

Studies of Carboxylate-Metal Ion Binding: Crystal Structure of Malonatodiaquacalcium(II)

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The crystal structure of malonatodiaquacalcium(II), $[\text{Ca}(\text{C}_3\text{H}_2\text{O}_4)(\text{H}_2\text{O})_2]$, has been determined from three-dimensional single-crystal x-ray diffraction data collected by counter methods on a computer-automated diffractometer. The structure was refined by a full-matrix least-squares procedure to a conventional R index of 0.029 for 748 reflections. The space group is C_2^3-C2 with unit cell dimensions $a = 13.955(13)$ Å, $b = 6.855(8)$ Å, $c = 6.835(5)$ Å, and $Z = 4$. The coordination polyhedron around the Ca(II) is that of a bicapped trigonal prism formed from six carboxylate oxygen atoms from four different malonate ligands and two water molecules. The two malonate carboxylate groups coordinate in different manners. One carboxylate group binds three different Ca(II) ions forming a four-membered chelate ring with one Ca(II) and unidentate bridge linkages to two other Ca(II) ions. The other carboxylate group chelates a lone Ca(II) ion. The crystal structure is highly polymeric because of the bridging. The structure and malonate conformation are compared with the structures of other metal-malonate compounds.

Introduction

Malonate ion, $^-\text{OOCCH}_2\text{COO}^-$, although a simple dicarboxylate ligand, exhibits a rather flexible stereochemistry and variable mode of binding with metal ions in the crystalline state. For example, in $\text{Eu}_2(\text{C}_3\text{H}_2\text{O}_4)_3 \cdot 8\text{H}_2\text{O}$ there are three different europium(III)-malonate stereochemistries involving both four- and six-membered malonate chelate rings as well as extensive bridging.¹ Still different modes of metal ion binding by malonate are found in crystalline Nd(III),² Sc(III),³ Cu(II),⁴ Co(III),⁵⁻⁷ and Cr(III)⁵ derivatives.

We have been interested in the versatility^{8,9} of metal ion coordination by carboxylate ligands and, in particular, the structural characteristics of carboxylate binding of hard cations, such as Ca(II), Mg(II), Mn(II), and Zn(II) which are of utmost importance in biological systems.¹⁰ Under investigation by us have been a series of malonate derivatives of divalent cations of the type $\text{MC}_3\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, where $\text{M} = \text{Ca(II)}$, Mg(II) ,¹¹ Fe(II) ,^{12,13} and Zn(II) .¹¹ Although the empirical formula units are similar, the indicated malonates are reported to crystallize in different space groups suggesting perhaps a variation in metal ion-malonate coordination.⁸ This paper reports on the crystal structure of the calcium(II) compound which exhibits a mode of malonate-metal ion binding not previously observed.

Experimental Section

Colorless single crystals of the title compound were readily grown by evaporation of a solution prepared by dissolving calcium carbonate in an aqueous solution of malonic acid. A well-formed crystal with approximate dimensions $0.14 \times 0.17 \times 0.20$ mm which gave sharp optical extinction under crossed polarizers was mounted along the longest crystal dimension which corresponded to the b^* direction. Indexed Weissenberg photographs revealed monoclinic symmetry and the only observed systematic absences, $h + k$ odd for hkl , were consistent with space groups $C2/m$, $C2$, and Cm . The unit cell parameters were determined at ambient room temperature from a least-squares refinement of the angular settings of 12 carefully centered reflections (2θ range $15-24^\circ$) on a Picker FACS-I automated (PDP-8/L) diffractometer using Mo $K\alpha$ radiation (λ 0.71069 Å).

