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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).



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MOLYBDENUM(VI) COMPLEXES OF (R)-CYSTEINE IN AQUEOUS SOLUTION

Complex formation between molybdate ions and (R)-cysteine has been studied, in aqueous solution, over a range of concentrations and pH, at 298K and $I=1 \text{ mol dm}^{-3}$ (NaCl), using UV, CD and NMR techniques. One main species is evident for $\text{pH} > 6.5$, in which cysteine is bonded as a tridentate ligand to Mo(VI), forming a 1:1 complex. This compound has a formation constant $\log K_f = 18.23 \pm 0.12$, determined by CD measurements. In solutions with pH values between 4.5 and 6.5, apart from this complex, there is evidence for at least three other species.

INTRODUCTION

Complexes of molybdenum(VI) with (R)-cysteine have been studied by a number of authors [1-5], as possible models for molybdenum-containing enzymes.

An early report [1], based on spectrophotometric studies, claimed the formation of complexes where ligand:Mo(VI) ratio varies from 3:1 to 1:1, in aqueous solutions, at pH values between 4.6 and 6.5. Conflicting results about the nature of the species formed and the pH region adequate for their study, have been subsequently reported [4,5]. Circular dichroism proved to be a very informative technique and was used over a wide pH range (4.5-9.5), with varying metal and ligand concentrations. A number of UV and NMR experiments linked our work with previous studies. We found

that redox chemistry, although being important in all conditions in which this and previous work have been carried out, has not been properly considered in previous studies.

At pH values higher than 6.5, a single complex, with Mo(VI):cysteine ratio equal to 1:1, has been identified and its formation constant determined. This species, and at least a second complex of Mo(VI), is present at lower pH values. However, in more acidic solutions (pH between 4.5 and 6.5) reduction of Mo(VI) is much faster, resulting in the formation of the known compound $[\text{Mo}_2\text{V}_2\text{O}_4(\text{cys})_2]^{2-}$.

RESULTS AND DISCUSSION

SPENCE and CHANG [1] have studied the complexes formed over a pH range from 4 to 6. Using Job's method of continuous variation they have suggested the formation of species where ligand:metal ratio varies from 3:1 to 1:1 and have estimated the formation constant for the first complex. We have used the same method for studying the species present in solutions with pH varying from 6.4 to 8.5 and concentrations of Mo(VI) and cysteine similar to those used by Spence and Chang. Some of the results are shown in Fig. 1. The molar ratios corresponding to the maxima of the curves vary with pH, total concentration and wavelength chosen. These results could be inter-

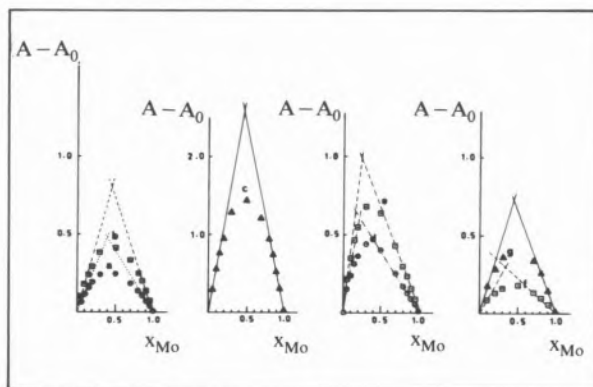


Fig. 1

Job's plots of absorbances for solutions of sodium molybdate and (R)-cysteine where

- $C_{\text{Mo}} + C_{\text{cys}} = 0.04 \text{ mol dm}^{-3}$, $\text{pH} = 8.5$, $l = 10 \text{ mm}$, and
(a) $\lambda = 370 \text{ nm}$, (b) $\lambda = 360 \text{ nm}$, (c) $\lambda = 340 \text{ nm}$;
- $C_{\text{Mo}} + C_{\text{cys}} = 0.04 \text{ mol dm}^{-3}$, $\text{pH} = 6.4$, $l = 5 \text{ mm}$, and
(d) $\lambda = 380 \text{ nm}$, (e) $\lambda = 360 \text{ nm}$;
- $C_{\text{Mo}} + C_{\text{cys}} = 0.016 \text{ mol dm}^{-3}$, $\text{pH} = 6.4$, $l = 5 \text{ mm}$,
(f) $\lambda = 360 \text{ nm}$, (g) $\lambda = 340 \text{ nm}$