Mixed Ligand Complexes of Copper(II) with π-Donor Ligands & Amino Acids

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Mixed ligand complexes of copper(II) with biguanides (HBG) and O-alkyl-1-amidinourea (HAAU) and amino acids (alanine and glycine) have been characterized on the basis of spectroscopic, polarographic and X-ray powder diffraction studies. The complexes have pseudooctahedral geometry and are monoclinic. The $E_{1/2}$ values of the complexes are less than those of the parent (HBG) and (HAAU) complexes of Cu(II).

Abbott and coworkers[1] have studied a series of copper(II) mixed ligand complexes with amino acids and imidazole. However, very few complexes of this type with N,N-donor, π-basic ligands such as biguanides (HBG) and O-alkyl-1-amidinourea (HAAU) have been reported. Dassarama and Ray[2] reported the synthesis of mixed ligand complexes of HBG and HAAU with amino acids such as glycine and alanine. Polarographic investigation of copper(II) and nickel(II) with these ligands was the subject of two papers published from our laboratory[3,4]. We report in this note the results of polarographic, spectroscopic, thermal and X-ray powder diffraction studies on the mixed ligand complexes of Cu(II) with amino acids (alanine and glycine) and HBG and HAAU.

The complexes were prepared and purified as given in the literature[2]. For polarographic investigation an LP-7 polarograph with EZ-7 line recorder was used. SCE was the reference electrode, connected by an agar-agar KCl-salt bridge. The capillary characteristics were 2.19 $mg^{2/3}s^{1/2}$ in open circuit in $1M$ KCl and 0.01% gelatin. Aqueous solutions of KCl ($2M$) and gelatin were used as supporting electrolyte and maxima suppressor respectively. The test solutions in doubly distilled water were completely deaerated by passing purified nitrogen. The thermal analyses was carried on a derivatograph system (Paulik, Paulik and Erdey). The X-ray diffraction pattern was obtained using a Deby-Scherrer camera.

The IR spectra of Cu(II) chelates of HBG and HAAU exhibit νNH_2 and νNH in the range 3200-3400 cm^{-1} (see ref. 5). This band undergoes a red shift in the mixed ligand complexes and appears as a broad band in the region 3100-3350 cm^{-1}, probably arising due to the presence of structurally different NH_2 and NH groups of comparable vibrational energies. A strong absorption band in the region $\simeq 1625\ cm^{-1}$ is attributed to $\nu_{as}\ COO^-$ (ref. 6). The band $\simeq 1535\ cm^{-1}$ is attributed to $\nu N \cdots C \cdots N$. The νCOO^- overlaps the $\nu C = N$ of the HBG and HAAU complexes[5]. The sharp peaks around 1000, 900 and 875 cm^{-1} may be due to the wagging rocking and twisting modes of water respectively. A weak peak at $\simeq 750$ and a sharp one at $\simeq 720\ cm^{-1}$ may be attributed to the $-NH$ wagging modes of vibration.

The electronic spectral band $\simeq 570$ nm in the mixed ligand complexes shows a red shift from those of HBG and HAAU ($\simeq 520$ nm) as expected for a distorted octahedral configuration. A new band at $\simeq 350$ nm has been attributed to charge transfer. However, there is no appreciable change in the position of the band at 250 nm assigned to π-π* transition in HBG and HAAU[7].

The thermogravimetric analyses of the mixed ligand complexes show an endothermic reaction at $\simeq 135°C$, the loss in mass corresponding to the loss of two molecules of water. Probably the water molecules are loosely coordinated to the metal ion. On exposing the complexes in air they again absorb two molecules of water. At around 245°C the amino acid part of the complexes starts decomposing with the evolution of N_2, CO_2 and H_2O. After this temperature, formation of a stable product continues upto 360°C, which finally decomposes to give CuO. These results show that the mixed ligand complexes are thermally less stable than the corresponding bis-biguanide and bis-O-alkyl-1-amidinourea copper(II) complexes[8].

All the complexes show one well-defined polarographic wave with $E_{1/2}$ around -0.4 V (Fig. 1). They are found to be diffusion-controlled, as revealed by the straight line plots of diffusion current versus concentration and $\sqrt{h_{eff}}$. Plots of log $i_E/i_d - i_E$ versus E_{dme} are linear with slopes showing the reversible nature of the waves. Polarographic studies have been carried out with complexes prepared *in situ* using different proportions of $CuCl_2$, [Cubis(ligand)]$Cl_2.2H_2O$, and free amino acids. As has been reported[3,4], polarogram of bis(HBG) copper(II) chloride dihydrate shows two distinct waves, the smaller first wave corresponding to the hydrolysed product of monoligand copper(II) complex (Eq. 1).

$$Cu(HBG)_2Cl_2 + 2H_2O = [Cu(HBG)(H_2O)_2]Cl_2 + HBG \qquad ...(1)$$
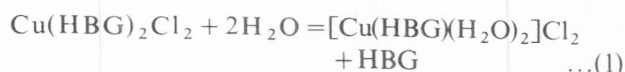
The half-wave potential of this system (Eq. 1) is around -0.15 V. Addition of $CuCl_2$ to the bis-

Table 1—Stability Constants of Mixed Ligand Complexes of Cu(II) with HBG and HAAU and Amino Acids

