



PS5.38 — TH

MARIA E. CURRY
DEREK J. HODGSON

Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514
U.S.A.

DRAKE S. EGGLESTON

Smith Kline & French Laboratories
P.O. Box 7929, Philadelphia, PA 19101
U.S.A.

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 $\text{Ca}_3(\text{Memal})_3 \cdot 4\text{H}_2\text{O}$, where Memal is the methylmalonato dianion, $\text{C}_4\text{H}_4\text{O}_4^{2-}$. 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

M. MADALENA CALDEIRA

NUNO OLIVEIRA

VICTOR M.S. GIL

CARLOS F.G. GERALDES

Department of Chemistry
University of Coimbra
Portugal

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:

	$\text{HO}_2\text{C}-\text{CH}_2-\text{CH}(\text{OH})-\text{CO}_2\text{H}$				J_{AX}	J_{BX}
	(A,B)	(X)				
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.