

the bands of (II) *ca* 1000 cm⁻¹ higher in energy than those in (I), consistent with the lower tetragonality of (II), 0.803, suggesting the tentative assignment of the electronic spectra with a $d_{x^2-y^2}$ ground state by analogy with the assignment of [Cu(beat)(HCO₂)]HCO₂, Table 7 (Bew, Dudley, Fereday, Hathaway & Slade, 1971).

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The Structure of Diaquasuccinatocalcium(II) Monohydrate

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Abstract

The crystal structure of the title compound, [Ca(C₄H₄O₄)(H₂O)₂].H₂O, C₄H₈CaO₆.H₂O, was determined from three-dimensional single-crystal X-ray diffraction data collected on an automated diffractometer.

The crystals are triclinic, space group $P\bar{1}$, with $a = 7.937$ (7), $b = 9.450$ (11), $c = 6.688$ (7) Å, $\alpha = 91.47$ (5), $\beta = 111.80$ (6), $\gamma = 71.60$ (6)°, $Z = 2$, $d_m = 1.61$ and $d_c = 1.59$ Mg m⁻³. The structure was refined by full-matrix least squares to a conventional R index of 0.030. There are two different succinate ions in the

structure, each lying on an inversion center. One succinate ion coordinates two Ca^{2+} ions, one through each of its two carboxylate groups, forming four-membered chelate rings. The other succinate binds a total of six Ca^{2+} ions. Each carboxylate group chelates a Ca^{2+} ion forming a four-membered ring and, in addition, each of the four carboxylate O atoms binds a Ca^{2+} *via* a unidentate bridge bond, which results in a highly polymeric structure. The eight-coordinate coordination polyhedron of the Ca^{2+} most closely approximates bicapped trigonal-prismatic geometry.

Introduction

Although simple α,ω -dicarboxylate ligands such as oxalate and malonate are known to exhibit extraordinary versatility in binding metal ions in the crystalline state, only relatively few crystal structural characterizations of metal-ion derivatives of succinate or higher α,ω -dicarboxylate homologs have been carried out (Reed, 1976; Karipides, Ault & Reed, 1977). For succinates these studies include copper(II) succinate dihydrate (O'Connor & Maslen, 1966), dilithium succinate (Klapper & Küppers, 1973), (*N,N*-diethylethylenediamine)succinatocopper(II) tetrahydrate (Pajunen & Pajunen, 1979), and potassium and cesium hydrogen succinates (McAdam, Currie & Speakman, 1971; McAdam & Speakman, 1971). In all these instances the succinate moiety binds the particular metal ions in different unidentate fashions. Bidentate chelation and four-membered-ring formation by succinate has been proposed in anhydrous cobalt(II) succinate on the basis of IR spectroscopy (Sharrock & Theophanides, 1975), and the presence of seven-membered succinate chelate rings has even been suggested in solutions of copper(II) succinate (Dillon & Rossotti, 1973).

As part of a program to investigate the structural characteristics of carboxylate-metal ion interactions, we have determined the crystal structure of calcium succinate trihydrate in order to determine the nature of succinate- Ca^{2+} binding, as well as to obtain information concerning the calcium(II) ion coordination polyhedron geometry.

Experimental

Colorless prismatic crystals of the title compound were grown by evaporation of a solution prepared by dissolving calcium carbonate in an aqueous solution of succinic acid. From oscillation and Weissenberg photographs, the crystals were found to be triclinic and the systematic absences $h + l$ odd for hkl indicated $B1$ or $B\bar{1}$ space-group symmetry (non-standard settings for $P1$ or $P\bar{1}$, respectively). A single crystal with

approximate dimensions $0.28 \times 0.30 \times 0.34$ mm was mounted on a Picker FACS-1 automated diffractometer and the unit-cell parameters were determined from a least-squares refinement of the angular settings of twelve carefully centered reflections. For the chosen B -centered cell the lattice constants are: $a = 14.759$ (10), $b = 9.450$ (11), $c = 6.688$ (7) Å, $\alpha = 91.47$ (5), $\beta = 86.92$ (6), $\gamma = 70.86$ (6)°.

