 2,3-dihydroxynaphthalene and en = ethylenediamine have been prepared by substitution reactions. The resulting compounds have been characterised by analytical, magnetic and I.R. spectral studies.

3. Study of some ternary complexes in solution., J.Indian Chem. Soc., 49(5), 469-474 (1972).

Mixed ligand formation constants K_{MAL} (where $M = Cu^{2+}$, Ni^{2+} , Zn^{2+} and Cd^{2+} ; $A =$ dipyridyl; $L =$ catechol, pyrogallol or protocatechuic acid) have been determined by using a modified form of Irving-Rossotti technique. Values of K_{MAL} have been found to be very close to K_{ML_1} in Ni^{2+} , Zn^{2+} and Cd^{2+} and $K_{MAL} > K_{ML_1}$ in $Cu(II)$ system. This relationship has been explained in terms of charge neutralization, π interaction and favourable geometry.

4. Studies in some heterochelates Part VII: Solution studies of $Ni(II)$, $Cu(II)$, $Zn(II)$ and $Cd(II)$ + dipyridyl + salicylic acid or thiosalicylic acid systems., Indian J.Chem., (in press).

Modified form of Irving-Rossotti titration technique has been applied to study the formation constants of mixed ligand complexes formed by the following reaction :



where $M = Cu(II)$, $Zn(II)$, $Ni(II)$ or $Cd(II)$; $A =$ dipyridyl and $L =$ salicylic acid or thiosalicylic acid at $17^\circ C$. in 50 % alcoholic solution. The value of mixed ligand formation constant K_{MAL}^{MA} is found to be almost equal to the value $K_{ML_1}^M$, in each case. This is because of $M \rightarrow$ dipyridyl π interaction. The behaviour of salicylic acid and thiosalicylic acid in the mixed ligand systems are same. In case of thiosalicylic acid complex, it is expected that metal ion having already donated π electrons to dipyridyl molecule should have less tendency to donate π electrons to the secondary ligand and hence the values of K_{ML_1} and K_{MAL} should have been significantly different. But $K_{MAL} \approx K_{ML_1}$,

where L = thiosalicylic acid. This is because the contribution of M-S π interaction is not very significant.

5. A study of Cu^{2+} , Ni^{2+} , Zn^{2+} and Cd^{2+} heterochelates.

Indian J.Chem., 10(9), 948 (1972).

The complexes of the type M.dipy.catechol, where M = Cu^{2+} , Ni^{2+} , Zn^{2+} and Cd^{2+} have been prepared and characterised on the basis of analytical, magnetic and spectral data. Zn(II) and Cd(II) complexes are diamagnetic whereas magnetic moments of Cu(II) and Ni(II) correspond to spin only moments of one and two electrons respectively. The data suggest a square planar and distorted octahedral structure for Cu(II) and Ni(II) complexes, respectively.

6. Studies of mixed ligand complexes of Cu^{2+} , Ni^{2+} , Zn^{2+} and Cd^{2+} , Indian J.Chem., 10(7), 742-743 (1972).

Irving-Rossotti technique has been applied to study the formation constant of the reaction $(\text{MA})^- + \text{L}^{2-} \rightleftharpoons (\text{MAL})^{3-}$ where LH_2 = catechol, pyrogallol and 2,3-dihydroxynaphthalene. A similar equation with L^{3-} represents coordination of protocatechuic acid. Metal.NTA 1:1 complexes are formed at lower pH and are stable at higher pH. The values of formation constants obtained for the mixed ligand system K_{MAL} are found to be less than the first formation constant in the binary system K_{ML} . This behaviour may be due to (i) the difference in electrostatic repulsions experienced by L^{2-} to add to $\text{M}^{2+}(\text{aq.})$, (ML) or M.NTA^- , or (ii) the NTA^{3-} occupying more coordination positions around metal ions than L^{2-} . The formation constants of binary copper complexes are higher

than that of Ni-chelates, Zn-chelates and Cd-chelates. However, in ternary system the magnitude of such difference is small. The observation has been explained in terms of Jahn-Teller distortion.

7. Study in some heterochelates III : Cu(II), Ni(II), Zn(II) or Cd(II) + Histidine or Ethylenediaminetetraacetic acid + Polyphenols Systems., Bull. Chem. Soc., (Japan), (in press).

An extension of Irving-Rossotti technique has been applied to study the formation constant of mixed ligand complexes as follows :



where M = Cu(II), Ni(II), Zn(II) and Cd(II); A = Histidine or Ethylenediaminetetraacetic acid and LH₂ = catechol, pyrogallol or 2,3-dihydroxynaphthalene. The values obtained for the mixed ligand formation constants are found to be less than the first formation constant K_{ML} , in the binary systems.