PHILLIPS, F. L. & SKAPSKI, A. C. (1975*c*). *Transition Met. Chem.* **1**, 28–32.
ROBBINS, A., JEFFREY, G. A., CHESNICK, J. P., DONOHUE, J., COTTON, F. A., FRENZ, B. A. & MURILLO, C. A. (1975). *Acta Cryst.* B**31**, 2395–2399.
RUNSINK, J., SWEN-WALSTRA, S. & MIGCHELSEN, T. (1972). *Acta Cryst.* B**28**, 1331–1335.
SCANE, J. G. (1967). *Acta Cryst.* **23**, 85.
SPAGNA, R. & ZAMBONELLI, L. (1973). *Acta Cryst.* B**29**, 2302–2304.
WEBSTER, M., MUDD, K. R. & TAYLOR, D. J. (1976). *Inorg. Chim. Acta*, **20** 231–235.
WELLER, F. (1979). Unveröffentlicht.
WELLER, F., MÜLLER, U., WEIHER, U. & DEHNICKE, K. (1980). *Z. Anorg. Allg. Chem.* **460**, 191–199.
WELLER, F., RUSCHKE, P. & DEHNICKE, K. (1980). *Z. Anorg. Allg. Chem.* Im Druck.
WET, J. F. DE & DU PREEZ, J. G. H. (1978). *J. Chem. Soc. Dalton Trans.* S. 592–597.

Acta Cryst. (1980). B**36**, 1081–1086

The Structures of Calcium Formate β-Ca(HCOO)$_2$ and δ-Ca(HCOO)$_2$, and the Tetragonal Mixed Crystals Ca(HCOO)$_2$–Sr(HCOO)$_2$

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(*Received* 4 *June* 1979; *accepted* 24 *December* 1979)

Abstract

The structure of β-Ca(HCOO)$_2$ has been determined independently by Matsui, Watanabé and Kamijo (hereafter MW & K) and by Lapp and Jacobson (hereafter L & J). It is tetragonal, $P4_12_12$, a = 6·776 (2), c = 9·453 (5) Å (MW & K)/a = 6·765 (2), c = 9·456 (3) Å (L & J), and Z = 4. The Ca^{2+} ions are coordinated by six O atoms at distances 2·311 (3)–2·484 (3) Å (MW & K)/2·301 (2)–2·478 (2) Å (L & J), plus two O atoms at a distance 2·944 (3) Å (MW & K)/2·950 (3) Å (L & J). The formate group is planar, and the two C—O distances are significantly different: 1·221 (5) and 1·242 (5) Å (MW & K)/1·230 (3) and 1·245 (3) Å (L & J). Endless chains, $[\cdots\mathrm{Ca}\cdots\mathrm{O{-}CH{-}O}\cdots]_\infty$, run parallel to the x and y directions and are cross-linked through the Ca^{2+} ions, forming networks. The structure of δ-Ca(HCOO)$_2$ was obtained from powder diffraction data at 603 K. It is tetragonal, $I4_1/amd$, with a = 6·75 (1), c = 10·04 (2) Å, and Z = 4. The structure of δ-Ca(HCOO)$_2$ is disordered but is derivable from that of β-Ca(HCOO)$_2$. The tetragonal mixed crystals between Ca(HCOO)$_2$ and Sr(HCOO)$_2$ have been prepared and these have been shown to have the same structure as β-Ca(HCOO)$_2$.

Introduction

Calcium formate exhibits four different modifications: α, β, γ and δ (Mentzen & Comel, 1974). The structure of α-Ca(HCOO)$_2$, stable at room temperature, was determined by Nitta & Osaki (1948), and was recently refined both by neutron diffraction (Burger, Fuess & Mason, 1977) and by X-ray diffraction (Watanabé & Matsui, 1978). It has been found possible to prepare single crystals of β-Ca(HCOO)$_2$, which enabled us to determine its structure. Although δ-Ca(HCOO)$_2$ can only be obtained as a crystalline powder, it was possible to arrive at a satisfactory structure which accounts well for the observed powder intensity data. In this paper, the structures of β-Ca(HCOO)$_2$ and δ-Ca(HCOO)$_2$ are given, followed by discussions of the relationship among the structures of the three phases, α-Ca(HCOO)$_2$, β-Ca(HCOO)$_2$ and δ-Ca(HCOO)$_2$.

