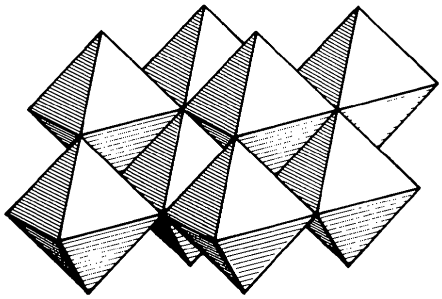

Fig. 2. The linkage of MoO_6 octahedra in the Mo_8O_{28} group.

MoO_6 as in $[H_2Mo_8O_{28}]^{6-}$ is found in an infinite chain of Mo_8O_{27} in crystals of $(NH_4)_6Mo_8O_{27}.4H_2O$ (Boschen, Buss & Krebs, 1974). The chain is constructed from the Mo_8O_{28} groups by sharing O atoms, corresponding to O(6) and its crystallographic equivalent in $[H_2Mo_8O_{28}]^{6-}$, of neighbouring groups.

All the C—C and C—N bond lengths in the three independent isopropylammonium cations are normal within experimental error. In each cation, the C—C—N angles are close to the tetrahedral values, whereas the C—C—C angle is significantly larger than 109·5°. All the NH_3 groups act as donors of hydrogen bonds to the O atoms of the polyanions and/or to water molecules. The water molecules are also bonded to the polyanion by weak hydrogen bonds. Thus, the crystal is held together mainly by the three-dimensional hydrogen-bond system shown with broken lines in Fig. 1.

When the crystals are irradiated with ultraviolet rays, some of the Mo^{VI} ions are reduced to Mo^{V}. ESR spectra of the irradiated crystals exhibit three hyperfine lines (1:2:1) owing to a superhyperfine interaction with two magnetically-equivalent H atoms (Yamase, 1978). The structure obtained suggests that the paramagnetic centre is produced at the Mo(4) site where a hydroxide group was originally coordinated, and that the two magnetically equivalent H atoms are probably bound to $O(6^i)$ and O(13) in positions *trans* to each other in the $Mo(4)O_6$ octahedron. A detailed discussion of the reduction mechanism is given elsewhere (Yamase, 1978).

The authors thank Professor Y. Iitaka for allowing them to use the automated four-circle diffractometer.

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A Redetermination of the Crystal Structures of α-Calcium Formate, α-Strontium Formate and Barium Formate by X-ray Analyses

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The crystal structure of α-calcium formate was refined to $R = 0.022$, and the result affords a good complement to the neutron analysis on the same compound [Burger, Fuess & Mason (1977). *Acta Cryst.* B**33**, 1968–1970]. The crystal structures of α-strontium formate and barium formate reported by previous workers were revised and refined to $R = 0.034$ and 0·027 respectively. These two formates are not isostructural, but the crystal structure of barium formate can be approximately transformed to that of α-strontium formate by a reorientation of one of the two independent formate groups in the asymmetric unit. The numbers of O atoms around the cations are (7 + 1) for α-calcium formate, 8 for α-strontium formate, and (8 + 1) for barium formate, where the additional terms are the number of O atoms situated at greater distances. The mean interatomic distances between the cations and their immediate neighbours are 2·421 Å for Ca^{2+}—O, 2·613 Å for Sr^{2+}—O, and 2·794 Å for Ba^{2+}—O.

Introduction

Schutte & Buijs (1964) have reported a new tetragonal modification of calcium formate. They call this new modification the β phase, and the hitherto known orthorhombic modification the α phase. Comel & Mentzen (1974) and Mentzen & Comel (1974) carried out an extensive study on the polymorphism of calcium and strontium formates, and not only confirmed the existence of the β phase, but also discovered two more modifications (γ and δ) for calcium formate, and two new modifications (β and δ) for strontium formate. Here again, the usual orthorhombic modification of anhydrous strontium formate, which crystallizes from aqueous solutions above 72°C (Ashton, Houston & Saylor, 1933), is called the α phase. No polymorphism has been reported for barium formate: a differential thermal analysis of this compound showed no phase transition from room temperature up to 300°C. It has been frequently mentioned that anhydrous strontium formate (α phase) and barium formate are isomorphous (Groth, 1910; Schutte & Buijs, 1964; Comel & Mentzen, 1974). However, the intensity distributions of Weissenberg photographs of α-strontium formate and barium formate are distinctly different, suggesting that these two formates have different crystal structures.