Crystal Data for $[\text{CaC}_3\text{H}_2\text{O}_4(\text{H}_2\text{O})_2]$: monoclinic, space group $C2$; $a = 13.955(13)$, $b = 6.855(8)$, $c = 6.835(5)$ Å; $\beta = 106.28(3)^\circ$; $V = 627.6$ Å³; $Z = 4$; $d_{\text{meas}} = 1.91(1)$ (by flotation in a mixture of CCl_4 and CH_3I), $d_{\text{calcd}} = 1.89$ g cm⁻³; mol wt = 178.16; $F(000) = 448$; $\mu(\text{Mo } K\alpha) = 9.4$ cm⁻¹.

Collection and Reduction of the Intensity Data. Three-dimensional x-ray intensity data were collected on the aforementioned diffractometer using zirconium-filtered Mo $K\alpha$ radiation. Data were collected for the quadrants $h, k \geq 0, \pm l$ in the range $0 < 2\theta \leq 55^\circ$ using the $\theta-2\theta$ scan technique. A $1^\circ/\text{min}$ scan rate and a scan range of $2\theta(\text{Mo } K\alpha_1) - 1.0^\circ$ to $2\theta(\text{Mo } K\alpha_2) + 1.0^\circ$ was used. Stationary crystal, stationary counter background counts were measured for 20 s at each

end of the scan. During the data collection the intensities of two standard reflections were monitored after every 50 measurements. Their intensities showed no significant variation which indicated little electronic or crystal instability during the data collection. No absorption corrections were applied in view of the small absorption coefficient and dimensions of the crystal. As a check on possible variations in transmission factors, the intensity of the 020 reflection was measured at $\chi = 90^\circ$ over a 360° range of ϕ angles; no significant difference in intensity (<4%) was noted suggesting that absorption effects could be ignored. The raw intensity data were assigned estimated standard deviations and reduced to values of F_o and $\sigma(F_o)$ in the manner previously described.¹⁴ A total of 748 reflections had $I > \sigma(I)$ and these were used in subsequent calculations.

Structure Determination and Refinement.¹⁵ The structure was solved by the application of heavy-atom techniques. The space group $C2$ was initially assumed and was subsequently confirmed by successful refinement of the structure. The x and z coordinates of the calcium ion were determined from the three-dimensional Patterson map, and the y coordinate was fixed to be 0.0 in order to specify the origin in space group $C2$. The carbon and oxygen atoms were found from a succession of difference Fourier synthesis which were phased by the atoms already located. After initial isotropic then anisotropic refinement of the nonhydrogen atoms by a full-matrix procedure, a difference Fourier synthesis revealed the positions of all hydrogen atoms. Each hydrogen atom was assigned an isotropic temperature factor of 5.0 Å². The entire structure was further refined by full-matrix least squares although the hydrogen atom parameters were not varied. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight, w , applied to each observation was taken to be $[\sigma(F_o)]^{-2}$. The structure refinement¹⁶ converged to a conventional R_1 index, $\sum ||F_o| - |F_c|| / \sum |F_o|$, of 0.029 and a weighted R_2 index, $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, of 0.041. The standard deviation of an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, was 1.81, where the number of observations (m) was 748 and the number of variable parameters (n) was 90 yielding a data:parameter ratio of 8.3:1. An analysis of the function $w(|F_o| - |F_c|)^2$ vs. $|F_o|$ or $(\sin \theta) / \lambda$ revealed no dependence on these quantities suggesting a reasonably chosen weighting scheme. The comparison of final $|F_o|$ and $|F_c|$ values for strong low-angle reflections showed no evidence for secondary extinction. A final three-dimensional Fourier difference map showed no residual electron density greater than 0.25 e Å⁻³ or less than -0.45 e Å⁻³. The neutral scattering factors for the nonhydrogen atoms were taken from Cromer and Mann^{17a} and included corrections for the real and imaginary anomalous dispersion^{17b} of the calcium ion. The hydrogen scattering factors were taken from Stewart, Davidson, and Simpson.¹⁸ A listing of the final observed and calculated structure factors as $10|F_o|$ and $10|F_c|$ is available.¹⁹ Final positional and thermal parameters are presented in Table I.