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0567-7408/80/051081-06$01.00

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The structures of β-Sr(HCOO)$_2$, δ-Sr(HCOO)$_2$ and of the tetragonal mixed crystals between calcium formate and strontium formate are also reported. The study of the structure of β-Ca(HCOO)$_2$ was also carried out to complement work being done on the development of a technique to use NMR to determine positions of H atoms in the solid (Vaughan, 1976).

The structure of β-Ca(HCOO)$_2$ was determined independently by Matsui, Watanabé and Kamijo and by Lapp and Jacobson. The atomic parameters obtained by these two investigations are in quite satisfactory agreement. Therefore these results will be described in parallel. Matsui, Watanabé and Kamijo are solely responsible for the rest of this paper.

The structure of β-Ca(HCOO)$_2$

Preparation of single crystals

Calcium formate crystallizes from aqueous solution in the rhombic bipyramidal class *mmm*, as described by Groth (1910), now known as α-Ca(HCOO)$_2$. This is the case when the temperature of the solution is kept below 333 K. It was found, however, that when the temperature was maintained above 338 K, crystals of a second morphology were also obtained, the yield of the latter increasing with temperature. Determination of the lattice constants and space group, as will be described later, indicated that this second morphology is identical with β-Ca(HCOO)$_2$, which had been obtained previously only as a crystalline powder (Schutte & Buijs, 1964; Mentzen & Comel, 1974). Single crystals thus obtained are tetragonal, colorless and transparent. Small crystals on the order of 0·1 mm are almost regular octahedra, because the axial ratio, $\sqrt{2}a/c$, is close to unity. Larger crystals show uneven development of faces and are often truncated. These crystals readily transform into α-Ca(HCOO)$_2$ in a moist atmosphere. They remain unchanged, however, when placed in a desiccator over silica gel, and can also be kept for a few days in a dry atmosphere. These properties are exactly the same as those reported for the crystalline powder of β-Ca(HCOO)$_2$.

Table 1. *Crystal data, the data collection and reduction of intensities and the least-squares refinement for* β-Ca(HCOO)$_2$ ($FW = 130{\cdot}12$) *at room temperature*

	MW & K	L & J
Space group	$P4_12_12$	$P4_12_12$
a (Å)	6·776 (2)	6·765 (2)
c (Å)	9·453 (5)	9·456 (3)
V (Å^3)	434·03	432·76
Z	4	4
D_x (Mg m^{-3})	1·991	1·997
D_m (Mg m^{-3})	1·996*	–
Diffractometer	Rigaku four-circle	Four-circle designed and built in the Ames Lab.
Radiation	Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å)	
Monochromator	Graphite	
Crystal shape	Octahedron	
Crystal size (mm) (length of the edge)	0·20	0·4
Scan mode	θ–2θ	ω
$2\theta_{\max}$ (°)	60	55
Number of reflections used for refinement	240 [$I > 2\sigma(I)$] hkl; $h \geq k$ half octant	504 [$F_o > 3\sigma(F_o)$] hkl octant
$\sigma(I)$ (counting statistics +)	$(0{\cdot}04I)^2$	$(0{\cdot}03C_T)^2 + (0{\cdot}03C_B)^2$†
Function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	
Least squares	Full-matrix	
Scattering factors for Ca^{2+}, O and C	*International Tables for X-ray Crystallography* (1974)	
for H	Stewart, Davidson & Simpson (1965)	
Thermal parameters	Anisotropic for the non-H atoms, isotropic for H	
Final R ($=\sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$)	0·024	0·049
Final R_w $\{=[\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}\}$	0·032	0·065

* Measured by flotation.

† C_T: total count. C_B: background count.