We are interested in the different crystal structures of calcium, strontium, and barium formates, and in the mechanism of the phase transitions, which should arise from various interactions between the alkaline-earth cations and the formate ions. As the first step of a programme, we reinvestigated the crystal structures of α-calcium formate, α-strontium formate, and barium formate, for although the crystal structures of these three compounds had been reported, it was felt that the accuracy of the result would not be sufficient. During the preparation of this manuscript, a paper on the neutron diffraction analysis of α-calcium formate at 100 and 296 K came to our notice (Burger, Fuess & Mason, 1977; hereafter referred to as BFM). It is still worthwhile to compare the positional parameters given by these authors with those obtained by us using Mo $K\alpha$ radiation. The structures of α-strontium formate and barium formate reported previously are to be revised. The correlation among the three crystal structures will be described. The crystal structure of β-calcium formate will be published in a separate paper.

Experimental

Single crystals of α-calcium formate and barium formate were obtained by slow evaporation from aqueous solutions at room temperature, and those of α-strontium formate at 80°C. All the crystals used for measurements were ground to spheres, the sizes of which are given in Table 1. The cell parameters and intensities of α-calcium formate were measured on a Rigaku four-circle diffractometer, and those for α-strontium formate and barium formate on a Philips four-circle diffractometer, always with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) at room temperature. In particular, for α-calcium formate one-quarter of the reciprocal sphere was scanned for the intensity collection. The space groups and cell parameters of the three formates reported by previous workers (Nitta & Osaki, 1948; Nitta & Saito, 1949; Sugawara, Kakudo, Saito & Nitta, 1951) were confirmed. The crystal data and experimental conditions are summarized in Table 1, where the cell parameters of α-calcium formate at 296 K reported by BFM are also given in square brackets for reference. The standard deviation of each intensity was calculated as $\sigma(I) = [\sigma^2(\text{counting statistics}) + (pI)^2]^{1/2}$, with p equal to 0·04 for α-calcium formate, 0·05 for α-strontium formate, and 0·02 for barium formate. For α-calcium formate, when symmetry-related reflexions were measured, the intensities were averaged and the standard deviations were set equal to $(\sigma_1^2 + \sigma_2^2)^{1/2}$, where σ_1 and σ_2 are the standard deviations of the two measurements respectively. The intensities were corrected for Lorentz and polarization factors, and absorption corrections were also made for α-strontium formate and barium formate.

Table 1. *Crystal data and some experimental conditions*

	α-Ca formate	α-Sr formate	Ba formate
FW	130·12	177·66	227·38
Space group	*Pbca*	$P2_12_12_1$	$P2_12_12_1$
a (Å)	13·407 (3) [13·407 (2)]*	6·864 (1)	6·794 (1)
b (Å)	10·192 (2) [10·168 (4)]*	8·752 (1)	8·890 (2)
c (Å)	6·282 (3) [6·278 (2)]*	7·262 (1)	7·655 (2)
V (Å^3)	858·40	436·26	462·35
Z	8	4	4
D_x (g cm^{-3})	2·014	2·705	3·266
D_m (g cm^{-3})	2·014†	2·696†	3·248†
Crystal size (mm) (radius of sphere)	0·10	0·12	0·09
Scan mode	θ–2θ	θ–2θ	θ–2θ
$2\theta_{\max}$ (°)	60	60	60
Scan width (°)	1·3 + 0·35 tan θ	1·7 + 0·3 tan θ	1·7 + 0·3 tan θ
Scan speed (° min^{-1})	4	4	4
Total data measured	2392	760	805
Total unique data	1252	760	805
Data with $I > 2\sigma(I)$ used for the refinement	977	509	774

* Burger, Fuess & Mason (1977).