Description and Discussion of the Structure

A view of a portion of the polymeric structure showing the coordination polyhedron about the Ca(II) ion and the atom-numbering scheme is presented in Figure 1. Interatomic

Table I. Positional^a and Thermal Parameters^{b,c} for $[\text{Ca}(\text{C}_3\text{H}_2\text{O}_4)(\text{H}_2\text{O})_2] (\times 10^4)$

| Atom | x | y | z | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|------|------------|-----------|------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Ca | 2227.1 (3) | 0 | 1231.7 (6) | 26.5 (3) | 62 (1) | 83 (1) | -2 (1) | 20.2 (4) | -6 (2) |
| O(1) | 3211 (4) | 1611 (8) | -899 (8) | 51 (4) | 73 (9) | 193 (15) | 24 (5) | 63 (6) | -5 (10) |
| O(2) | 3246 (4) | -1587 (7) | -916 (7) | 44 (4) | 69 (10) | 141 (13) | -3 (4) | 44 (6) | -30 (9) |
| O(3) | 3506 (4) | 1587 (9) | -5861 (8) | 50 (4) | 126 (11) | 144 (13) | 22 (5) | 6 (5) | 25 (10) |
| O(4) | 3536 (4) | -1609 (7) | -5812 (6) | 50 (3) | 51 (8) | 80 (10) | 22 (4) | 13 (4) | -0 (7) |
| O(5) | 1243 (1) | -32 (9) | 3616 (3) | 37.4 (9) | 78 (4) | 123 (4) | 11 (6) | 32 (2) | -8 (11) |
| O(6) | 869 (2) | 88 (16) | -1799 (4) | 38 (1) | 486 (14) | 173 (6) | -27 (9) | 6 (2) | 122 (18) |
| C(1) | 3528 (2) | -68 (12) | -1406 (3) | 22 (1) | 55 (6) | 63 (4) | 7 (5) | 6 (2) | -30 (10) |
| C(2) | 4301 (2) | -82 (14) | -2634 (4) | 22 (1) | 90 (7) | 90 (5) | -16 (5) | 17 (2) | -2 (10) |
| C(3) | 3756 (2) | 41 (14) | -4921 (3) | 22 (1) | 89 (5) | 95 (5) | -12 (7) | 23 (2) | -14 (15) |

| Atom | x | y | z | Atom | x | y | z |
|--------|------|-------|-------|--------|------|------|-------|
| H1(C2) | 4783 | 1125 | -2209 | H2(O5) | 1366 | -977 | 4363 |
| H2(C2) | 4722 | -1372 | -2339 | H1(O6) | 520 | -750 | -1700 |
| H1(O5) | 1386 | 972 | 4373 | H2(O6) | 602 | 1003 | -1511 |

^a The estimated standard deviations in the least significant figures are given in parentheses here and in other tables. ^b The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^c Hydrogen atoms were assigned a fixed isotropic temperature factor of 5.0 \AA^2 .

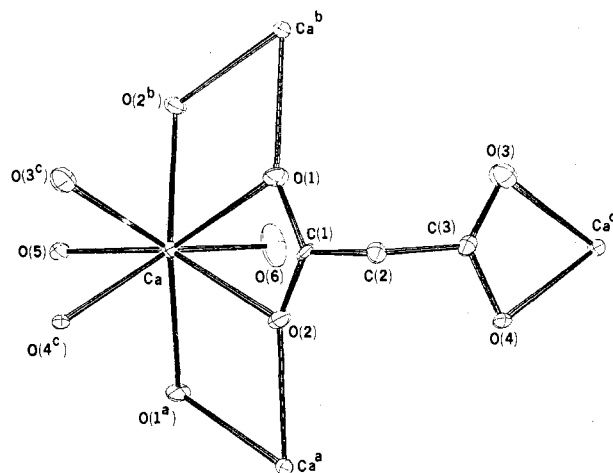


Figure 1. A view of a portion of the polymeric structure showing the metal-ligand coordination polyhedron and the atom-numbering scheme. The atoms with superscript letters are related to the corresponding atom positions given in Table I by the following symmetry transformations: (a) $x, y - 1/2, z$; (b) $x, y + 1/2, z$; (c) $x, y, z + 1$; (d) $x, y, z - 1$.

