MIXED COMPLEXES OF Cu(II) WITH BIOLOGICALLY ACTIVE LIGANDS

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Mixed ligand complexes are very likely to be formed in biological fluids since potential ligands like amino acids, peptides, proteins, vitamins etc. are present along with metal ions. Due to the close association with life and related activities, pyridoxine has rightly attracted the attention of research workers in recent years for co-ordination studies. Some of its derivatives have been investigated by Manousek and Zuman [1]. The polarographic measurements of formation constants of Copper(II) complexes with pyridoxine in ortho phosphate medium have been reported by Pella and Purdy [2].

In continuation of our earlier work [3-6] the polarographic study of different metal ions with amino acids and other biologically active ligands, studies on the formation of mixed ligand complexes by Cu(II) with the above cited amino acids as primary ligand and pyridoxine (Vitamin B_6) as secondary ligand are reported in this paper.

EXPERIMENTAL

All chemical used were of AnalaR grade. Pyridoxine, aspartic acid, isoleucine, glycine, glutamic acid and valine, were used as a complexing agent. The ionic strength was kept constant at 1.0 M by using potassium nitrate. 0.004% gelatin was also used in the final solution to suppress the maxima observed. Experiments were performed with 0.5 mM copper. The pH of all the solutions was maintained with an Elico digital pH meter (Model LI-120). Purified nitrogen was passed through the solution to remove the oxygen. Polarograms of the solutions were taken using a manual polarograph. Saturated calomel electrode was used as reference electrode. The capillary had the following characteristics: m = 1.96 mg/sec t = 4.05 sec/drop and h_{corr} = 40.0 cm (at 303 ± 1°K in 1.0 M KNO_3 in open circuit).

RESULTS AND DISCUSSION

The Simple Systems

Tne stepwise formation constant of the complexes of Cu(II) with pyridoxine and aspartic acid, isoleucine, glycine, glutamic acid and valine, were determined separately under identical conditions before the study of mixed ligand systems using the Deford and Hume [7] method. The results are summarized in Table 1.

The Mixed-Ligand Systems

The copper-aspartate-pyridoxinate, copper-isoleucinate-pyridoxinate, copper-glycinate-pyridoxinate, copper-glutamate-pyridoxinate and copper-valinate-pyridoxinate systems were studied by keeping the concentration of the weaker ligand (pyridoxinate) constant at 0.2 M while varying the concentration of second ligand for each system. The free ligand concentration for each system has been calculated with the help of pH of the solution, pK value and amount of the ligand. All the systems were studied at pH$\geq$7. The pK values of amino acids were calculated by the method of Albert and Serjeant [8] at 303 ± 1°K.

In all the cases, the single well defined and diffusion controlled wave had a slope of 30± 2 mV for the log plots indicating that the reduction is reversible and involves two electrons.

As the concentration of aspartate, isoleucinate, glycinate, glutamate and valinate is increased, the half wave potential shifts towards more negative values. This shift in half-wave potential is greater in the presence of weaker ligand (pyridoxinate) than in its absence. It indicates mixed-ligand complex formation. The Schaap and McMasters [9] treatment was applied for calculating the F functions and Leden's graphical extrapolation method [10] to calculate the A, B and C at 0.2 M [Pyr] values. The stability constants were evaluated from the values of A, B and C. The stability constants log β_{11} of all the systems are presented in Table 2. The stabi-

TABLE 1

FORMATION CONSTANTS FOR Cu BINARY COMPLEXES

Ligand	log β_1	log β_2
Pyridoxine	1.7	2.70
Aspartate	8.5	15.50
Isoleucinate	8.3	15.30
Glycinate	8.4	15.25
Glutamate	8.2	15.10
Valinate	8.0	14.90

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TABLE 2

STABILITY CONSTANTS OF MIXED - LIGAND COMPLEXES OF Cu(II) WITH AMINO ACIDS AND PYRIDOXINATE

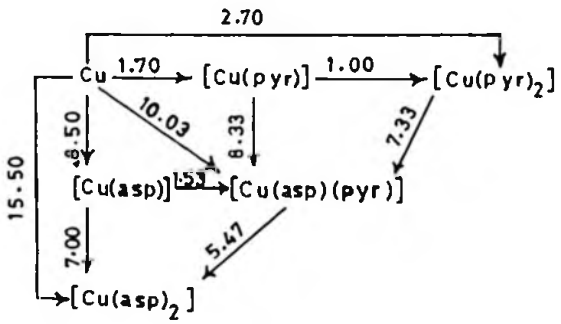
System	log B_{11}
Cu-asp-pyr	10.03
Cu-iso-pyr	9.90
Cu-gly-pyr	9.82
Cu-glu-pyr	9.79
Cu-val-pyr	9.65

lity constant equilibria are summarized in the Schemes (I-V).

