

nation ( $\text{NH}_2$ ,  $\text{N}^-$ ,  $\text{N}^-$ ) and  $\text{CuH}_3\text{L}$  to NNNN co-ordination ( $\text{NH}_2$ ,  $\text{N}^-$ ,  $\text{N}^-$ ,  $\text{N}^-$ ).

Comparison of the formation constants of  $\text{CuH}_1\text{L}$  and  $\text{CuH}_2\text{L}$  complexes (Table I) with those of the comparable species in the Cu(II) — tetraglycine system shows the influence of Asp-2 in the system studied. For example the  $\text{CuH}_1\text{L}$  complex ( $\log \beta = 2.28$ ) is significantly more stable than with tetraglycine ( $\log \beta = -0.4$ , ref. [1]). This comparison indicates clearly the involvement of  $\text{COO}^-$  of the Asp-2 residue in metal ion binding. The formation of the additional chelate ring when  $\text{COO}^-$  is bound to the Cu(II) ion in this NN species leads to the creation of a very stable complex with a maximum concentration reaching 100% around pH 7 (see Fig. 1).

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## THERMODYNAMIC AND SPECTROSCOPIC STUDY OF METAL COMPLEX FORMATION WITH CYCLOPEPTIDES: Cu(II)- AND Zn(II)-CYCLO-L-HISTIDYL-L-HISTIDYL

Cyclic peptides can be very useful models for the study of protein-metal ion interactions. Cyclic peptides have the advantage over linear peptides

that no free terminal amino and carboxylate groups are present to bind to the cation. Thus, cyclopeptide complexes of metal ions represent simple model compounds for the study of metal ion interaction with amido groups and side chains in proteins and polypeptides.

We have investigated copper(II) and zinc(II) complexation with cyclo-L-histidyl-L-histidyl (cyhis). Our interest in this type of ligand is well justified in light of work reported previously in the literature. LANGEBECK *et al.* [1] found that cyhis catalyzes the oxidation of DOPA and that the addition of Cu(II) to the reaction system accelerates the oxidation. HORI *et al.* [2] have obtained the crystal structure of  $\text{Cu}(\text{cyhis})_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  by X-ray crystallography. On this basis it was proposed that cyhis may be a good model for elucidating interactions between metal ions and the imidazole group of the histidine residue of some enzymes.

In light of the problems associated with extrapolating solid state properties to solution species, we began an investigation of the coordination chemistry of the title ligand in aqueous solution. Specifically, we determined by potentiometric titration the stability constants of the species formed between the ligand and either copper(II) or zinc(II). The species  $\text{M}(\text{cyhis})_2^{2+}$  was present in the pH range 4.0 to 5.5 and was the principal complex species observed.

The ligand protonation constants determined potentiometrically were 6.53 and 5.49, for  $\log K_1$  and  $\log K_2$  respectively, at 25°C and  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ ).

Calorimetric measurements were also carried out to determine  $\Delta H$  and  $\Delta S$  values for the formation of the metal complexes. These data helped in ascertaining whether or not the imidazole nitrogen is involved in the complexation process.

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### STRUCTURAL INVESTIGATIONS OF MAGNESIUM- AND COPPER(II)- -HYDROGENURATES

Uric acid, uric acid dihydrate, sodium hydrogenurate monohydrate and ammonium hydrogenurate occur as crystalline solids in human urinary calculi. Sodium hydrogenurate monohydrate microcrystals in addition are the cause (or a consequence?) of gouty arthritis. Beside these well known facts some chemical but no structural information is available about the interaction of uric acid with bio-metals, e.g. Ca, Mg, Fe, Co, Cu or Zn.

We have grown single crystals of two different phases of  $\text{Mg}(\text{hydrogenurate})_2 \cdot 8\text{H}_2\text{O}$  and of  $\text{Cu}(\text{hydrogenurate})_2 \cdot 6\text{H}_2\text{O}$ , determined their crystal structures and investigated the thermal decomposition of the compounds with different methods of thermal analysis. Relevant crystal data are:  $\text{Mg}(\text{C}_5\text{H}_3\text{N}_4\text{O}_3)_2 \cdot 8\text{H}_2\text{O}$  phase I,  $a = 9.573(2)$ ,  $b = 14.627(3)$ ,  $c = 7.170(1)$  Å,  $\beta = 101.91(1)^\circ$ , space group  $P 2_1/c$ ;  $\text{Mg}(\text{C}_5\text{H}_3\text{N}_4\text{O}_3)_2 \cdot 8\text{H}_2\text{O}$  phase II,  $a = 10.397(2)$ ,  $b = 14.306(3)$ ,  $c = 6.732(1)$  Å,  $\beta = 104.64(2)^\circ$ , space group  $P 2_1/c$ ;  $\text{Cu}(\text{C}_5\text{H}_3\text{N}_4\text{O}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $a = 6.929(4)$ ,  $b = 18.229(4)$ ,  $c = 14.559(5)$  Å,  $\beta = 102.70(3)^\circ$ , space group  $P 2_1/n$ .

The structures of both phases of  $\text{Mg}(\text{C}_5\text{H}_3\text{N}_4\text{O}_3)_2 \cdot 8\text{H}_2\text{O}$  contain isolated, slightly distorted octahedral  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  cations, hydrogenurate anions and two molecules of water of crystallization per formula unit. A structural formula representing these facts is

$[\text{Mg}(\text{H}_2\text{O})_6](\text{hydrogenurate})_2 \cdot 2\text{H}_2\text{O}$ . No bonding interaction between magnesium and hydrogenurate is observed. According to literature data the first deprotonation site of uric acid in solution should be N(9). The hydrogenurate phases described here however are deprotonated at N(3) (the positions of the hydrogen atoms could be located in difference fourier maps). Differences in details of the geometry between the hydrogenurate anion and uric acid may be described in terms of three additional resonance structures distributing the formal negative charge at N(3) within the pyrimidine (but not the imidazole) ring of uric acid. In both phases pairs of hydrogen-bonding of the type N(1)-H(1)...O(8) and O(6)...H(9)-N(9) result in infinite chains of hydrogenurate molecules along the b-axis of the cell.

$\text{Cu}(\text{hydrogenurate})_2 \cdot 6\text{H}_2\text{O}$  represents the first example of a hydrogenurate d-metal complex as evidenced by its crystal structure analysis. Deprotonation of uric acid has occurred at N(9), and copper exhibits a distorted square-pyramidal coordination by two N(9) atoms of hydrogenurate and three water molecules. There are three additional molecules of water of crystallization per formula unit. The hydrogen-bonding scheme is different from that of the magnesium salts and is dominated by pairs of the type N(1)-H(1)...O(8) and O(2)...H(7)-N(7).