distances and angles are given in Table II. The space group $C2$ imposes no symmetry constraints on the structure which contains one $\text{CaC}_3\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the asymmetric unit. The calcium(II) ion is eight-coordinate and is bound to six oxygen atoms from four different malonate ions and two water molecules. All four oxygen atoms of a malonate ligand participate in binding $\text{Ca}(\text{II})$ ions. Each carboxylate group chelates a $\text{Ca}(\text{II})$ ion forming a four-membered ring while, in addition, oxygens O(1) and O(2) of one of the carboxylate groups each bind separate $\text{Ca}(\text{II})$ ions through monodentate bridging bonds. The crystal structure thus consists of a tightly knitted three-dimensional polymeric array as a result of cross-linking of malonato- $\text{Ca}(\text{II})$ chains by the unidentate bridge interactions. The observed bond distances and angles (Table II) for the CaO_8 polyhedron as well as the malonate ligand approach the values found previously.

The problems of identifying the type of coordination polyhedron in eight-coordinate structures have been discussed by Porai-Koshits and Aslanov,²⁰ and a formalism^{20,21} has been presented to allow unambiguous specification of the coordination polyhedron in the family of eight-atom shaped structures in terms of angular parameters, δ and ϕ . The δ angles are the dihedral angles between pairs of faces which intersect along the four edges connecting B vertices while the

Table II. Bond Distances and Angles

| Distances, \AA | | | |
|-----------------------|-----------|-------------|-----------|
| Ca-O(1) | 2.520 (6) | C(1)-C(2) | 1.541 (3) |
| Ca-O(1 ^a) | 2.397 (5) | C(2)-C(3) | 1.537 (3) |
| Ca-O(2) | 2.555 (5) | C(3)-O(3) | 1.238 (9) |
| Ca-O(2 ^b) | 2.424 (5) | C(3)-O(4) | 1.281 (9) |
| Ca-O(3 ^c) | 2.516 (6) | C(2)-H1(C2) | 1.05 |
| Ca-O(4 ^c) | 2.563 (4) | C(2)-H2(C2) | 1.05 |
| Ca-O(5) | 2.408 (2) | O(5)-H1(O5) | 0.85 |
| Ca-O(6) | 2.384 (2) | O(5)-H2(O5) | 0.81 |
| C(1)-O(1) | 1.313 (8) | O(6)-H1(O6) | 0.77 |
| C(1)-O(2) | 1.194 (8) | O(6)-H2(O6) | 0.77 |