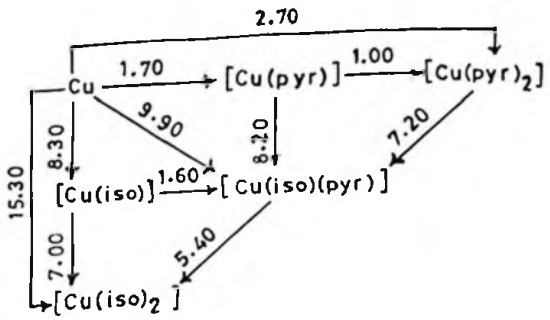
A number of interesting observations can be made. The tendency to add a given ligand X to CuX and to CuY (where X is pyridoxinate and Y is aspartate, isoleucinate, glycinate, glutamate and valinate) can be compared. The log K values are (1.00, 1.53) (1.00, 1.60) (1.00, 1.42) (1.00, 1.59) (1.00, 1.65) respectively. Because the statistical factor is only 2 in favour of the mixed complex, the largest part of the difference in log K must be attributed to entropy effects which would favour the formation of complex. The corresponding tendency to add Y to Cu(X) and to Cu(Y) can also be compared. The log K values (8.33, 7.00) (8.20, 7.00) (8.12, 6.75) (8.09, 6.90) and (7.95, 6.90) for all systems respectively, show that the formation of the mixed complex is favoured by an amount corresponding to that predicted by the statistical factor.

For comparing the stabilities of simple and mixed complexes. One should measure, the disproportionation constant (K^D) for the equilibrium.

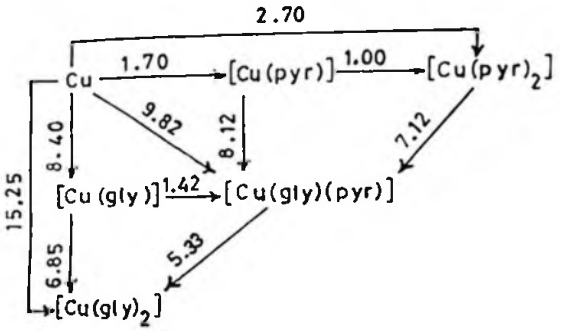
$$2\ Cu(XY) \rightleftharpoons Cu(X)_2 + Cu(Y)_2$$



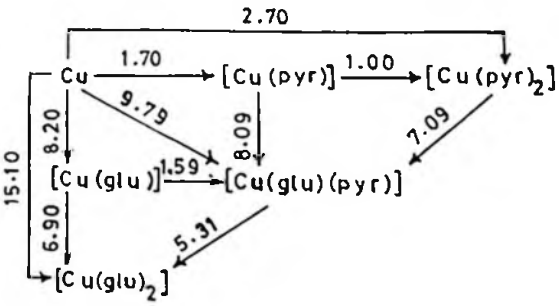
Scheme I. Copper-aspartate-pyridoxinate System



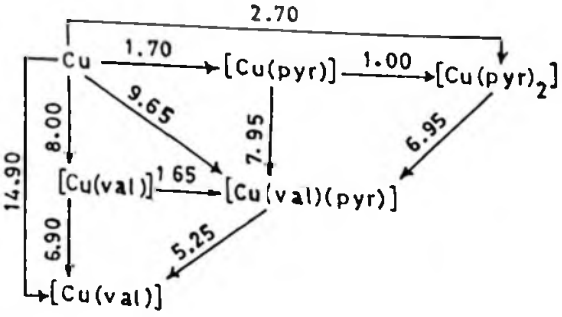
Scheme II. Copper-isoleucinate-pyridoxinate System



Scheme III. Copper-glycinate-pyridoxinate System



Scheme IV. Copper-glutamate-pyridoxinate System



Scheme V. Copper-valinate-pyridoxinate System

The value of log K^D is -0.6 statistically but the observed values are found to be -1.83, -1.80, -1.70, -1.78, and -1.70, for copper-aspartate-pyridoxinate, copper-isoleucinate-pyridoxinate, copper-glycinate-pyridoxinate, copper-glutamate-pyridoxinate and copper-valinate-pyridoxinate respectively. Log K^D for each equilibria, show that mixed ligand complex formation is affected by some other factors such as steric and electrostatic effects.

REFERENCES

1. O. Manousek, P. Zuman, *Colln. Czech. Chem. Commun.* **29(6))**, (1964). 1432.
2. P.A. Pella, W.C. Purdy, *J. Electroanal. Chem.*, **10(1)**, (1965) 51.
3. S.K. Shah, C.M. Gupta, *Talanta*, **27** (1980) 455.
4. C.P.S. Chandel, C.M. Gupta, *Chemica Scripta*, **20** (1982) 229.
5. Rajani Kumari, C.P.S. Chandel, C.M. Gupta *Bull. Chem. Soc. Japan*, 58,(1985) 721.
6. C.M. Rajani, C.P.S Chandel, Gupta, *J. Electrochem. Soc. India*. 35-1, (1986) 61.
7. D.D. DeFord, D.N. Hume, *J. Amer. Chem. Soc.*, **73**, (1951) 5321.
8. A. Albert and E.P. Serjeant, *The Determination of Ionization Constants*, (Chapman and Hall, London) 1971.
9. W.B. Schaap, D.L. McMasters, *J. Amer. Chem. Soc.*, **83**, (1961) 4699.
10. I. Ledin, *Z. Phys. Chem.*, **188A** (1941) 160.

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