atomes C(1) et C(2) qui se trouvent sur les pseudo-axes d'ordre 6_3 et 3 partagent les atomes d'oxygène avec les polyèdres [MO_{10}] en formant des couches parallèles à (001) et des canaux vides le long des pseudo-axes 6_3. Il y a deux couches par période *c* de la maille, les polyèdres [MO_{10}] partagent aussi une arête en commun ce qui relie les couches entre elles. Les polyèdres [NaO_8] sont reliés entre eux par des faces communes, ils forment des colonnes en zigzag selon la direction de l'axe *c*. L'ensemble des couches de polyèdres [MO_{10}] et des colonnes [NaO_8] sont reliés entre eux par des faces communes et des groupements carboxyles en formant d'autres canaux vides le long des pseudo-axes 3 (Fig. 2).

Comme le taux d'occupation de *M*(1) 1,114 (3) est plus élevé que celui de *M*(2) 0,947 (3) et *M*(3) 0,962 (3), nous pouvons imaginer que les sites *M*(1) sont occupés d'une manière préférentielle par les atomes les plus lourds c'est à dire par les terres rares. Nous remarquons dans le Tableau 2 que les distances moyennes Na—O sont égales pour les trois sites à 2,48 Å; alors que pour *M*, elles sont légèrement différentes: *M*(1)—O (2,61 Å) plus petite que *M*(3)—O (2,63 Å) et que *M*(2)—O (2,64 Å).

Les valeurs des distances interatomiques O—O varient pour [MO_{10}] de 2,745 à 3,755 Å, pour [NaO_8] de 2,901 à 3,562 Å et pour le groupement carboxyle de 2,174 à 2,241 Å.

Il est fort probable que la majorité des minéraux de type burbankite cristallise dans le système monoclinique et est pseudo-hexagonale.

Nous remercions Dr F. Cesbron de nous avoir proposé cette étude et fourni le cristal.

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The Structure of Lithium Formate

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Abstract. LiHCOO, $M_r = 51{\cdot}956$, monoclinic, $C2/c$, $a = 12{\cdot}054\ (5)$, $b = 12{\cdot}063\ (4)$, $c = 13{\cdot}518\ (5)$ Å, $\beta = 100{\cdot}96\ (1)^\circ$, $V = 1929{\cdot}6\ (9)$ Å^3, $Z = 32$, $D_x = 1{\cdot}431$ Mg m^{-3}, Mo $K\bar{\alpha}$ $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}115$ mm^{-1}, $F(000) = 832$, $T = 295$ K. The refined structure gave $R(F^2) = 0{\cdot}047$ for 1422 observed reflections with $F^2 > 2\sigma(F^2)$. Every O atom in the structure is bound to two Li$^+$ ions and every Li$^+$ ion is tetrahedrally bound to four O atoms, forming a succession of ionic ring systems involving four, six, eight, *etc.* members. The Li—O distances lie in the range 1·927 (2)–1·967 (2) Å; the C—O distances in the range 1·232 (2)–1·245 (2) Å.

Introduction. The structure of the title compound has been determined in order to explore similarities and differences in the anhydrous and hydrated lithium formate, and other alkali and alkaline earth formates. The lithium formate monohydrate structure has been the subject of several X-ray studies (Mohana Rao & Viswamitra, 1971; Torre, Abrahams & Bernstein, 1971; Thomas, Tellgren & Almlöf, 1975; Harkema, de With & Keute, 1977; Thomas, 1978) and one neutron diffraction investigation (Tellgren, Ramanujam & Liminga, 1974), all at room temperature. No anhydrous structure has been reported in the literature, however.