| Angles, Deg | | | |
|--|------------|--|-----------|
| O(6)-Ca-O(1 ^a) | 79.8 (3) | O(2 ^b)-Ca-O(4 ^c) | 127.0 (2) |
| O(6)-Ca-O(5) | 97.07 (8) | O(3 ^c)-Ca-O(1) | 83.4 (2) |
| O(6)-Ca-O(2 ^b) | 76.6 (3) | O(3 ^c)-Ca-O(2) | 104.6 (2) |
| O(6)-Ca-O(3 ^c) | 152.9 (3) | O(3 ^c)-Ca-O(4 ^c) | 51.12 (7) |
| O(6)-Ca-O(1) | 85.2 (2) | O(1)-Ca-O(2) | 51.19 (6) |
| O(6)-Ca-O(2) | 86.9 (2) | O(1)-Ca-O(4 ^c) | 105.1 (2) |
| O(6)-Ca-O(4 ^c) | 155.9 (3) | O(2)-Ca-O(4 ^c) | 83.2 (2) |
| O(1 ^a)-Ca-O(5) | 82.9 (2) | O(1)-C(1)-O(2) | 121.9 (2) |
| O(1 ^a)-Ca-O(2 ^b) | 150.59 (8) | O(1)-C(1)-C(2) | 119.2 (7) |
| O(1 ^a)-Ca-O(3 ^c) | 126.8 (2) | O(2)-C(1)-C(2) | 118.9 (7) |
| O(1 ^a)-Ca-O(1) | 122.4 (2) | O(3)-C(3)-O(4) | 121.0 (2) |
| O(1 ^a)-Ca-O(2) | 72.6 (2) | O(3)-C(3)-C(2) | 124.2 (7) |
| O(1 ^a)-Ca-O(4 ^c) | 76.4 (2) | O(4)-C(3)-C(2) | 114.8 (7) |
| O(5)-Ca-O(2 ^b) | 82.9 (1) | H1(C2)-C(2)-H2(C2) | 109.1 |
| O(5)-Ca-O(3 ^c) | 83.2 (2) | H1(C2)-C(2)-C(1) | 109.6 |
| O(5)-Ca-O(1) | 154.4 (2) | H2(C2)-C(2)-C(1) | 110.0 |
| O(5)-Ca-O(2) | 154.1 (2) | H1(C2)-C(2)-C(3) | 109.4 |
| O(5)-Ca-O(4 ^c) | 83.0 (1) | H2(C2)-C(2)-C(3) | 109.4 |
| O(2 ^b)-Ca-O(3 ^c) | 76.6 (2) | H1(O5)-O(5)-H2(O5) | 106.9 |
| O(2 ^b)-Ca-O(1) | 72.8 (1) | H1(O6)-O(6)-H2(O6) | 103.3 |
| O(2 ^b)-Ca-O(2) | 122.8 (1) | | |

ϕ angles are a measure of the degree of nonplanarity of the two intersecting trapezoids. For an idealized D_{2d} dodecahedron, $\delta_1 = \delta_2 = \delta_3 = \delta_4 = 29.5^\circ$ and $\phi_1 = \phi_2 = 0^\circ$; for a C_{2v} bicapped trigonal prism, $\delta_1 = 0^\circ$, $\delta_2 = 21.8^\circ$, $\delta_3 = \delta_4 = 48.2^\circ$, and $\delta_1 = \delta_2 = 14.1^\circ$; and for a D_{4d} square antiprism, $\delta_1 = \delta_2 = 0^\circ$, $\delta_3 = \delta_4 = 52.4^\circ$, and $\phi_1 = \phi_2 = 24.5^\circ$. The observed values for the CaO_8 polyhedron in malonatodiaquacalcium(II) are $\delta_1 = 0.37^\circ$, $\delta_2 = 40.8^\circ$, $\delta_3 = 45.9^\circ$, $\delta_4 = 47.3^\circ$, $\phi_1 = 6.1^\circ$, and $\phi_2 = 10.2^\circ$. Thus, the CaO_8 coordination polyhedron is best described as being derived from a bicapped trigonal prism. This is the first reported instance of this coordination geometry for a $\text{Ca}(\text{II})$ eight-coordinate polyhedron. Another indicator of the bicapped trigonal prism geometry is the close planarity of each of the three quadrilateral faces of the trigonal prism. The pertinent mean plane information is summarized in Table III. The atoms O(1^a) and O(2^b) are "capped" over faces O(2)-O(6)-O(5)-O(4^c) and O(1)-O(6)-O(5)-O(3^c), respectively. The "uncapped"