Table 2. *Fractional coordinates for* β-Ca(HCOO)$_2$ *at room temperature with e.s.d.'s in parentheses*

The results of MW & K are given first, those of L & J second.

	x	y	z
Ca	0·2169 (1)	0·2169 (1)	0
	0·2170 (1)	0·2170 (1)	0
O(1)	0·2766 (4)	0·0651 (4)	0·2353 (3)
	0·2765 (3)	0·0657 (3)	0·2348 (2)
O(2)	0·2813 (4)	0·3793 (3)	0·2851 (3)
	0·2804 (4)	0·3806 (3)	0·2856 (3)
C	0·3039 (6)	0·2061 (6)	0·3170 (4)
	0·3045 (4)	0·2061 (4)	0·3176 (3)
H	0·354 (7)	0·173 (7)	0·412 (5)
	0·361 (5)	0·186 (5)	0·415 (4)

Structure determination

The experimental procedures and the determinations of the structure used by MW & K and L & J are similar and are relatively routine. Relevant data are shown in Table 1. As a general check on electronic and crystal stability, three standard reflections were remeasured after every 50 (MW & K)/75 (L & J) reflections. These standards were not observed to vary significantly throughout the entire data-collection period. No absorption correction was made. A Howells, Phillips & Rogers (1950) test made by L & J indicated a non-centrosymmetric space group. Since the symmetry of the crystal is enantiomorphous, the space group of the crystal used for investigation was determined using sets of reflections hkl and $h\bar{k}l$ before the final refinement was made (MW & K). In order to minimize the extinction effect, three reflections with small scattering angles and large $|F_o|$ values were omitted in the final refinement by MW & K. A small secondary-extinction effect was noted and corrected by L & J. The final atomic coordinates* are listed in Table 2.

Description of the structure

The projection of the structure along [001] is shown in Fig. 1. There exist endless chains, $[\cdots Ca\cdots O{-}CH{-}O\cdots]_\infty$, running parallel to the x and y directions. These chains are cross-linked through the Ca^{2+} ions, forming networks, which are stacked along the z direction through the 4_1 operation. The Ca^{2+} ion environment is shown in Fig. 2. The Ca^{2+} ion lies on the twofold axis, and four O atoms, $O(1^{ii})$, $O(1^{iii})$, $O(2^{iv})$ and $O(2^{v})$, from four different formate groups are coordinated in a square-planar fashion to the Ca^{2+} ion; the four O atoms O(1), O(2), $O(1^{i})$ and $O(2^{i})$ from two formate groups are coordinated to the Ca^{2+} ion above and below the square plane. The $Ca^{2+}{-}O$ distances are listed in Table 3, along with the bond distances and angles of the formate group. There is one independent formate group in the asymmetric unit, and it is found to be planar within the standard deviations. The two C—O distances are significantly different however. All the formate groups in structures reported previously are planar with an equal distance for the two C—O bonds, except for one of the two independent formate groups in α-Ca(HCOO)$_2$ (Watanabé & Matsui, 1978). The formate groups in β-Ca(HCOO)$_2$ afford another example of incomplete resonance. As is shown in Fig. 3, the shorter C—O bond is associated with the longest Ca^{2+} distance. A similar effect has already been noted in α-Ca(HCOO)$_2$.

