

be explained if the band is indeed a N-N vibration. In a symmetrical molecule, the N-N vibration is infrared forbidden. In the neutral ligand it should be allowed but is probably very weak. For the uni-negative ligand, however, the vibration becomes more intense and this is explained by the X-ray studies¹⁰ which show that the C=N double bond is almost completely localized in the C-N^{II} region. Hence, the N^{II} and N^{III} atoms are very much different. The position of the band at lower energy is also consistent with the observed lengthening of the N^{II}-N^{III} bond. In all the three thiosemicarbazido complexes, in addition to bands due to $\delta(\text{NH})$, amide, $\nu(\text{CN}) + \delta(\text{NH}_2)$ and $\nu(\text{C}=\text{S})$, a sharp band appears at 950 cm^{-1} indicating uninegative bidentate nature of the ligand^{8,9}. Dithiocarbamate can behave as a bidentate or a monodentate ligand. The former exhibits $\nu(\text{CS})$ near 1000 cm^{-1} as a single band, whereas the latter shows a doublet in the same region¹¹. Also the $\nu(\text{C}=\text{N})$ of the former (above 1485 cm^{-1}) is higher than that of the latter (below 1485 cm^{-1})¹². In the present case, the ligand dithiocarbamate exhibits $\nu(\text{C}=\text{N})$ band at 1505 cm^{-1} and a singlet at 1005 cm^{-1} due to $\nu_{\text{as}}(\text{CS})$ indicating that the chelate is coordinated to manganese(III) ion through both the sulphur atoms as a uninegative bidentate ligand. Similar observations for manganese tris (dithiocarbamates) have been reported by Prabhakaran and Patel¹³ and Das and Ramana Rao¹⁴. In the acetylacetonato complexes, the bands due to $\nu(\text{C} \cdots \text{O})$ and $\nu(\text{C} \cdots \text{C})$ were obtained at ~ 11600 and 1520 cm^{-1} respectively indicating the uninegative bidentate coordination of the ligand as suggested by Graddon¹⁵. In the compounds containing picolinate group, the band due to free carboxyl group at 1710 cm^{-1} was found to be absent. Other bands due to $\nu_{\text{as}}(\text{CO}_2)$ and pyridine ring were found to be present indicating the coordination of the ligand through the nitrogen and oxygen atoms as an uninegative bidentate one as suggested by Fowles *et al.*¹⁶.

The electronic spectra of the complexes show three bands at ~ 13500 , ~ 22900 , and $\sim 25000\text{ cm}^{-1}$. Only one spin-allowed transition ${}^5E_g \rightarrow {}^5T_{2g}$ is expected for weak field octahedral manganese(III) complexes^{17,18}. The presence of three bands in these complexes indicates lowering of the O_h symmetry due to Jahn-Teller distortion. The complexes are expected to be tetragonally distorted with D_{4h} symmetry and the bands can be assigned to the transitions, ${}^5B_{1g} \rightarrow {}^5A_{1g}$ ($\sim 13500\text{ cm}^{-1}$), ${}^5B_{1g} \rightarrow {}^5B_{2g}$ ($\sim 22900\text{ cm}^{-1}$) and ${}^5B_{1g} \rightarrow {}^5E_g$ ($\sim 25000\text{ cm}^{-1}$) as suggested by Davis *et al.*¹⁹ and Lever²⁰. The lowest band of all the complexes was found to be broad which confirms the Jahn-Teller distortion experien-

ced by these complexes. Thus, in the light of the above evidences, it is suggested that the five mixed chelate manganese(III) complexes reported here are six-coordinated with tetragonally distorted octahedral stereochemistries.

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Polarographic Studies on Mixed Ligand Complexes Involving Amino Acids : Ternary Systems, Cd- α -Alanine-Oxalate & Cd- β -Alanine-Oxalate

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Ternary complexes of cadmium(II) with oxalate as primary ligand and α - and β -alanines as secondary ligands have been studied polarographically. Formation of three mixed complex species, $[\text{Cd}(\text{amino acid})(\text{oxalate})]$, $[\text{Cd}(\text{amino acid})(\text{oxalate})_2]$ and $[\text{Cd}(\text{amino acid})_2(\text{oxalate})]$, is observed in each case. The reduction is reversible and diffusion-controlled. The stability constants have been evaluated using the method of McMasters. The α -alanine complexes are found to be more stable than the corresponding β -alanine complexes.

IN continuation of our studies on the ternary systems, Cd-oxalate-glycinate¹ and Cd-oxalate-valinate², we report here the results of similar studies on Cd-oxalate- α -alanine and Cd-oxalate- β -alanine systems.