Table III. Least-Squares Planes^a

| Atom | Deviation from plane, Å | Atom | Deviation from plane, Å |
|--|-------------------------|-----------------|-------------------------|
| Plane 1: $-0.9856X - 0.0196Y - 0.1676Z + 4.515 = 0.0$ | | | |
| O(3 ^c) | -0.003 | O(1) | -0.003 |
| O(4 ^c) | +0.003 | O(2) | +0.003 |
| Plane 2: $-0.3245X - 0.9451Y - 0.0378Z + 0.4274 = 0.0$ | | | |
| O(3 ^c) | +0.19 | O(6) | +0.17 |
| O(5) | -0.18 | O(1) | -0.19 |
| Plane 3: $-0.3265X - 0.9431Y - 0.0626Z + 0.4757 = 0.0$ | | | |
| O(4 ^c) | -0.005 | O(6) | -0.004 |
| O(5) | +0.004 | O(2) | +0.005 |
| Interplanar Dihedral Angles, Deg | | | |
| Plane 1-plane 2 | 72.1 | Plane 2-plane 3 | 38.5 |
| Plane 1-plane 3 | 69.4 | | |

^a The planes are defined in orthogonal coordinates where $X = ax + c(\cos \beta)z$; $Y = by$; $Z = c(\sin \beta)z$. All atoms in each plane were given unit weights.

face is O(1)-O(2)-O(3^c)-O(4^c) (Figure 1).

There are two kinds of four-membered rings in the structure. The first are the chelate rings formed by coordination from each end of the malonate ligand to separate Ca(II) ions. Each Ca-O-C-O chelate ring is slightly buckled with the Ca(II) ions lying -0.21 and -0.73 Å from the O(1)-C(1)-O(2) and O(3)-C(4)-O(4) carboxylate planes, respectively. This kind of coordination is a common structural characteristic in calcium carboxylates.²²⁻²⁸

The second kind of four-membered rings are the Ca-O-Ca-O rings formed as a result of the bridging structure (Figure 1). These rings are planar with a maximum atom deviation from the plane of 0.004 Å. The Ca(II)---Ca(II) distance across this ring is only 3.9852 (4) Å which compares with the Ca---Ca internuclear distance of 3.96 Å found in calcium metal^{29,30} and emphasizes the tightness of the polymeric unit packing.

The carboxylate groups in calcium malonate differ in the number of calcium(II) ions coordinated to each. Thus, one carboxylate group, C(1)-O(1)-O(2), binds three Ca(II) ions while the other C(3)-O(3)-O(4) coordinates to only one Ca(II). This unsymmetrical coordination of calcium(II) ions by dicarboxylate anion ligands is found also in the calcium(II) derivatives of fumaric,²⁶ garcinia,³¹ and terephthalic²⁵ acids. In fact, in each of the latter, Ca(II) binding occurs through only one of the two available carboxylate groups. Examination of the crystal structures of all these unsymmetrically coordinated compounds reveals that the least Ca(II)-bound carboxylate in each is involved in hydrogen bonding and it appears that hydrogen bonding is an effective means for dissipating the negative charge of a carboxylate group. Hence, it is

probably unlikely that the two carboxylate groups in these compounds differ greatly in negative charge as had been suggested in the case of the Ca(II) derivative of garcinia acid.³¹ Furthermore, a recent study³² on the mechanism of reduction of polynuclear μ -terephthalato-cobalt(III) complexes has shown that the terephthalato ligand does not mediate electrons efficiently between the carboxylate groups through the aromatic ring. We would expect, therefore, even less redistribution of negative charge across the aliphatic backbones of ligands such as malonate or the anion of garcinia acid.