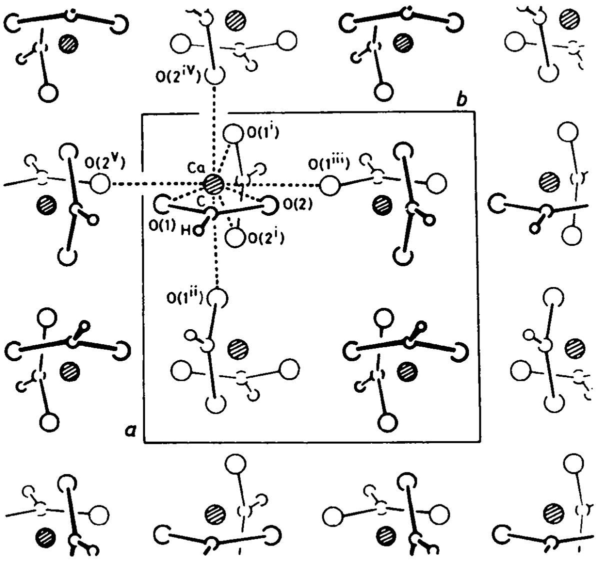

Fig. 1. Crystal structure of β-Ca(HCOO)$_2$ along [001]. Symmetry codes are: (i) y,x,z; (ii) $\frac{1}{2}+y, \frac{1}{2}-x, -\frac{1}{4}+z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$; (iv) $-\frac{1}{2}+y, \frac{1}{2}-x, -\frac{1}{4}+z$; (v) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{4}-z$.

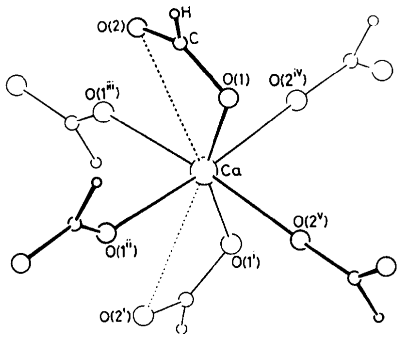

Fig. 2. The Ca^{2+} ion environment in β-Ca(HCOO)$_2$. Symmetry codes are the same as in Fig. 1.

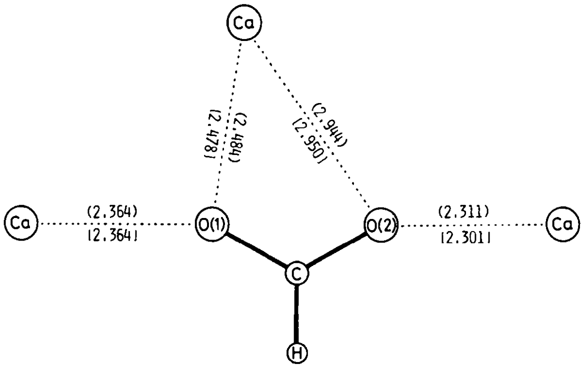

Fig. 3. The formate group environment in β-Ca(HCOO)$_2$. The $Ca^{2+}{-}O$ distances (Å) obtained by MW & K are given in parentheses and those by L & J in square brackets.

Table 3. *Interatomic distances* (Å) *and bond angles* (°) *in* β-Ca(HCOO)$_2$ *with e.s.d.'s in parentheses*

	Ca–O(1)	Ca–O(2)	Ca–O(1^{ii})	Ca–O(2^{iv})
MW & K	2·484 (3)	2·944 (3)	2·364 (3)	2·311 (3)
L & J	2·478 (2)	2·950 (3)	2·364 (2)	2·301 (2)
	Chelate coordination		Square coordination	

	C–O(1)	C–O(2)	C–H
MW & K	1·242 (5)	1·221 (5)	0·99 (5)
L & J	1·245 (3)	1·230 (3)	1·01 (3)

	O(1)–C–O(2)	O(1)–C–H	O(2)–C–H
MW & K	124·6 (4)	116 (3)	119 (3)
L & J	123·9 (3)	122 (1)	114 (1)

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* Lists of thermal parameters and structure factors obtained by the two independent investigations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35072 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure of δ-Ca(HCOO)$_2$

δ-Ca(HCOO)$_2$ has only been obtained as a crystalline powder, and exists at a temperature range of 573–633 K (Mentzen & Comel, 1974). The material used for this investigation was prepared as described by Mentzen & Comel.

