

Fig. 1. Molecules R_1 and L_2 as located in the unit cell.

The ethyl group, being the most flexible moiety, has large thermal motion and hence less accurate bond lengths and angles.

This analysis shows that the ethoxy substituent of the butadienyl moiety [O(3)—C(8)—C(9)] is *trans* to the single bond C(5)—C(6).

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Neutron Diffraction of α -Calcium Formate at 100 and 296 K

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Abstract. α -Ca(HCOO)₂, orthorhombic, *Pcab*; $T = 100$ K: $a = 10.231$ (3), $b = 13.239$ (3), $c = 6.263$ (1) Å; $T = 296$ K: $a = 10.168$ (4), $b = 13.407$ (2), $c = 6.278$ (2) Å; $Z = 8$; $\mu(\lambda = 0.9106 \text{ Å}) = 0.74$ (6) cm⁻¹.

The Ca²⁺ ions are coordinated to eight O atoms and form chains parallel to *c* which are laterally bound through formate ions. The formate groups, strongly influenced by crystal-field effects, contract with increasing temperature.

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Introduction. Small colourless orthorhombic bipyramidal crystals were obtained by neutralizing a

solution of formic acid with calcium carbonate. At both temperatures a sphere of 1.87 (1) mm diameter was used. The unit cell and intensities were measured by neutron diffraction on the D8-facility at the HFR of the Institute Laue-Langevin (Grenoble). The space group *Pcab* (Nitta & Osaki, 1948) was confirmed at 100 K. Lattice parameters were obtained by least squares from the setting angles of 36 reflexions at 100 K and 16 reflexions at 296 K. Data collection was carried out by ω -scan techniques with variable scan and step widths. The range was $\sin \theta/\lambda \leq 0.55$ at 296 K and $\sin \theta/\lambda \leq 0.645$ at 100 K. 575 symmetry-independent reflexions at 296 K and 937 at 100 K were measured. The data reduction was carried out with the minimal $\sigma(I)/I$ method (Lehmann & Larsen, 1974); 540 and 869 symmetry-independent reflexions had $I > 2\sigma(I)$ above background [$\sigma^2(F^2) = \sigma_c^2(F^2) + (0.02 F^2)^2$, where σ_c is based on counting statistics].

The absorption coefficient was measured by transmission experiments [$\mu = 0.74$ (6) cm^{-1}] and the calculated transmission coefficients are constant within a standard deviation. The function minimized by full-matrix least squares was $\sum w(|F_o| - |F_c|)^2$ where the summation extends over all reflexions with unit weights for $F_o \geq 2\sigma$ and with $w = 0.1$ for those with $F_o < 2\sigma$. H atoms were located from difference maps. The last stage of refinement was carried out with isotropic extinction and anisotropic temperature factors. The extinction coefficients y , defined as the ratio of the observed intensity to the kinematical value, are for all reflexions greater than 0.973.

The final R for the reflexions with $F_o \geq 2\sigma$ was 0.025 (100 K) and 0.029 (296 K); for all reflexions, $R_w(F) = \sum w(|F_o| - |F_c|)^2 / \sum w F_o^2$ was 0.03 and 0.033 respectively. Atomic positional parameters are shown in Table 1.* Neutron scattering lengths were $b(\text{Ca}) = 0.466$, $b(\text{C}) = 0.6648$, $b(\text{O}) = 0.5804$ and $b(\text{H}) = -0.3740 \times 10^{-12}$ cm.

Discussion. The neutron investigation of $\alpha\text{-Ca}(\text{HCOO})_2$ is part of a study on the crystal chemistry

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32477 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester, CH1 1NZ, England.

Table 1. Positional parameters at $T = 100$ K and $T = 296$ K (second row)

	<i>x</i>	<i>y</i>	<i>z</i>
Ca	-0.13506 (10)	-0.10668 (7)	-0.03159 (16)
O(1)	-0.1345 (2)	-0.1073 (1)	-0.0277 (3)
	-0.03372 (9)	0.04840 (7)	-0.19165 (14)
	-0.0357 (2)	0.0473 (1)	-0.1906 (3)
O(2)	-0.20144 (9)	-0.0126 (7)	-0.36897 (14)
	-0.2014 (2)	-0.0144 (1)	-0.3665 (3)
O(3)	-0.20112 (8)	-0.20243 (7)	0.28129 (13)
	-0.2001 (1)	-0.2014 (1)	0.2848 (3)
O(4)	-0.02277 (9)	-0.29887 (7)	0.28374 (14)
	-0.0236 (2)	-0.2981 (1)	0.2894 (3)
C(1)	-0.11130 (8)	0.05095 (6)	-0.34690 (12)
	-0.1130 (1)	0.0489 (1)	-0.3444 (2)
C(2)	-0.12546 (7)	-0.26665 (6)	0.36576 (12)
	-0.1260 (1)	-0.2659 (1)	0.3683 (2)
H(1)	-0.5989 (2)	-0.1102 (2)	-0.0321 (3)
	-0.6013 (4)	-0.1071 (3)	-0.0369 (7)
H(2)	-0.6542 (2)	-0.7050 (2)	-0.0241 (3)
	-0.6555 (4)	-0.7059 (3)	-0.0224 (7)