	$E_{1/2}$	j	$\log K_{\text{instab}}$
Cu(HBG)$_2$Cl$_2$ + Alanine	−0.43	2.1	6.37
Cu(HBG)$_2$Cl$_2$ + Glycine	−0.40	2.3	7.94
Cu(MeHAAU)$_2$Cl$_2$ + Alanine	−0.36	2.0	8.51
Cu(MeHAAU)$_2$Cl$_2$ + Glycine	−0.32	2.0	8.92

complex increases the height of the first wave at the expense of the second wave which completely disappears at a Cu(HBG)$_2$Cl$_2$:CuCl$_2$ ratio of 1:1.5. The addition of CuCl$_2$ in fact produces mono-ligand complexes in accordance with Eq.(2).

$$[Cu(HBG)_2]Cl_2 + CuCl_2 + H_2O$$
$$\rightleftharpoons 2[Cu(HBG)Cl.H_2O]Cl \qquad \ldots(2)$$

The half-wave potential of this system (Eq. 2) is around −0.2 V, which is almost identical to the $E_{1/2}$ values of the first wave due to bis(ligand) copper(II) complexes. On adding different amounts of amino acids, viz. glycine and alanine to the above system (Eq. 2), keeping [Cu(HBG)$_2$]Cl$_2$:CuCl$_2$ ratio at 1:1.5, a second wave appears in addition to the existing one. With increase in the concentration of the amino acids, the height of the second wave increases at the cost of the first and attains a definite height at [Cu(HBG)Cl.H$_2$O]Cl: amino acid ratio of 1:1.5, beyond which further addition of amino acid has no effect on the polarograms. From the difference in $E_{1/2}$ at two concentrations we have

$$\Delta E_{1/2} = -p\frac{0.059}{n} \times \Delta \log[\text{amino acid}]$$

Thus from the slope of $\Delta \log$ [amino acid] versus $E_{1/2}$ plot we get a value of $p \sim 2$, showing that only one amino acid molecule is taking part in the reaction satisfying two coordination numbers.

The half-wave potentials of these waves are between −0.3 V and −0.4 V depending on the nature of the amino acid (see Table 1). That these waves are different from those due to simple copper amino acid complexes has been verified by recording polarograms of CuCl$_2$ with varying amounts of amino acid. It has also been observed that addition of free amino acid to the solution of bis(ligand) complexes does not form mixed ligand complexes as the polarograms show no appreciable change (Fig. 1). This is probably due to the fact that bis(ligand) copper(II) complexes being very stable with $E_{1/2}$ values −0.56 V, it is impossible on the part of an amino acid to replace one biguanide molecule in the complex.

The stability constants of these complexes have been calculated using the equation

$$(E_{1/2})_{\text{Cu(HBG)(AA)Cl}} - (E_{1/2})_{\text{Cu(HBG)H}_2\text{OCl}}$$

$$= -\frac{0.059}{n}\log K_{\text{instab}} - p\frac{0.059}{n}\log(\text{AA}).$$

These values are recorded in Table 1. As has been observed for bis(HBG) copper(II) and bis(HAAU) copper(II) complexes[3,4] the HBG mixed ligands are more stable than the HAAU complexes. Also the alanine complexes are more stable than the glycine complexes.

Since good single crystals could not be obtained, no detailed X-ray studies could be undertaken. However, X-ray powder diffraction photographs of [Cu−(HBG)(Gly)]Cl 1.5 H$_2$O, have been taken and indexed by Ito's method. The values of the repeat distances obtained are a = 4.50, b = 3.95 and c = 3.60. Hence the complexes have monoclinic structure.
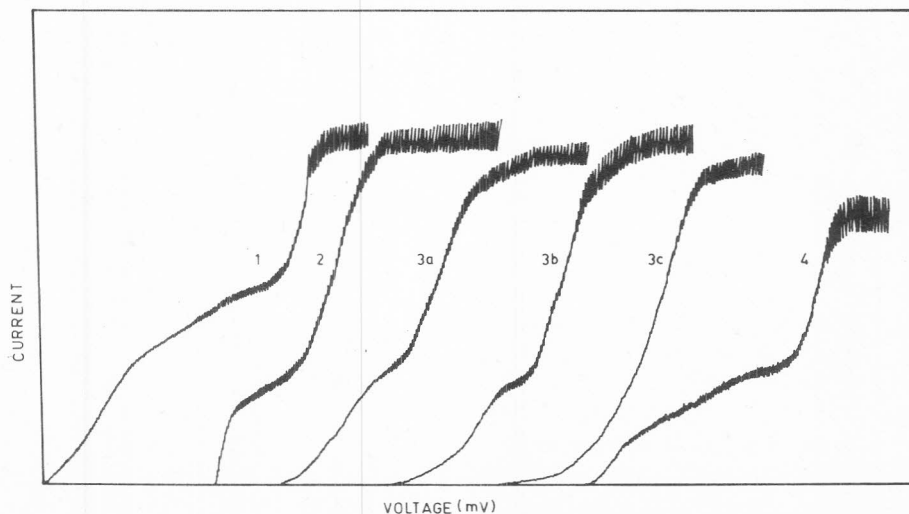

Fig. 1—Polarograms of (1) Cu(HBG)$_2^{2+}$ (2) Cu(HBG)$_2^{2+}$ + CuCl$_2$ (1:1) (3) Cu(HBG)$_2^{2+}$ + CuCl$_2$ (4) Cu(HBG)$_2^{2+}$ + alanine (1:1) + alanine {(a) 1:1:0.5; (b), 1:1:1; (c), 1:1:1.5}

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