The amino acids used were BDH reagents. All other chemicals used were of AR grade.

The polarograms were recorded on an automatic polarograph (OH-105 RadelKis Hungary) using d.m.e. with $m = 2.54$ mg/s and $t = 4.7$ s (in open circuit). The pH of all the experimental solutions was maintained constant at 8.0 with the help of HNO₃/NaOH solution and measured with a Beckman

Expandomatic SS-2 pH-meter. Temperature was kept constant at 303K with a U-10 ultra thermostat. The fixed concentration of metal ion used was $2 \times 10^{-4}M$ and ionic strength was kept constant at 0.3 M with KNO₃ as the supporting electrolyte. The [free ligand] of the amino acids was calculated from the reported value³ of pK_2 (α -ala = 9.70, β -ala = 10.09) at 303K.

A solution of Cd(II) under experimental conditions gave reversible waves. The stability constants of binary systems were calculated by the method of De Ford and Hume⁴. The values obtained are as follows :

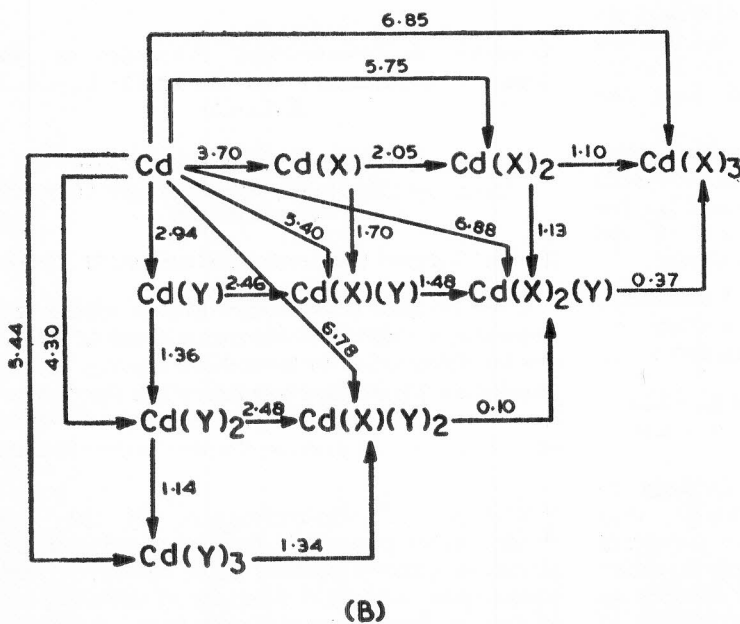
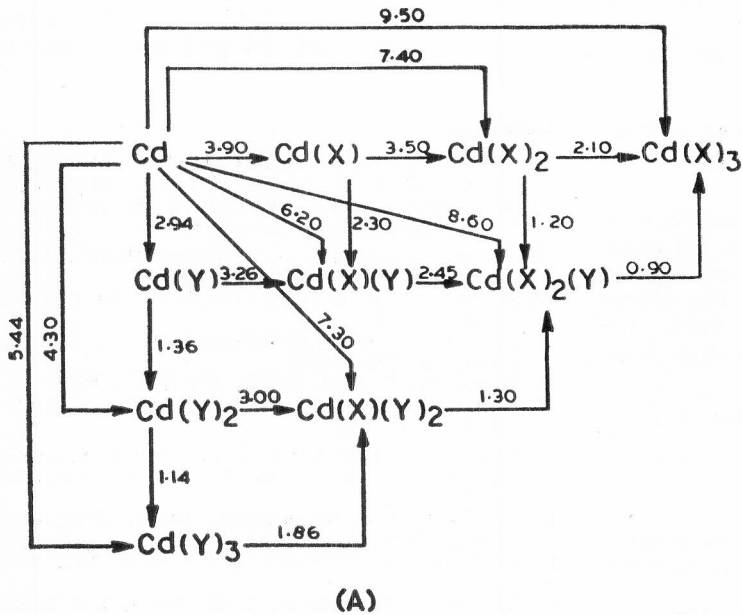


Fig. 1 — Complex equilibria in the ternary system Cd-oxalane [A, α -alanine; B, β -alanine].

| Cd-ox | Cd- α -ala | Cd- β -ala |
|-------------------------|-------------------------|-------------------------|
| log β_{01} = 2.94 | log β_{10} = 4.40 | log β_{10} = 3.70 |
| log β_{02} = 4.30 | log β_{20} = 7.40 | log β_{20} = 5.75 |
| log β_{03} = 5.44 | log β_{30} = 9.50 | log β_{30} = 6.85 |