$T = 100$ K

g 1.08 (9) $\times 10^{-3}$
 $R(F)$ 0.025
 $R_w(F)$ 0.029

$T = 296$ K

g 1.3 (1) $\times 10^{-3}$
 $R(F)$ 0.030
 $R_w(F)$ 0.033

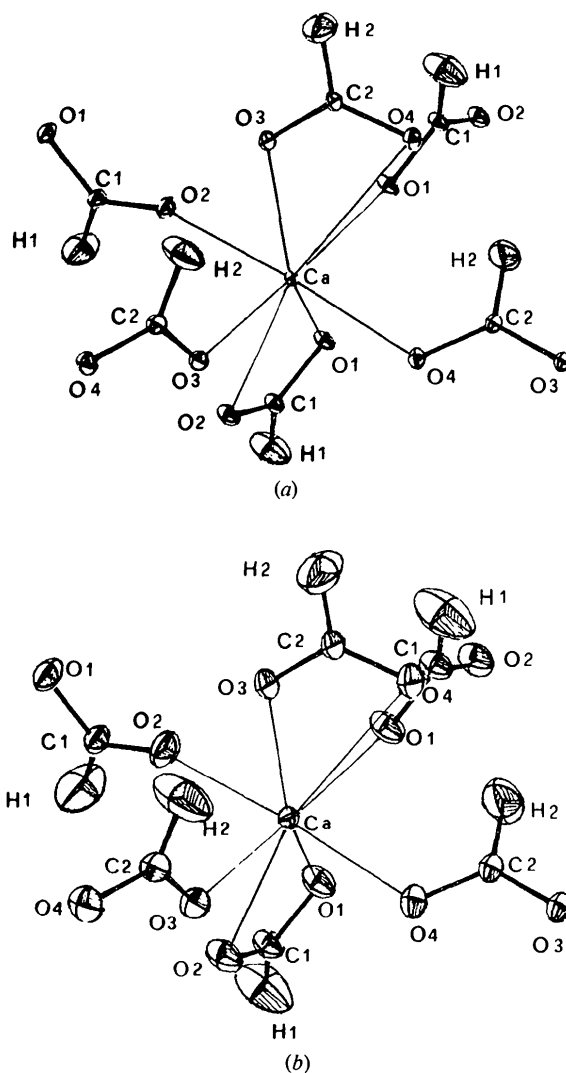


Fig. 1. The coordination of the calcium ion (a) at 100 K and (b) at 296 K. The thermal vibration ellipsoids are at a 50% probability level.

Table 2. Bond distances (\AA) and angles ($^\circ$) at 100 K and 296 K

Metal-oxygen coordination	100 K	296 K
Ca-O(1)	2.509 (1)	2.520 (2)
Ca-O(2)	2.546 (1)	2.556 (3)
Ca-O(3)	2.430 (1)	2.426 (2)
Ca-O(4)	2.347 (1)	2.347 (2)
Ca-O(1')	2.352 (1)	2.350 (2)
Ca-O(2')	2.323 (1)	2.315 (2)
Ca-O(3')	2.405 (1)	2.409 (2)
Ca-O(4')	3.420 (1)	3.433 (2)
Formate groups	100 K	296 K
C(1)-H(1)	1.098 (2)	1.085 (5)
C(1)-O(1)	1.256 (1)	1.245 (2)
C(1)-O(2)	1.254 (1)	1.244 (2)
O(1)-C(1)-O(2)	122.17 (8)	122.0 (2)
O(1)-C(1)-H(1)	118.7 (1)	118.4 (3)
O(2)-C(1)-H(1)	119.1 (1)	119.5 (3)
C(2)-H(2)	1.100 (2)	1.081 (4)
C(2)-O(3)	1.266 (1)	1.261 (2)
C(2)-O(4)	1.245 (1)	1.232 (2)
O(3)-C(2)-O(4)	125.02 (8)	125.3 (2)
O(3)-C(2)-H(2)	116.3 (1)	116.5 (3)
O(4)-C(2)-H(2)	118.7 (1)	118.2 (3)

of metal formates. Results on $\text{Zn}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ have been published (Burger & Fuess, 1977).

Comel & Mentzen (1974) have shown that a second modification, β - $\text{Ca}(\text{HCOO})_2$, exists at room temperature and report two high-temperature forms.

The present work confirms that α - $\text{Ca}(\text{HCOO})_2$ is stable between 100 and 296 K. The temperature factors are smaller at 100 K by a factor of about 2.4. The structure of α - $\text{Ca}(\text{HCOO})_2$ consists of chains of Ca^{2+} ions which are laterally bound through formate groups. Calcium formate has therefore some highly anisotropic physical properties (elastic, thermoelectric, dielectric and optical constants, coefficients of thermal expansion

and thermal conductivity, hardness) (Haussühl, 1963). The first coordination sphere around the Ca^{2+} ion is formed by seven O atoms at distances between 2.3228 (4) and 2.5577 (6) \AA at 100 K and 2.3147 (5) and 2.5562 (6) \AA at 296 K (Fig. 1). The coordination polyhedron is completed by an eighth O atom at 3.4197 (5) (100 K) and 3.4331 (5) \AA (296 K). At the two temperatures the C-O distances and angles of the formate groups are significantly different (Table 2). This corresponds to a splitting of the fundamental frequencies observed by Raman spectroscopy (Krishnan & Ramanujam, 1973) and may be explained by crystal-field effects due to the asymmetric environment of the Ca^{2+} ion. Bond lengths within the formate group tend to shorten with increasing temperature, a finding already reported by de With, Harkema & van Hummel (1976) for $\text{Mg}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$. These authors found also a smaller volume of the unit cell at low temperature despite a lengthening of one of the cell constants [$T = 130$ K: $c = 9.400$ (7) \AA , $T = 293$ K: $c = 9.382$ (7) \AA].

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