Crystals of α-Ca(HCOO)$_2$ were pulverized and placed on the heating stage of a Rigaku diffractometer, Geigerflex-2013. The specimen was heated to 613 K, followed by cooling to room temperature, and again heated at a heating rate of 10 K min^{-1} and maintained at 603 ± 1 K during exposure to Cu $K\alpha$ radiation (λ = 1·5418 Å) filtered through Ni foil. By subjecting the specimen to several transitions, preferred orientation effects were minimized. The observed powder diffraction lines of δ-Ca(HCOO)$_2$ are consistent with a tetragonal unit cell containing four formula units having a = 6·75 (1) and c = 10·04 (2) Å, in good agreement with those reported by Mentzen & Comel (1974). The observed extinction conditions are: hkl with $h + k + l = 2n$, $hk0$ with $h(k) = 2n$, and hhl with $2h + l = 4n$, corresponding to the space group $I4_1/amd$. The observed X-ray diffraction data are listed in Table 4. Since there are four formula units in the unit cell, atoms can be assigned to the following equivalent positions in the unit cell: 4 Ca at (a) (0,0,0) *etc.*, 8 C at (e) $(0,0,z_C)$ *etc.*, 8 H at (e) $(0,0,z_H)$ *etc.*, and 16 O at (h) $(0,x_o,z_o)$ *etc.* (*International Tables for X-ray Crystallography*, 1969). The positions (c) or (d) for C and H, and the positions (g) or (f) for O lead to no discrete HCOO$^-$ groups. If we assume an isosceles triangle with 1·24 Å for C—O and 125° for ∠OCO, and neglecting H, the structure can be characterized by one z value, say z_o for O. Fairly good agreement between the observed and calculated intensities was obtained for z_o = 0·255. However, in this model an anomalously small value (1·77 Å) is obtained for the shortest interatomic H···H distance if we assume 1·00 Å for C—H. We are therefore led to the conclusion that the actual structure is a disordered one at least for C and H, but is one which can be derived from the model mentioned above. Thus the formate groups are distributed symmetrically on both sides of the mirror planes running parallel to the ac and bc planes. This can be achieved either by statistical orientations or by rigorous thermal motions of the formate groups. As a simplified yet tangible structure, it is assumed that the atoms in the unit cell occupy the following equivalent positions:

$$(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})+$$

$$\begin{array}{rlrl} 4 & \text{Ca} & (a) & 0,0,0;\ 0,\tfrac{1}{2},\tfrac{1}{4} \\ 8 & \text{C} & \tfrac{1}{2}\times(h) & \left.\begin{array}{l} 0,x,z;\ 0,\bar{x},z;\ 0,\tfrac{1}{2}+x,\tfrac{1}{4}-z; \\ 0,\tfrac{1}{2}-x,\tfrac{1}{4}-z;\ x,0,\bar{z};\ \bar{x},0,\bar{z}; \\ x,\tfrac{1}{2},\tfrac{1}{4}+z;\ \bar{x},\tfrac{1}{2},\tfrac{1}{4}+z \end{array}\right. \\ 8 & \text{H} & \tfrac{1}{2}\times(h) & \\ 16 & \text{O} & (h) & \end{array}$$

Table 4. *X-ray data for* δ-Ca(HCOO)$_2$ *at* 603 K

$h\,k\,l$	$10^4 \sin^2\theta$ (obs)	$10^4 \sin^2\theta$ (calc)	I_{obs}	I_{calc}
1 0 1	187	189	100	100·0
2 0 0	519	522	78	80·4
1 0 3	660	661	51	52·3
0 0 4	941	943	18	21·6
2 2 0	1043	1043	6	3·5
2 1 3	*	1183	*	4·4
3 0 1	1232	1233	20	18·4
2 0 4	1467	1465	8	10·7
3 1 2	*	1540	*	11·0
1 0 5	1603	1604	2	1·6
3 0 3	1708	1705	9	11·4
3 2 1	1757	1755	4	5·2

* Superimposed with Pt line.

where a statistical weight of $\frac{1}{2}$ is given to C and H. A comparison of the observed and calculated intensities, using the following parameter values, x = 0·042, z = −0·304 for C; x = 0·117, z = −0·391 for H; x = 0·163, z = 0·255 for O, is listed in Table 4. In this model, the shortest interatomic H···H distance is calculated to be 2·46 Å. The isotropic thermal parameters used for the calculation are 6·0 Å^2 for Ca^{2+} and 9·0 Å^2 for the others.