† Ashton, Houston & Saylor (1933).

Structure determination and refinement

α-Calcium formate

A refinement was made with the initial atomic parameters reported by Nitta & Osaki (1948). Full-matrix least squares, with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for H, including the anomalous-dispersion term for Ca, and using non-zero reflexions, gave a final $R = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}022$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}029$.* The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. In the final cycle, three reflexions with small scattering angles and large $|F_o|$ values were excluded. The final atomic coordinates are listed in Table 2, where the atomic coordinates at 296 K reported by BFM are also shown in square brackets for reference.

Although the maximum disagreement in the coordinate values of the two independent investigations is 6σ, the average difference is only $1{\cdot}1\sigma$, except for H.

α-Strontium formate and barium formate

Refinements based on the atomic coordinates given by previous workers (Nitta & Saito, 1949; Sugawara, Kakudo, Saito & Nitta, 1951) failed to converge, so the usual standard heavy-atom methods were applied.

The H atoms were omitted from the refinements of the two structures since they did not converge even at the final stages. The structures were first refined by anisotropic full-matrix least squares, using all the non-zero reflexions, which gave the reliability indices $R = 0{\cdot}043$ and $R_w = 0{\cdot}050$ for α-strontium formate, and $R = 0{\cdot}029$ and $R_w = 0{\cdot}041$ for barium formate. Further refinements were performed, including the imaginary parts of the atomic scattering factors and omitting three reflexions for α-strontium formate and two for barium formate. The final reliability indices are $R = 0{\cdot}034$, $R_w = 0{\cdot}040$ for α-strontium formate, and $R = 0{\cdot}027$, $R_w = 0{\cdot}039$ for barium formate.*† The final atomic coordinates are listed in Tables 3 and 4 respectively.

The scattering factors for Ca^{2+}, Sr^{2+}, Ba^{2+}, O and C, and the anomalous-scattering factors for Ca, Sr and Ba were taken from *International Tables for X-ray Crystallography* (1974), and the scattering factors for H from the table given by Stewart, Davidson & Simpson (1965). All the calculations were performed on a NEAC 2200-250B computer at this university.

Table 2. *Fractional coordinates in α-calcium formate with e.s.d.'s in parentheses*

BFM's results are given in square brackets. [Values in square brackets are the transforms of those of BFM: $x' = -y$, $y' = -x$, $z' = -z$ for the non-hydrogen atoms, $x' = y$, $y' = -\frac{1}{2} - x$, $z' = \frac{1}{2} + z$ for H(1), and $x' = 1 + y$, $y' = -\frac{1}{2} - x$, $z' = -\frac{1}{2} + z$ for H(2).]

	x	*y*	*z*
Ca	0·10744 (2)	0·13432 (2)	0·02777 (4)
	[0·1073 (1)]	[0·1345 (2)]	[0·0277 (3)]
O(1)	−0·04761 (8)	0·03572 (11)	0·19072 (17)
	[−0·0473 (1)]	[0·0357 (2)]	[0·1906 (3)]
O(2)	0·01435 (9)	0·20134 (11)	0·36681 (18)
	[0·0144 (1)]	[0·2014 (2)]	[0·3665 (3)]
O(3)	0·20145 (8)	0·20018 (10)	−0·28472 (16)
	[0·2014 (1)]	[0·2001 (1)]	[−0·2848 (3)]
O(4)	0·29822 (8)	0·02314 (10)	−0·28871 (17)
	[0·2981 (1)]	[0·0236 (2)]	[−0·2894 (3)]
C(1)	−0·04873 (11)	0·11308 (14)	0·34326 (24)
	[−0·0489 (1)]	[0·1130 (1)]	[0·3444 (2)]
C(2)	0·26593 (11)	0·12572 (13)	−0·36703 (21)
	[0·2659 (1)]	[0·1260 (1)]	[−0·3683 (2)]
H(1)	−0·0999 (14)	0·1044 (21)	0·4406 (32)
	[−0·1071 (3)]	[0·1013 (4)]	[0·4631 (7)]
H(2)	0·2898 (17)	0·1542 (18)	−0·5068 (33)
	[0·2941 (3)]	[0·1555 (4)]	[−0·5224 (7)]