Three-dimensional X-ray intensity data were collected in this setting on the aforementioned diffractometer using Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Data were collected in the quadrants $\pm h, k \geq 0, \pm l$ in the range $0 < 2\theta \leq 55^\circ$ using the θ - 2θ scan technique. During the data collection the intensities of two standard reflections, which were monitored after each 50 measurements, did not show any significant variation. 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 (Reed & Karipides, 1976). Absorption corrections were not applied in view of the small absorption coefficient and dimensions of the crystal. 2050 unique data were collected. Of these, 1919 reflections had $I > \sigma(I)$ and were used in the structure refinement.

The transformation matrix which converts the chosen end-centered cell to the reduced primitive cell is

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_P = \begin{pmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_B$$

The reduced-primitive-cell constants, which were determined using the program *TRACER* II (Lawton, 1973), and other crystal data are presented in Table 1.

Initially, the structure was solved using Patterson and Fourier methods assuming the non-centrosymmetric space group $P1$. However, subsequent examination clearly revealed the centrosymmetric nature of the structure and final analysis was carried out in the centrosymmetric space group $P\bar{1}$. After all the non-hydrogen atoms were located, the trial structure was refined by a full-matrix least-squares procedure assuming at first isotropic then anisotropic motion for the nonhydrogen atoms. At this stage a difference Fourier synthesis revealed the positions of all H atoms. The entire structure, including the H atoms,

Table 1. *Crystal data for diaquasuccinatocalcium(II) monohydrate*

$[\text{Ca}(\text{C}_4\text{H}_4\text{O}_6)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	Space group $P\bar{1}$
$a = 7.937$ (7) Å	$Z = 2$
$b = 9.450$ (11)	$d_m = 1.61$ (1) Mg m^{-3}
$c = 6.688$ (7)	$d_c = 1.59$
$\alpha = 91.47$ (5)°	$F(000) = 220$
$\beta = 111.80$ (6)	$V = 439.6$ Å ³
$\gamma = 71.60$ (6)	$\mu(\text{Mo } K\alpha) = 0.69$ mm^{-1}

was further refined by full-matrix least squares. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight, w , applied to each observation was taken to be $[1/\sigma(F_o)]^2$. 149 parameters were refined yielding a data:parameter ratio of 12.9:1. The structure refinement converged to a conventional R_1 index, $\sum ||F_o| - |F_c|| / \sum |F_o|$, of 0.030 and a weighted R_2 index, $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, of 0.032. The goodness-of-fit is 1.6. An analysis of $w(|F_o| - |F_c|)^2$ as a function of $|F_c|$ or $\sin \theta/\lambda$ revealed no dependence on these quantities, suggesting that the weighting scheme used was adequate. A final three-dimensional electron density map showed no unusual features. In the final least-squares cycle no parameter varied by more than 0.01 of its estimated standard deviation.

Attempts at refinement in the non-centrosymmetric space group $P1$ did not improve the structure and although the residuals were slightly lower, $R_1 = 0.027$ and $R_2 = 0.031$, the errors in individual parameters were about eight times greater than in the centrosymmetric refinement. We did not observe any singularities or near-singularities in the refinement (Schomaker & Marsh, 1979); however, convergence was very slow and even after six cycles there were many parameter shift/error's greater than 0.5 with little tendency to improve. Thus, the structure is best described in $P\bar{1}$.

The neutral scattering factors for all atoms were taken from *International Tables for X-ray Crystallog-*

Table 2. Positional parameters and their standard deviations ($\times 10^4$) for nonhydrogen atoms

	x	y	z
Ca	5740.4 (4)	-4173.0 (3)	2870.0 (4)
O(1)	3080 (2)	-2036 (1)	312 (2)
O(2)	3375 (2)	-1999 (1)	3712 (2)
O(3)	3595 (2)	-5483 (1)	283 (2)
O(4)	3325 (2)	-5238 (1)	3406 (2)
O(5)	8089 (2)	-6786 (1)	3715 (2)
O(6)	7791 (2)	-2665 (2)	3787 (2)
O(7)	5796 (4)	355 (2)	2569 (3)
C(1)	2481 (2)	-1472 (2)	1752 (2)
C(2)	652 (3)	-136 (2)	1167 (3)
C(3)	2707 (2)	-5511 (1)	1484 (2)
C(4)	780 (2)	-5758 (2)	536 (2)