The unidentate carboxylate bridge bonds, Ca-O(1^a) and Ca-O(2^b), found in malonatotriaquacalcium(II) are also common structural features in metal-carboxylate complexes. In particular, in calcium(II) carboxylates there is usually an extensive network of bridging interactions.^{22-28,33-35} These bridge bonds are responsible for the extensive polymeric units commonly found in such derivatives and are obviously important in determining the crystalline structures. In Ca(II) malonate it is noteworthy that the Ca-O(1^a), 2.397 (5) Å, and Ca-O(2^b), 2.424 (5) Å, bridge bonds are shorter than all the nonbridging Ca(II) carboxylate oxygen separations (Table II). The importance of these bridge interactions in establishing the structural characteristics of species present in aqueous solutions is diminished somewhat since there would be considerable disruption of the polymeric units to accommodate solvent water molecules in the coordination sphere. Still the great prevalence of bridging in the crystalline state does suggest that under the right conditions such interactions can become increasingly important in solution leading to the formation of oligomeric species. This idea is supported by the results from a detailed solution dynamics study^{36,37} of aqueous calcium ascorbate where aggregations of Ca(II) and ascorbate ions, such as Ca₃(ascorbate)₃ and Ca₃(ascorbate)₄³⁻ were formed. In crystalline calcium ascorbate extensive bridging occurs.^{38,39} Similarly, other investigations,⁴⁰⁻⁴² including electron spin resonance, of aqueous solutions of copper(II) and zinc(II) hydroxycarboxylates has revealed the presence of dimers and higher oligomers. In these instances bridging carboxylate interactions are strongly implicated in stabilizing the aggregates in aqueous solution.

The versatility of malonate ion binding of metal ions in the solid state is shown in Figure 2. There is a decided preference for six-membered chelate ring formation by malonate although that is not mirrored in the Ca(II) and one of the Nd(III) complexes² where only four-membered chelate rings are formed. The variety of observed bridging interactions underscores their importance in carboxylate-metal crystalline structures. The differences in binding illustrated in Figure 2 are of interest in view of the idea that trivalent lanthanides may be suitable paramagnetic replacement probes for Ca(II)

Table IV. O-C-C-C Dihedral Angles and C-C-C Bond Angles in Metal-Malonate Compounds

| Compd | Dihedral angles, deg | | Bond angle, deg C(1)-C(2)-C(3) | Ref |
|---|---|---|-----------------------------------|-----------|
| | O(1)-C(1)-C(2)-C(3), O(2)-C(1)-C(2)-C(3) | O(3)-C(3)-C(2)-C(1), O(4)-C(3)-C(2)-C(1) | | |
| Ca(C ₃ H ₂ O ₄)·2H ₂ O | -86.0, 94.5 | 86.6, -91.0 | 109.3 (2) | This work |
| [Cu(N-Meen) ₂](C ₃ H ₂ O ₄)·H ₂ O ^a | 75.1, -103.6 | 90.0, -91.3 | 108.8 (14) | 4 |
| Cu(N-Meen)(C ₃ H ₂ O ₄)·2H ₂ O ^a | 43.1, -137.4 | -45.3, 134.1 | 115.9 (7) | 4 |
| Na(+) _{5,6} -[Co(en)(C ₃ H ₂ O ₄) ₂]·2H ₂ O | 46.0, -150.1 | -30.2, 151.9 | 116.2 (25) | 7 |
| | 31.7, -153.4 | -45.4, 139.6 | 118.2 (26) | 7 |
| (-) _{5,6} -[Co(en)(NO ₂) ₂](+) _{5,6} -[Co(en)(C ₃ H ₂ O ₄) ₂] | -7.4, 171.7 | -10.2, 174.4 | 124 (3) | 6 |
| | -19.7, 168.7 | -0.9, 178.6 | 125 (3) | 6 |
| Sc(OH)(C ₃ H ₂ O ₄)·2H ₂ O | 35.3, -145.6 | -42.8, 140.1 | 115.7 (8) | 3 |
| Nd ₂ (C ₃ H ₂ O ₄) ₃ ·6H ₂ O | 68.1, -110.6 | 68.1, -110.6 | 104 (2) | 2 |
| | -33.0, 145.3 | 44.9, -142.8 | 118 (1) | 2 |
| Eu ₂ (C ₃ H ₂ O ₄) ₃ ·8H ₂ O | -44.6, 128.0 | 45.1, -128.0 | 115 (4) | 1 |
| | 26.3, -145.5 | -26.3, 145.5 | 122 (3) | 1 |
| | -54.4, 130.5 | 54.4, -130.5 | 115 (5) | 1 |

^a Meen = *N*-methylethylenediamine.