Experimental. *Crystal preparation.* A small single crystal of LiHCOO was prepared from analytical grade LiHCOO.H_2O by heating approximately 0·5 g of the monohydrate in a melting-point microscope above the dehydration temperature (≃ 367 K) and up to the melting point of the anhydrous salt (≃ 543 K). At the

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Table 1. *Data collection details and R values for* LiHCOO

Diffractometer	Stoe
λ(Mo $K\bar{\alpha}$)	0·71069 Å
Temperature	295 K
Scan type	ω–2θ
Step (2θ)	0·03°
Scan range	$3 \le 2\theta \le 50°$
$(\sin\theta/\lambda)_{\max}$	0·595 Å^{-1}
h,k,l range	$-14 \le h \le 14, -14 \le k \le 14,$ $0 \le l \le 16$
Time/step	0·5–2·0 s ($3 \le 2\theta \le 30°$) 0·5–3·0 s ($30 \le 2\theta \le 50°$)
No. of steps/reflection	70
No. of test reflections	5
Interval between tests	180 min
No. of reflections collected	6008
No. of unique reflections	1697
No. of reflections with $F^2 > 2\sigma(F^2)$	1422
Transmission factor range	0·969–0·978
$R_{\rm int} = \sum(\lvert F_o - \langle F_o \rangle \rvert)/\sum F_o$	0·028
$S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m-n)]^{1/2}$	2·01
$R(F^2) = \sum\lvert F_o^2 - F_c^2\rvert / \sum F_o^2$	0·048 (all reflections) 0·047 [$F_o^2 > 2\sigma(F_o^2)$]
$wR(F^2) = [\sum w(\lvert F_o^2 - F_c^2\rvert)^2/\sum wF_o^4]^{1/2}$	0·060 (all reflections)

Table 2. *Fractional positional parameters and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$$

	x	y	z	$U_{\rm eq}$
O(11)	0·56023 (8)	0·40047 (8)	0·38576 (7)	0·0362
O(12)	0·67930 (8)	0·44638 (9)	0·28656 (7)	0·0369
O(21)	0·35107 (8)	0·39821 (9)	0·43992 (7)	0·0393
O(22)	0·16672 (8)	0·42167 (9)	0·38948 (7)	0·0372
O(31)	0·42798 (8)	0·03445 (8)	0·35046 (7)	0·0375
O(32)	0·48159 (9)	0·16972 (8)	0·45954 (7)	0·0373
O(41)	0·59425 (8)	0·19043 (8)	0·67853 (7)	0·0384
O(42)	0·56706 (9)	0·36503 (8)	0·63026 (7)	0·0399
C(1)	0·65503 (12)	0·40587 (12)	0·36446 (10)	0·0418
C(2)	0·25214 (11)	0·39573 (13)	0·45218 (10)	0·0417
C(3)	0·44423 (12)	0·13305 (12)	0·37408 (10)	0·0403
C(4)	0·60861 (12)	0·29147 (12)	0·69023 (11)	0·0424
Li(1)	0·49659 (19)	0·32850 (19)	0·49178 (16)	0·0399
Li(2)	0·41925 (19)	0·47767 (19)	0·34017 (16)	0·0348
Li(3)	0·66981 (19)	0·06151 (19)	0·74564 (16)	0·0341
Li(4)	0·48832 (18)	0·09612 (19)	0·58820 (16)	0·0347
H(1)	0·720 (2)	0·370 (1)	0·414 (1)	0·071
H(2)	0·242 (1)	0·367 (1)	0·520 (1)	0·067
H(3)	0·425 (1)	0·189 (1)	0·320 (1)	0·067
H(4)	0·654 (2)	0·318 (2)	0·755 (1)	0·072

melting point, the temperature was carefully adjusted until only one crystal seed remained in the melt. Very slow cooling then produced a large single crystal, from which a smaller crystal with well developed faces was cut.

Unit-cell determination. Unit-cell determination (and data collection) was performed on a MicroVAXII-controlled four-circle Stoe diffractometer using graphite-monochromatized Mo $K\bar{\alpha}$ radiation ($\lambda = 0{\cdot}71069$ Å) at room temperature. The crystal was sealed in a glass capillary. Unit-cell dimensions were determined using 24 well centered reflections with $10 \le 2\theta \le 30°$. The systematic absences showed the space group to be either *Cc* (No. 9) or *C*2/*c* (No. 15). Data collection details are given in Table 1.