Table 3. Hydrogen atom positional parameters ($\times 10^3$)

	x	y	z
H1(C2)	114 (5)	86 (4)	158 (6)
H2(C2)	11 (4)	-13 (4)	219 (5)
H1(C4)	56 (3)	-611 (2)	168 (3)
H2(C4)	77 (3)	-650 (3)	-49 (4)
H1(O5)	775 (3)	-720 (3)	450 (4)
H2(O5)	783 (3)	-721 (2)	263 (4)
H1(O6)	728 (4)	-184 (3)	356 (4)
H2(O6)	888 (4)	-277 (3)	452 (4)
H1(O7)	599 (5)	79 (4)	176 (6)
H2(O7)	598 (4)	78 (3)	366 (5)

raphy (1974) and included corrections for the real and imaginary anomalous dispersion of Ca. The following programs or modifications were used: *FORDAP* (Zalkin, 1979), *ORFLS* and *ORFFE* (Busing, Martin & Levy, 1962, 1964), *ORTEP II* (Johnson, 1970) and *PLANES* (Smith, 1962). The final positional parameters are given in Tables 2 and 3 and, along with the structure factors lists,* are based on the reduced primitive cell given in Table 1.

Description of the structure and discussion

A view of portions of the polymeric units occurring in the unit cell, showing the coordination polyhedron

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35096 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

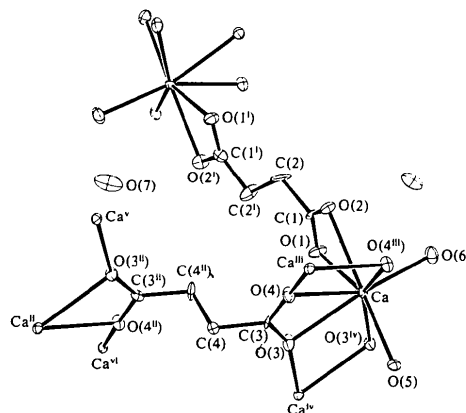


Fig. 1. A portion of the polymeric unit showing the spatial relationship between the two independent succinate ions, the CaO_8 coordination polyhedron, and the mode of succinate- Ca^{2+} binding. Hydrogen atoms have been omitted for clarity. The superscripts specify the symmetry-related positions of the atoms given in Table 2: (i) $-x, -y, -z$; (ii) $-x, -1-y, -z$; (iii) $1-x, -y-1, 1-z$; (iv) $1-x, -y-1, -z$; (v) $-x, y, z$; (vi) $-x, y, -z$.

Table 4. Bond distances (\AA) and angles ($^\circ$)

Superscripts are defined in Fig. 1.

Ca-O(1)	2.503 (1)	C(1)-O(1)	1.262 (2)
Ca-O(2)	2.521 (1)	C(1)-O(2)	1.261 (2)
Ca-O(3)	2.541 (1)	C(1)-C(2)	1.517 (2)
Ca-O(3 ^{iv})	2.348 (1)	C(2)-C(2 ^v)	1.492 (4)
Ca-O(4)	2.562 (1)	C(3)-O(3)	1.255 (2)
Ca-O(4 ⁱⁱⁱ)	2.345 (1)	C(3)-O(4)	1.247 (2)
Ca-O(5)	2.505 (1)	C(3)-C(4)	1.514 (2)
Ca-O(6)	2.395 (1)	C(4)-C(4 ⁱⁱ)	1.541 (3)
O(1)-C(1)-O(2)	121.3 (1)	O(3)-C(3)-O(4)	120.9 (1)
O(2)-C(1)-C(2)	118.0 (1)	O(4)-C(3)-C(4)	119.4 (1)
O(1)-C(1)-C(2)	120.7 (1)	O(3)-C(3)-C(4)	119.5 (1)
C(1)-C(2)-C(2 ^v)	115.4 (2)	C(3)-C(4)-C(4 ⁱⁱ)	108.3 (1)

about Ca^{2+} , the spatial relationship between the two unique succinate ions, the mode of Ca^{2+} binding by the succinates and the atom-labeling scheme, are presented in Fig. 1. Intermolecular bond distances and angles are given in Table 4.