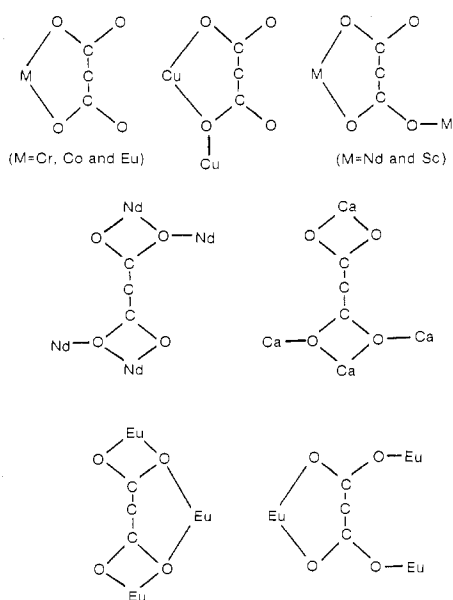


Figure 2. Modes of malonate-metal ion binding: Cr,⁵ Co,^{6,7} Eu,¹ Cu,⁴ Nd,² Sc,³ Ca (this work).

and display similar modes of binding in biological systems. However, in the crystalline state, at least, this is not the case for the simple dicarboxylate, malonate.

The conformation of the malonate ligand in malonato-diaquacalcium(II) differs considerably from that found in other metal-malonate compounds (Table IV) and this again emphasizes the flexibility of malonate coordination. The planes of both carboxylate groups in the Ca(II) complex are twisted such that they are approximately perpendicular to the C-C-C malonate backbone plane. In contrast to those malonate derivatives in which there is a six-membered chelate ring, the planes of the two carboxylate groups are twisted considerably closer to the C-C-C plane and there appears to be a significant concomitant opening of the C(1)-C(2)-C(3) bond angle (Table IV), although the error limits on some of the reported angles in Table IV are rather large. In bis(*N*-methylethylenediamine)copper(II) malonate dihydrate,⁴ the malonate ion is not coordinated to the copper(II) ion and it exhibits a conformation similar to that observed in calcium malonate. Furthermore, in the Ca(II) and Nd(III)² derivatives not involving a six-membered chelate ring as well as the "uncoordinated" malonate ion occurring in the copper(II) complex, the C(1)-C(2)-C(3) angles approach more closely the expected tetrahedral value suggesting considerable relaxation of bond angle strain.

Finally, the hydrogen bonding scheme in this highly polymeric structure is not extensive and involves only the hydrogen atoms of the O(5) water molecule. The structural parameters in terms of the donor atom (D) and acceptor atom (A) for the D...A and H...A distances and the D-H...A angle are 2.748 (8) Å, 1.94 Å, and 172° and 2.755 (7) Å, 1.92 Å, and 169° for the hydrogen bonds, O(5)-H1(O5)...O(3) ($1/2 - x, y - 1/2, z$) and O(5)-H2(O5)...O(4) ($1/2 - x, y + 1/2, z$), respectively.

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Registry No. [Ca(C₃H₂O₄)(H₂O)₂], 18923-49-4.

Supplementary Material Available: A listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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- (16) An attempt was made to refine the structure in space group *C2/m*. Atoms Ca, O(5), O(6), C(1), C(2), and C(3) were constrained in special positions (4i) (*m* point symmetry) and atoms O(1), O(3), H1(C2), H1(O5), and H1(O6) placed in the general positions of space group *C2/m*. Under these conditions three cycles of full-matrix least-squares refinement led to unacceptably high discrepancy indices of 0.19 and 0.26 for *R*₁ and *R*₂, respectively. Refinement in space group *Cm* was also unsuccessful.
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