The projection of the structure along [001] is shown in Fig. 4. Each Ca^{2+} ion lies on $\bar{4}2m$ and is surrounded by eight O atoms from six different formate groups. The Ca^{2+}—O distances are found to be 2·28 Å (×4) and 2·79 Å (×4). The two structures, β-Ca(HCOO)$_2$ and δ-Ca(HCOO)$_2$, are closely related. Starting from the structure of β-Ca(HCOO)$_2$, if we displace the Ca^{2+} ions along the twofold symmetry axis on which they lie by approximately 0·3 Å, and give small displacements and statistical orientations to the formate groups, the Ca^{2+} ion site could possess $\bar{4}2m$ symmetry, and the structure becomes that of δ-Ca(HCOO)$_2$.

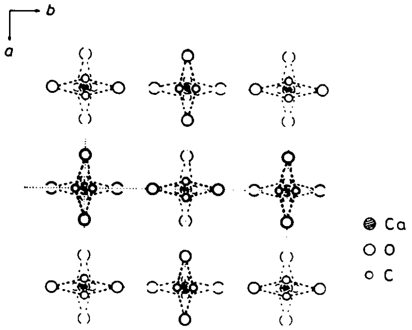

Fig. 4. Crystal structure of δ-Ca(HCOO)$_2$ projected along [001]. The formate groups are positioned on the two sides of the mirror planes, ac and bc, with a statistical weight $\frac{1}{2}$. The H atoms are omitted for simplification. See also Fig. 5.

Structure relations among α-Ca(HCOO)$_2$, β-Ca(HCOO)$_2$ and δ-Ca(HCOO)$_2$

Now that the structures of α-Ca(HCOO)$_2$, β-Ca(HCOO)$_2$ and δ-Ca(HCOO)$_2$ are established, it is worth describing the structural relations among the three. A schematic drawing of the surroundings of the Ca^{2+} ions in the three structures is given in Fig. 5. In all three structures the four O atoms from four different formate groups are coordinated in a square-planar fashion to the Ca^{2+} ion, and two more formate groups are placed above and below the square plane. The main difference lies in the orientations of these two formate groups to the Ca^{2+} ion. In α-Ca(HCOO)$_2$ the two formate groups are non-equivalent, and one of the two formate groups is coordinated to the Ca^{2+} ion acting as a chelate ligand, while the other formate group is coordinated to the Ca^{2+} ion with only one of the two O atoms. In β-Ca(HCOO)$_2$ the two formate groups which are related by the twofold axis passing through the Ca^{2+} ion are coordinated to the Ca^{2+} ion acting as chelate ligands with considerably different Ca^{2+}–O distances, as is shown in Table 3. In δ-Ca(HCOO)$_2$ the two formate groups, which are also symmetry-related, are coordinated to the Ca^{2+} ion with O atoms acting as symmetrical chelate ligands with an equal distance of 2·79 Å for Ca^{2+}–O. In the three structures, the Ca^{2+}–O distances of the chelate formate groups are always found to be longer than the other Ca^{2+}–O distances. Also in each of the three structures, there exist endless chains of the form $[\cdots\text{Ca}\cdots\text{O–CH–O}\cdots]_\infty$, which are cross-linked by the Ca^{2+} ions. In β-Ca(HCOO)$_2$ these chains are nearly planar and the C–H vectors in each chain are pointing in the same direction, while in δ-Ca(HCOO)$_2$ the C–H vectors in each chain are distributed statistically in two directions. In α-Ca(HCOO)$_2$ the chains are more complicated and the C–H vectors are pointing in four directions.

Tetragonal mixed crystals Ca(HCOO)$_2$–Sr(HCOO)$_2$

By slow evaporation of aqueous solutions containing various amounts of calcium formate and strontium formate at 353 K, a series of tetragonal mixed crystals were obtained. From the crystal habit, and more definitely from the axial ratios as well as the densities obtained by an analysis of Weissenberg photographs and by pycnometry, respectively, these crystals were found to be the same as those that Groth (1910) described as the third modification of the pseudo-binary system Ca(HCOO)$_2$–Sr(HCOO)$_2$. The space group is determined to be $P4_12_12$ (or $P4_32_12$). The lattice constants increase with the concentrations[*] of strontium and vary from 6·841 (2) to 6·976 (3) Å for a and 9·523 (4) to 9·571 (4) Å for c, as shown in Fig. 6. The β phase described in the preceding sections is nothing but the end component of these tetragonal mixed crystals.