The studies were made at two fixed concentrations (0.01 and 0.1 M) of oxalate so chosen that predominantly one and two oxalate ions per Cd(II) ion would exist respectively in the Cd-oxalate system. The functions F_{00} , F_{10} , F_{20} and F_{30} were calculated following the method of Schaap and McMasters⁵. The functions A , B , C and D were calculated by Leden's⁶ extrapolation method. From the values of B and B' at two different concentrations of oxalate ions, the formation constants of $[\text{Cd}(\alpha\text{-ala}/\beta\text{-ala})(\text{ox})]^-$ and $[\text{Cd}(\alpha\text{-ala}/\beta\text{-ala})(\text{ox})_2]^{3-}$ have been calculated. The values are as follows :

| | | |
|-------------------|-------------------------|-------------------------|
| α -alanine | log β_{11} = 6.20 | log β_{12} = 7.30 |
| β -alanine | log β_{11} = 5.40 | log β_{12} = 6.78 |

From the values of C and C' the formation constants (log β_{21}) were calculated for both the amino acids. The average values for log β_{21} are 8.60 and 6.88 for α -ala and β -ala respectively. The average values of D and D' were obtained as 9.49, 6.85 which are in agreement with log β_{30} values found experimentally (9.5, 6.85).

The mixing constant, $K_M = \beta_{11}/\sqrt{(\beta_{02}\beta_{20})}$ and stabilization constants (log $K_S = \log K_M - \log 2$)⁷ were calculated for the above systems. The values obtained are :

| | | |
|---------------|-------------------|-------------------|
| α -ala | log K = 0.350 | log K_S = 0.049 |
| β -ala | log K_M = 0.375 | log K_S = 0.074 |

The positive values of mixing constants and stabilization constants show that the ternary complexes are slightly more stable than the binary complexes; also, the values are more positive for β -alanine than for α -alanine. The positive values of stabilization constants have also been observed by Brookes and Pettit⁸, Gergely and Sovago⁹ and Ting and Wancollas¹⁰.

The equilibria between various species formed in solution in the two ternary systems, Cd-ox- α -ala and Cd-ox- β -ala are shown in Figs 1 A and B. The numerical values are the log K values and Y and X refer to oxalate and α -ala/ β -ala respectively.

The stability constants of mixed ligand complexes were also calculated by the method of Watters and De Witt¹¹. The results obtained are as under :

| | | | |
|-----------------|--------------------------|--------------------------|-------------------------|
| α -ala : | log β_{11} = 5.74, | log β_{12} = 7.26, | log β_{21} = 8.60 |
| β -ala : | log β_{11} = 4.86, | log β_{12} = 6.38, | log β_{21} = 6.84 |

It can be seen that it is easier for α -ala/ β -ala to add to $[\text{Cd}(\text{ox})]$ than to $[\text{Cd}(\alpha\text{-ala}/\beta\text{-ala})]$, thus formation of ternary complex is more favoured than that of the binary complex. The log K values for substitution are 2.30 and 1.70, while there is no tendency to substitute (ox) due to weaker nature of the oxalate ligand. The higher experimental values

may be accounted for by the electrostatic and steric factors as also concluded by Hughes *et al.*¹².

A comparison of the present data with those reported in our previous communications^{1,2} reveals that the stability of the ternary complexes $[\text{Cd}(\text{aa})_n(\text{ox})_{2-n}]$ decreases in the order: gly > α -ala > val > β -ala which is in agreement with the increasing bulkiness of the alkyl group and the expected relative behaviour of the amino acids. It is interesting to note that the binary complexes of β -alanine are much weaker than those of α -alanine as expected on account of the larger size of ring in the case of β -alanine chelates. But in ternary system there is not much of difference in the stabilities which may be due to the fact that amino acid occupies one axial and the equatorial position in the ternary systems.

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Synthesis & Ion-exchange Properties of Niobium Selenite : Separation of La-Th, Th-Cu, Pb-Cd, Zn-Pb & La-Ce

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A new inorganic ion-exchanger, niobium selenite, has been prepared by mixing 0.1M niobium pentoxide and 0.1M sodium selenite in different ratios. Its ion-exchange capacity, composition, chemical stability etc. have been determined. Distribution studies have been carried out to study its selectivity. On the basis of differential selectivity a number of separations have been achieved.

INORGANIC ion-exchangers of the type of zirconium phosphate have received considerable attention because of their high selectivity which is based upon their rigid structure of definite pore size. Materials based on niobium have, however, not received the same attention though a number of