Table 3. *Fractional coordinates in α-strontium formate with e.s.d.'s in parentheses*

	x	*y*	*z*
Sr	0·24569 (13)	0·08570 (6)	0·50895 (7)
O(1)	0·0030 (10)	−0·0239 (6)	0·2475 (7)
O(2)	−0·1248 (9)	0·1469 (7)	0·4313 (8)
O(3)	0·5960 (9)	0·3555 (6)	0·1700 (7)
O(4)	0·3894 (9)	0·1575 (7)	0·1902 (7)
C(1)	−0·1394 (12)	0·0506 (8)	0·3062 (10)
C(2)	0·4771 (13)	0·2591 (10)	0·1023 (10)

Table 4. *Fractional coordinates in barium formate with e.s.d.'s in parentheses*

	x	*y*	*z*
Ba	0·32737 (6)	0·08618 (5)	0·53803 (6)
O(1)	−0·0038 (9)	0·0761 (9)	0·3256 (9)
O(2)	−0·2717 (10)	0·1115 (8)	0·4884 (8)
O(3)	0·6176 (10)	0·3316 (8)	0·1705 (9)
O(4)	0·4014 (11)	0·1450 (8)	0·1859 (9)
C(1)	−0·1778 (13)	0·0454 (9)	0·3714 (12)
C(2)	0·5026 (14)	0·2396 (10)	0·1041 (11)

Description of the structure

α-Calcium formate

The coordination of the Ca ion is shown in BFM. There are seven O atoms at distances less than 2·6 Å from the Ca ion and one more, O(4), at 3·432 Å (see

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* Lists of structure factors and thermal parameters for the three crystals have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33580 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See previous footnote.

† Almost the same result for barium formate was obtained independently by Kakudo (private communication, October, 1977).

Table 5). We may take the seven O atoms as the immediate neighbours. Two of these, O(1) and O(2), are from the same formate group acting as chelate ligand (see type I in Fig. 6), and the rest are from five different formate groups. Distinct elongations of the Ca—O distances for the chelate O atoms [2·526 Å for Ca—O(1), 2·561 Å for Ca—O(2)], as compared with those for the other O atoms (2·321–2·428 Å), are found. The decahedron formed by the seven O atoms can be regarded as a deformed oblique pentagonal bipyramid. Each decahedron shares three edges [O(1)—O(1^{i}), O(2)—O(3^{iii}) and O(2^{ii})—O(3)], forming a hexagonal network of a pleated layer running parallel to the *bc* plane. These pleated layers stack along the *a* axis through the operations *a* and *b*, at an interval of *a*/2, and are held together through the C atoms of the formate groups at three corners [O(3), O(3^{iii}) and O(4^{iv})] of each decahedron. We shall call this mode of linkage 'carbon bridge'. The carbon bridges between the pleated layers can be seen in Fig. 1.

Table 5. *Interionic distances* (Å) *with e.s.d.'s in parentheses*

α-Ca(HCOO)$_2$		α-Sr(HCOO)$_2$	
Ca—O(1)	2·526 (1)	Sr—O(1)	2·702 (6)
—O(1^{i})	2·352 (1)	—O(1^{i})	2·504 (6)
—O(2)	2·561 (1)	—O(2)	2·659 (6)
—O(2^{ii})	2·321 (1)	—O(2^{ii})	2·541 (5)
—O(3)	2·428 (1)	—O(3^{iii})	2·599 (5)
—O(3^{iii})	2·413 (1)	—O(3^{iv})	2·633 (5)
—O(4^{iv})	2·346 (1)	—O(4)	2·594 (5)
—O(4)	3·432 (1)	—O(4^{i})	2·669 (6)