There are two independent succinate ions in the structure which are specified by atoms O(1), O(2), C(1), C(2), C(2'), C(1'), O(1'), O(2') (succinate *A*) and O(3), O(4), C(3), C(4), C(4''), C(3''), O(3''), O(4'') (succinate *B*). Both succinate ions lie on inversion centers and, thus, each has imposed crystallographic $\bar{1}$ symmetry. The succinate ligands (*A*) and (*B*) bind to Ca^{2+} ions in different manners. Succinate (*A*) chelates two Ca^{2+} ions through each of its two carboxylate groups forming in each case a four-membered ring. Succinate (*B*) forms similar four-membered rings through coordination from both carboxylate groups to Ca^{2+} ions. However, succinate (*B*) is also involved extensively in bridging interactions. The carboxylate O(3) and O(4) atoms each link a Ca^{2+} ion by unidentate bridging bonds. Each succinate (*A*) ion, therefore, binds two different Ca^{2+} ions and each succinate (*B*) ion binds six Ca^{2+} ions, resulting in a highly complex, tightly knitted, three-dimensional array.

The dimensions of the succinate ions given in Table 4 are similar to the values found in previous structures containing the succinate dianion (O'Connor & Maslen, 1966; Klapper & Küppers, 1973; Pajunen & Pajunen, 1979). In calcium succinate the range in C—C—C angles at the CH_2 carbons from 108.3 (1) to 115.4 (2)° suggests that these angles are particularly susceptible to deformation in order to accommodate the steric demands of the crystal packing.

Although in this structure both succinate ions chelate Ca^{2+} ions through each carboxylate, this bidentate mode of binding has not been observed previously in succinates. Thus, in dilithium succinate (Klapper & Küppers, 1973), copper(II) succinate dihydrate (O'Connor & Maslen, 1966), (*N,N*-diethylethylenediamine)succinatocopper(II) tetrahydrate (Pajunen & Pajunen, 1979), potassium hydrogen succinate (McAdam, Curie & Speakman, 1971) and cesium hydrogen succinate monohydrate (McAdam & Speakman, 1971), the succinate ions are involved in only unidentate linkages through the carboxylate groups.

The two carboxylate groups in each of the succinates (*A*) and (*B*) are *trans* with the respective dihedral angles C(1)—C(2)—C(2')—C(1') and C(3)—C(4)—C(4'')—C(3'') of 180°. This *trans* orientation is the same as that occurring in lithium succinate and the hydrogen succinates of potassium and cesium, but differs from the *gauche* structure found in copper(II) succinate dihydrate and (*N,N*-diethylethylenediamine)succinatocopper(II) tetrahydrate. However, the detailed conformations of the two succinate ligands

are different with respect to the orientation of the carboxylate group planes and the C—C—C backbone plane.

In succinate (*A*), each of the two carboxylate group planes is twisted approximately towards the C(1)—C(2)—C(2')—C(1') backbone plane. The dihedral angle between these planes is 18.4°. In succinate (*B*), the situation is quite the opposite with each of the carboxylate groups almost perpendicular to the C(3)—C(4)—C(4'')—C(3'') plane (the dihedral angle between these planes is 94.6°). This difference in ligand conformation is undoubtedly the result of the substantial difference in metal binding by each succinate. The conformation found in dilithium succinate, where each carboxylate oxygen is also involved in bridging interactions, is similar (dihedral angle, 89.0°) to that found for succinate (*B*).

The Ca^{2+} ion is eight-coordinate and the CaO_8 polyhedron consists of the Ca^{2+} ion surrounded by succinate (*A*) carboxylate oxygens O(1), O(2), succinate (*B*) oxygens O(3), O(4), O(3''), O(4''), and two water molecules O(5) and O(6). The nature of the eight-coordinate geometry for the CaO_8 polyhedron can be determined using the formalism developed by Porai-Koshits & Aslanov (1972) and extended by Muetterties & Guggenberger (1974). Porai-Koshits & Aslanov have defined δ and φ shape parameters that measure the extent to which an observed coordination polyhedron deviates from the idealized polyhedron. The theoretical values for the shape parameters for idealized eight-coordinate polyhedra as well as the observed values in diaquasuccinatocalcium(II) monohydrate are given in Table 5. The CaO_8 polyhedron most closely approximates a bicapped trigonal prism although the polyhedron is somewhat distorted towards D_{4d} square-antiprismatic geometry. In the CaO_8 polyhedron the atoms O(3'') and O(4'') are 'capped' over the faces O(5)—O(6)—O(3)—O(1) and O(5)—O(6)—O(4)—O(2), respectively. The 'uncapped' face is O(1)—O(2)—O(3)—O(4). A bicapped trigonal prismatic structure was also found for the CaO_8 polyhedron in diaquamalonatocalcium(II) (Karipides, Ault & Reed, 1977). To the

