PS5.38 — TH

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CALCIUM BINDING TO METHYLMALONATE ION

In an endeavor to model the binding of calcium(II) ions to γ-carboxyglutamic acid (gla) residues, we have determined the crystal and molecular structure of the calcium(II) complex of methylmalonic acid, which is an excellent structural model for the functional groups at the γ-carbon center of gla. The complex crystallizes as a hydrate of formulation $Ca_3(Memal)_3.4H_2O$, where Memal is the methylmalonato dianion, $C_4H_4O_4^{2-}$. The complex crystallizes in the monoclinic space group C2/c with four formula units in a cell of dimensions $a = 16.886$ (7), $b = 18.959$ (10), $c = 6.640$ (8) Å, $\beta = 90.76$ (8)°. The structure contains two independent and distinct types of calcium atom. One calcium atom is eight-coordinate, binding to two water molecules and to six carboxylate oxygen atoms; the only chelation at this center involves oxygen atoms from a single carboxylate group. The other calcium atom is seven-coordinate, coordinating to one water molecule and six carboxylate oxygen atoms. In this case, however, one of the two chelates is formed by atoms from the two different carboxylate groups of a single methylmalonato ion; this type of chelation is not available to glutamic or aspartic acid residues, but is available to gla residues and may be significant in the binding of calcium to gla-containing proteins.

PS5.39 — MO

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MULTINUCLEAR NMR STUDIES OF VANADIUM(V) COMPLEXES WITH LACTIC AND MALIC ACIDS

Complexation of vanadium(V) with lactic and malic acids, in aqueous solution, is being investigated using ^1H, ^{13}C and ^{51}V NMR spectroscopy [1].
Two main complexes are formed in each case, with relative concentrations depending on pH and on ionic strength. The vanadium-lactic acid complexes have 1:2 and 1:1 composition, the acid acting as a bidentate ligand in both. The two dominant vanadium-malic acid complexes have a 1:1 stoichiometry, the ligand being bidentate in one (involving the OH and the α carboxyl group) and terdentate in the other (involving also the other carboxyl group). These latter results are established on the basis of the ^{13}C shifts and the vicinal HH coupling constants observed on complexation:

	HO_2C-CH_2-CH(OH)-CO_2H (A,B)		(X)		J_{AX}	J_{BX}
a. Bidentate	0.4	0.4	6.1	5.8 ppm	4.2	9.8 Hz
b. Terdentate	4.6	2.0	10.0	6.0	1.9	4.9

An attempt is made to interpret the vanadium shifts observed on complexation.
Formation constants are being estimated and exchange and metal reduction phenomena investigated.

REFERENCE

[1] For similar studies see M. MADALENA CALDEIRA, VICTOR M.S. GIL, *Can. J. Chem.*, **62**, 2094-2100 (1984), and references therein.

PS5.40 — TU

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SPECTROSCOPIC AND POTENTIOMETRIC STUDIES OF COPPER(II) COMPLEXES OF D-GLUCOSAMINE

Because of the involvement in many bioinorganic systems, the interaction of metal ions with simple amino sugars such as D-glucosamine has been studied [1,2], but no precise description of the complexes is really available. We have investigated the Cu(II)-D-glucosamine system in aqueous solution by using spectroscopic (ESR, absorption and CD) and potentiometric techniques.

According to the potentiometric results, five distinct complex species are formed over the pH range 5-9.5 (Table I).

The CuL_2 complex, the major species around pH 7 (~55% at pH 6.9), is easily distinguished by spectral measurements. Indeed, the *d-d* absorption maximum (660 nm, $\epsilon = 44$), the ESR parameters ($g_{\parallel} = 2.317$, $A_{\parallel} = 175 \times 10^{-4}$ cm^{-1}) and the CD data (640 nm, $\Delta\epsilon = +0.06$) strongly support the involvement of two nitrogen atoms in metal coordination [3-4].

Above pH 7 two other complexes, namely

Table I

Logarithm of stability constants (log β_{pqr}) of complex species $M_pH_qL_r$ (M = Cu(II), L = D-glucosamine) in 0.15 M NaCl at 25°C

p	q	r	log β_{pqr}
0	1	1	7.70
1	0	1	3.06
1	0	2 (CuL_2)	8.76
1	−1	2	0.83
1	−2	2 ($CuH_{-2}L_2$)	−5.82
1	−3	2	−15.08

$CuH_{-1}L_2$ (~10% at pH 7.4) and $CuH_{-2}L_2$ (~90% at pH 8.1), are formed. The minor species, $CuH_{-1}L_2$, which is not shown by any used spectroscopic technique, results from the deprotonation of one of the hydroxyl groups of a glucosamine ligand and, thereby, involves a chelate (*N,O*) ring. The $CuH_{-2}L_2$ species ($\lambda_{max} = 620$ nm, $g_{\parallel} = 2.255$, $A_{\parallel} = 196 \times 10^{-4}$ cm^{-1}) involves two chelate (*N,O*) rings because of the coordination of two amino groups and two deprotonated hydroxyls. The formation of $CuH_{-2}L_2$ gives rise to strong negative CD effects centered around 730 nm ($\Delta\epsilon = -0.15$).

Positive Cotton effects, attributable to $NH_2 \rightarrow Cu(II)$ charge transfer transitions, are observed in the UV region (CuL_2: 315 nm, $\Delta\epsilon = +0.6$; $CuH_{-2}L_2$ at pH ~8: 300 nm, $\Delta\epsilon = +2.2$).

The formation of $CuH_{-3}L_2$, which predominates above pH 10, does not result in any distinguishable variation of absorption or ESR spectra.

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