Ba(HCOO)$_2$			
Ba—O(1)	2·777 (6)	Ba—O(3^{iv})	2·794 (7)
—O(1^{i})	2·892 (6)	—O(4)	2·792 (7)
—O(2^{ii})	2·778 (7)	—O(4^{i})	2·814 (7)
—O(2^{v})	2·760 (7)	—O(1^{ii})	3·379 (7)
—O(3^{iii})	2·746 (7)		

Symmetry codes: (i) $-x,-y,-z$; (ii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, -y, \frac{1}{2}+z$ for α-calcium formate; and (i) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (iv) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (v) $1+x, y, z$ for α-strontium formate and barium formate.

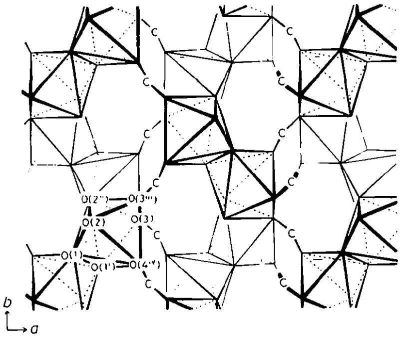

Fig. 1. Structure of α-calcium formate, showing the linkage between the pleated layers.

α-Strontium formate

Fig. 2 shows the atomic arrangement projected along the *a* axis. Each Sr ion is surrounded by eight O atoms at the distances shown in Table 5. Two of these eight O atoms [O(1) and O(2)] are from a chelate formate group, and the rest are from six different formate groups. A similar tendency towards the elongation of the Sr—O distances for the chelate O atoms is found, but the effect is not so marked as in α-calcium formate. The dodecahedron formed by these eight O atoms may be regarded, roughly speaking, as a deformed antiprism. A similar coordination of O atoms around a Sr ion is reported in the structure of strontium formate dihydrate (Galigné, 1971), and it is interesting that the mean Sr—O distances for the two antiprisms agree quite well: 2·615 Å in $Sr(HCOO)_2.2H_2O$ and 2·613 Å in α-$Sr(HCOO)_2$. The linking of coordination polyhedra is quite different from that in α-calcium formate. Each dodecahedron shares its two faces [O(1), O(3^{iv}), O(4), and O(1^{i}), O(3^{iii}), O(4^{i})] to form a column running along the *c* axis, as is shown in Fig. 3, and these columns are stacked together by virtue of the screw operations, 2_1, along the *a* and *b* axes. These columns are linked together in two ways: (1) by the carbon bridges at four corners [O(3^{iii}), O(3^{iv}), O(4) and O(4^{i})] and (2) by sharing two corners [O(2) and O(2^{ii})] of each dodecahedron. Pauling's electrostatic valence rule is satisfied.

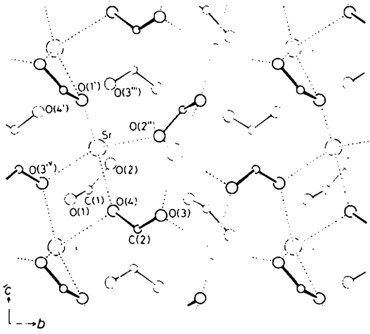

Fig. 2. Structure of α-strontium formate projected along [100].

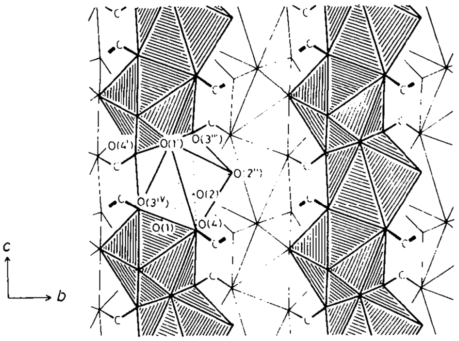

Fig. 3. Structure of α-strontium formate, showing the linking of coordination polyhedra.