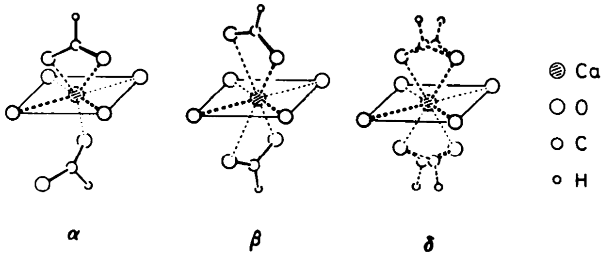

Fig. 5. The Ca^{2+} ion environments in the three modifications, α-Ca(HCOO)$_2$, β-Ca(HCOO)$_2$ and δ-Ca(HCOO)$_2$. The site symmetries of the Ca^{2+} ion are 1, 2 and $\bar{4}2m$ for α, β and δ, respectively.

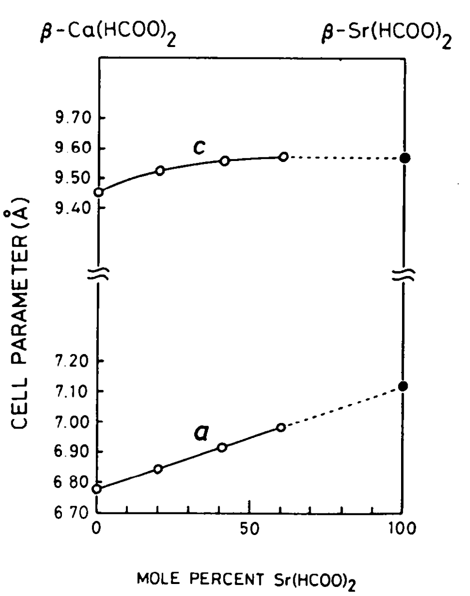

Fig. 6. Variations of the cell parameters of the mixed crystals, Ca(HCOO)$_2$–Sr(HCOO)$_2$, with concentration. The open circles indicate the values obtained from single-crystal diffraction data and the solid ones from powder diffraction data.

Mentzen & Comel (1974) reported two new modifications of strontium formate, β-Sr(HCOO)$_2$ and δ-Sr(HCOO)$_2$. The space groups and the lattice parameters obtained by these authors and redetermined by us are: $P4_12_12$ (or $P4_32_12$), a = 7·12 (1) and c = 9·57 (2) Å at room temperature for β-Sr(HCOO)$_2$, and $I4_1/amd$, a = 7·07 and c = 10·12 Å at 553 K for δ-Sr(HCOO)$_2$. The lattice parameters of β-Sr(HCOO)$_2$ lie close to the extrapolated curves prepared from those of the mixed crystals having different compositions, as can be seen in Fig. 6.

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[*] The content of strontium in each mixed crystal was determined by its formula weight M_r[Ca$_{1-x}$Sr$_x$(HCOO)$_2$], which was calculated by the equation $M_r = \rho NV/Z$, where ρ is the observed density, N Avogadro's constant, V the cell volume and Z the number of formula units contained in the unit cell.

Therefore, β-Sr(HCOO)$_2$ can be taken as the other end component of the tetragonal mixed crystals. Observed powder diffraction intensities of β-Sr(HCOO)$_2$ and δ-Sr(HCOO)$_2$ are well accounted for by the structures of β-Ca(HCOO)$_2$ and δ-Ca(HCOO)$_2$, and therefore it is established that both the two pairs β-Ca(HCOO)$_2$ and β-Sr(HCOO)$_2$, and δ-Ca(HCOO)$_2$ and δ-Sr(HCOO)$_2$ are, respectively, isostructural.