Table 5. *Shape parameters for* $[\text{Ca}(\text{C}_4\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ *and theoretical values for idealized eight-coordinate polyhedra*

Parameter	Observed value (°)	Theoretical value (°)		
		C_{2v} bicapped trigonal prism	D_{4d} square antiprism	D_{2d} dodecahedron
δ_1	13.1	0	0	29.5
δ_2	47.1	21.8	0	29.5
δ_3	48.3	48.2	52.4	29.5
δ_4	53.4	48.2	52.4	29.5
φ_1	12.6	14.1	24.5	0
φ_2	24.8	14.1	24.5	0

best of our knowledge, these examples represent the only reported instances of bicapped trigonal-prismatic geometry for CaO_8 coordination polyhedra.

The Ca—O bond lengths in calcium succinate follow the trends previously observed in calcium carboxylate structures (Einspahr & Bugg, 1977). The average Ca—O bond distance for the unidentate bridge bonds is 2.346 Å, which is shorter than the four non-bridging Ca—carboxylate or two Ca—water interactions. These bridge bonds are responsible for the extensive polymeric units and this shortening of the bridge bonds emphasizes their importance in determining the crystal-line structure.

There are two different kinds of four-membered rings in the structure. The first are the Ca—O—C—O chelate rings formed by the bidentate coordination of Ca^{2+} ions at each end of both succinate ions. Each of these chelate rings is slightly buckled with the respective Ca^{2+} ions lying 0.26 and 0.71 Å from the O(1)—C(1)—O(2) and O(3)—C(3)—O(4) carboxylate planes, respectively. The average Ca—O bond length involving the bidentate carboxylate interactions is 2.532 Å, which compares well with the 2.54 Å found for similar interactions in other calcium carboxylates (Einspahr & Bugg, 1977). The average O—Ca—O and Ca—O—C angles in these four-membered chelate rings are 51.2 and 93.3°, respectively.

The second, but less common, four-membered rings in this structure are the Ca—O—Ca—O rings formed as a result of the bridging structure (Fig. 1). These rings, which are planar, serve to form the rigid framework for the polymeric structure. The Ca...Ca distances across these rings are only 3.977 (1) and 4.008 (1) Å, which compare with the Ca...Ca distance of 3.96 Å in metallic calcium (Martínez-Ripoll & Brauer, 1974). The average Ca—O—Ca and O—Ca—O angles in these rings are 109.2 and 70.8°, respectively.

There is an extensive network of hydrogen bonds utilizing all six H atoms from the water molecules. One of the three independent water molecules is not coordinated to Ca^{2+} but, as a water of hydration, is involved in the hydrogen-bonding scheme. In addition

to water molecules, only the O atoms of succinate (*A*) participate in hydrogen bonding. This fact is not surprising since all of the succinate (*B*) carboxylate O atoms are involved in binding two Ca ions each and, thus, cannot participate readily in hydrogen bonding. The pertinent hydrogen-bonding parameters are summarized in Table 6.

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Table 6. *Hydrogen-bond distances (Å) and angles (°)*

Donor (*D*) and hydrogen atoms have the coordinates listed in Tables 2 and 3. Superscripts specify the symmetry-related positions of the acceptor (*A*) atoms. Superscripts (iii) and (iv) are the same as those given in Fig. 1, (vii) 1 - *x*, -*y*, -*z*; (viii) 1 - *x*, -*y*, 1 - *z*; (ix) *x*, *y*, *z*; (x) 2 - *x*, -*y* - 1, 1 - *z*.

Hydrogen bond	<i>D</i> ... <i>A</i>	H... <i>A</i>	∠ <i>D</i> -H... <i>A</i>
O(5)—H1(O5)...O(2 ⁱⁱⁱ)	2.840 (2)	2.01 (4)	173 (2)
O(5)—H2(O5)...O(1 ^{iv})	2.828 (2)	2.02 (2)	171 (2)
O(6)—H1(O6)...O(7 ^{ix})	2.761 (3)	2.02 (3)	174 (3)
O(6)—H2(O6)...O(5 ^x)	2.944 (2)	2.16 (3)	174 (3)
O(7)—H1(O7)...O(1 ^{vii})	3.058 (2)	2.29 (4)	173 (3)
O(7)—H2(O7)...O(2 ^{viii})	2.875 (2)	2.07 (3)	173 (3)