Barium formate

Fig. 4 shows the atomic arrangement projected along the *a* axis. When compared to Fig. 2, a close resemblance between the structures of barium formate and α-strontium formate can be seen. The main difference lies in the orientation of each of the two independent formate groups in the two structures. It follows that, in the structure of barium formate, around each Ba ion, in addition to eight O atoms as immediate neighbours (at 2·746–2·892 Å) there is another O atom at 3·379 Å (see Table 5). No chelate ligand is found, and this is reflected in the interatomic distances between the Ba ion and the surrounding O atoms. These eight O atoms form an undecahedron, since O(1^{i}), O(2^{ii}), O(2^{v}) and O(3^{iii}) are found to be almost coplanar: the maximum deviation from the best plane being only 0·03 Å. Each undecahedron shares its two faces [O(1), O(3^{iv}), O(4) and O(1^{i}), O(3^{iii}), O(4^{i})], as in the structure of α-strontium formate, to form a column and these columns are stacked together along the *c* axis. The columns are linked together by the carbon bridges at all corners of the undecahedron, and also by sharing two corners [O(2^{ii}) and O(2^{v})]. The linking of the coordination polyhedra is shown in Fig. 5, where the similarity of the two structures is again clear. Pauling's electrostatic valence rule is satisfied.

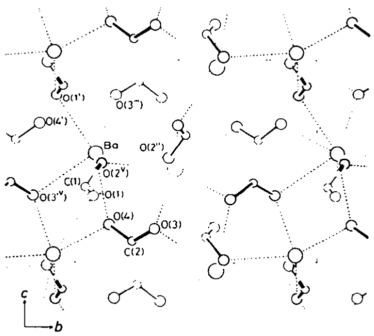

Fig. 4. Structure of barium formate projected along [100].

The size of the formate groups

There are two independent formate groups in each of the asymmetric units of the three formate structures, and the accuracy of the results permits us to discuss the differences in size of these six formate groups in terms of their environments or of the structural principles. The modes of coordination of the six formate groups to the cations are shown schematically in Fig. 6, and the bond distances and valence angles in these six formate groups are given in Table 6. A summary of the results follows.

α-Calcium formate

This is the most carefully studied, and it is interesting to see a close agreement between the coordinates of the non-hydrogen atoms obtained with Mo *Kα* radiation and those with neutrons by BFM. The differences in the C–H bond distances from the two investigations can also be compared to those reported in similar complementary researches. The H, C and O atoms in both type I and type II are found to be coplanar, the maximum deviations from the least-squares planes being 0·005 Å for both type I and type II.

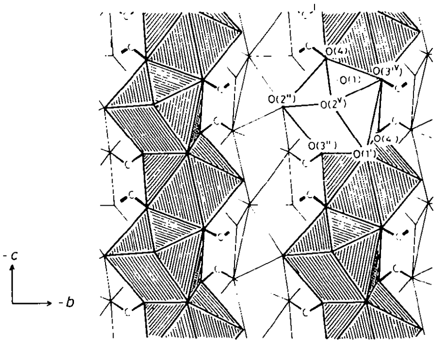

Fig. 5. Structure of barium formate, showing the linking of coordination polyhedra.

Table 6. *Bond distances* (Å) *and angles* (°) *in the formate groups with e.s.d.'s in parentheses*

BFM's results are given in square brackets.