Mentzen & Comel (1974) reported, further, that the transition β-Sr(HCOO)$_2$ $\rightleftharpoons$ δ-Sr(HCOO)$_2$ is progressive, the lattice constants of the one changing continuously into the other with temperature; this is undetected by differential thermal analysis. On the other hand, the transformation from β-Ca(HCOO)$_2$ to δ-Ca(HCOO)$_2$ occurs stepwise through an intermediate phase which they call γ-Ca(HCOO)$_2$. The two transitions β-Ca(HCOO)$_2$ $\rightleftharpoons$ γ-Ca(HCOO)$_2$ and γ-Ca(HCOO)$_2$ $\rightleftharpoons$ δ-Ca(HCOO)$_2$ involve heats of transition. The mechanism of transition β-Sr(HCOO)$_2$ $\rightleftharpoons$ δ-Sr(HCOO)$_2$ can be readily explained as a displacive type, as evidenced by the structures of the two modifications. The transition β-Ca(HCOO)$_2$ into δ-Ca(HCOO)$_2$ may need the intermediate phase because of stronger interactions between the Ca^{2+} and formate ions.

This work was supported in part (L & J) by the US Department of Energy, contract No. W-7405-Eng-82, Division of Materials Science, budget code No. AK-01-02-03-1.

References

Burger, N., Fuess, H. & Mason, S. A. (1977). *Acta Cryst.* B**33**, 1968–1970.

Groth, P. (1910). *Chemische Kristallographie*, Vol. 3, p. 10. Leipzig: Engelmann.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210–214.

International Tables for X-ray Crystallography (1969). Vol. I, p. 245. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–98. Birmingham: Kynoch Press.

Mentzen, B. F. & Comel, C. (1974). *J. Solid State Chem.* **9**, 214–223.

Nitta, I. & Osaki, K. (1948). *X-rays*, **5**, 37–42 (in Japanese).

Schutte, C. J. H. & Buijs, K. (1964). *Spectrochim. Acta*, **20**, 187–195.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Vaughan, R. W. (1976). Private communication.

Watanabé, T. & Matsui, M. (1978). *Acta Cryst.* B**34**, 2731–2736.

Acta Cryst. (1980). B**36**, 1086–1091

Structure de l'Iodure de Tris(éthylènediamine)cobalt(III) Monohydraté

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(*Reçu le* 6 *juillet* 1979, *accepté le* 1 *janvier* 1980)

Abstract

The crystal structure of (±)[Co(en)$_3$]I$_3$.H$_2$O has been determined by single-crystal X-ray diffraction analysis. It is orthorhombic with space group *Pbca*. The lattice constants are $a = 11{\cdot}516$ (3), $b = 13{\cdot}449$ (4) and $c = 23{\cdot}35$ (1) Å with eight formula units in the unit cell; $V = 3616$ Å^3, $d_x = 2{\cdot}343$ Mg m^{-3}. The structure was refined by full-matrix least-squares methods with anisotropic thermal parameters to a final $R = 0{\cdot}034$ for 3660 reflexions. The configuration of the complex ion (+)[Co(en)$_3$]$^{3+}$ is $\Lambda(\lambda\lambda\delta)$; the correlation between hydrogen bonds and conformation is discussed. (±)[Co(en)$_3$]I$_3$.H$_2$O is isostructural with (±)[Cr(en)$_3$]I$_3$.H$_2$O and [Cr(en)(tn)$_2$]I$_3$.H$_2$O: this can be justified by the structural filiation established for all the tris(ethylenediamine) complexes [M(en)$_3X_m$].

0567-7408/80/051086-06$01.00

Introduction

Les bromures et chlorures racémiques de tris(éthylènediamine)métal(III) sont isomorphes (maille trigonale, groupe spatial $P\bar{3}c1$), quel que soit le métal central (Co^{3+}, Cr^{3+}, Rh^{3+}...) (Whuler, Brouty, Spinat & Herpin, 1975, 1976).

Mais cet isomorphisme ne s'étendrait pas à tous les halogénures complexes de ce type puisque Jaeger (1918) a prévu, par mesures goniométriques, que les iodures cristallisent dans le système orthorhombique

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