α-Ca(HCOO)$_2$			α-Sr(HCOO)$_2$		Ba(HCOO)$_2$	
C(1)–O(1)	1·241 (2)	[1·245 (2)]	C(1)–O(1)	1·25 (1)	C(1)–O(1)	1·26 (1)
–O(2)	1·244 (2)	[1·244 (2)]	–O(2)	1·24 (1)	–O(2)	1·25 (1)
–H(1)	0·92 (2)	[1·085 (5)]				
C(2)–O(3)	1·261 (2)	[1·261 (2)]	C(2)–O(3)	1·27 (1)	C(2)–O(3)	1·24 (1)
–O(4)	1·234 (2)	[1·232 (2)]	–O(4)	1·25 (1)	–O(4)	1·25 (1)
–H(2)	0·98 (2)	[1·081 (4)]				
O(1)–C(1)–O(2)	122·9 (2)	[122·0 (2)]	O(1)–C(1)–O(2)	122·7 (8)	O(1)–C(1)–O(2)	125·2 (8)
–H(1)	117 (1)	[118·4 (3)]				
O(2)–C(1)–H(1)	120 (1)	[119·5 (3)]				
O(3)–C(2)–O(4)	125·9 (2)	[125·3 (2)]	O(3)–C(2)–O(4)	125·7 (7)	O(3)–C(2)–O(4)	125·7 (8)
–H(2)	114 (1)	[116·5 (3)]				
O(4)–C(2)–H(2)	120 (1)	[118·2 (3)]				

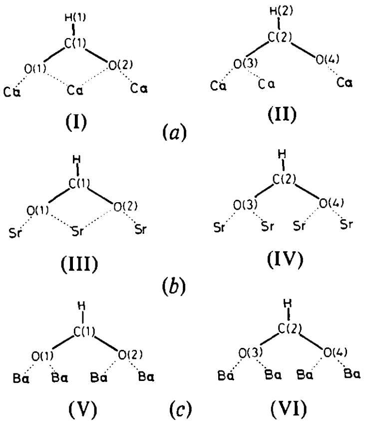

Fig. 6. Environments of the formate groups in (*a*) α-$Ca(HCOO)_2$, (*b*) α-$Sr(HCOO)_2$ and (*c*) $Ba(HCOO)_2$.

The C—O *bond distances*

Except for type II, the two C—O bonds are disposed symmetrically, as in most other formate structures. The mean distances of the symmetrical C—O bonds are 1·243 Å for α-calcium formate and 1·25 Å for both α-strontium formate and barium formate. These values can be compared with those reported for $Li(HCOO).H_2O$ (1·244, 1·248 Å; Enders-Beumer & Harkema, 1973), Na(HCOO) (1·246 Å; Markila, Rettig & Trotter, 1975), and $Mg(HCOO)_2.2H_2O$ (at 293 K, 1·241–1·254 Å; de With, Harkema & van Hummel, 1976). Type II shows a rather unusual unsymmetrical disposition of the two C—O bonds (incomplete resonance). The shorter C—O bond is coordinated to one cation, and the longer to two cations. A similar example is reported for the N—O bonds of nitrate groups in $Ca(NO_3)_2.3H_2O$ (Leclaire, 1976).

The O—C—O *bond angles*

As can be seen in Fig. 6, type I and type III both have the chelate-like structure with the cation. The O—C—O bond angles of these formate groups (122·9 and 122·7°) are definitely smaller than those of the others (125·2–125·9°) (see Table 5). The latter values compare well with those reported for $Li(HCOO).H_2O$ (125·5°), Na(HCOO) (126·3°), and $Mg(HCOO)_2.2H_2O$ (125·8 and 125·9°).

The effective ionic radius of the O *atom in the formate group*

The mean interatomic distances between the cations and their neighbouring O atoms in the three formates are 2·421 Å for Ca^{2+}—O, 2·613 Å for Sr^{2+}—O, and 2·794 Å for Ba^{2+}—O. If we subtract from these values the effective ionic radii of these cations assigned by Shannon & Prewitt (1969) (1·07 Å for $^{VII}Ca^{2+}$, 1·25 Å for $^{VIII}Sr^{2+}$, and 1·42 Å for $^{VIII}Ba^{2+}$), we obtain the values 1·35, 1·36 and 1·37 Å, respectively. We may therefore assign 1·36 ± 0·01 Å as the effective ionic radius of the O atom in the formate group, which is, incidentally, the same as that assigned by Shannon & Prewitt for $^{III}O^{2-}$.

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