Data collection. A total of 6008 reflections ($\pm h,\pm k,l$) were collected: one data set in the range $3 \le 2\theta \le 30°$ using a primitive unit cell (*C*-centering check) and two independent data sets in the range $30 \le 2\theta \le 50°$ using a *C*-centered cell.

Intensities were corrected for background by a profile analysis procedure (Lehmann & Larsen, 1974), and for a small intensity loss (in total $\simeq$ 6%) on the basis of the variation of the five test reflections. Lorentz, polarization and absorption corrections were made [crystal size: 0·210 × 0·275 × 0·280 mm; crystal volume: 0·022 mm^3; crystal faces: $\{010\}$, $\{10\bar{1}\}$, $(11\bar{3})$, $(\bar{3}0\bar{1})$]. After averaging, the remaining 1697 unique reflections [1422 with $F^2 > 2\sigma(F^2)$] were used in the subsequent structure determination and refinements. The calculations were carried out on a MicroVAXII computer at the Institute of Chemistry, Uppsala University, and on a VAX 8650 at the State Computer Center, Espoo.

Table 3. *Bond lengths* (Å) *and angles* (°) *in* LiHCOO

HCOO$^-$ ions			
C(1)–O(11)	1·232 (2)	O(11)–C(1)–O(12)	126·6 (1)
C(1)–O(12)	1·245 (2)	O(11)–C(1)–H(1)	117·0 (10)
C(1)–H(1)	1·03 (2)	O(12)–C(1)–H(1)	116·4 (10)
C(2)–O(21)	1·235 (2)	O(21)–C(2)–O(22)	126·7 (1)
C(2)–O(22)	1·243 (2)	O(21)–C(2)–H(2)	114·3 (10)
C(2)–H(2)	1·01 (2)	O(22)–C(2)–H(2)	118·9 (10)
C(3)–O(31)	1·238 (2)	O(31)–C(3)–O(32)	126·5 (1)
C(3)–O(32)	1·239 (2)	O(31)–C(3)–H(3)	117·6 (10)
C(3)–H(3)	0·99 (2)	O(32)–C(3)–H(3)	115·9 (10)
C(4)–O(41)	1·237 (2)	O(41)–C(4)–O(42)	126·3 (1)
C(4)–O(42)	1·241 (2)	O(41)–C(4)–H(4)	118·2 (11)
C(4)–H(4)	1·00 (2)	O(42)–C(4)–H(4)	115·4 (11)
Li$^+$ environments			
Li(1)–O(11)	1·953 (2)	Li(3)–O(12$^{\rm iii}$)	1·951 (2)
Li(1)–O(21)	1·951 (2)	Li(3)–O(31$^{\rm iv}$)	1·958 (2)
Li(1)–O(32)	1·965 (2)	Li(3)–O(22$^{\rm v}$)	1·962 (2)
Li(1)–O(42)	1·953 (2)	Li(3)–O(41)	1·938 (2)
Li(2)–O(11)	1·933 (2)	Li(4)–O(32)	1·941 (2)
Li(2)–O(12$^{\rm i}$)	1·927 (2)	Li(4)–O(31$^{\rm iv}$)	1·967 (2)
Li(2)–O(21)	1·958 (2)	Li(4)–O(22$^{\rm vi}$)	1·961 (2)
Li(2)–O(42$^{\rm ii}$)	1·940 (3)	Li(4)–O(41)	1·955 (2)

Codes refer to the following equivalent positions: (i) $1-x, y, \frac{1}{2}-z$; (ii) $1-x, 1-y, 1-z$; (iii) $\frac{3}{2}-x, \frac{1}{2}-y, 1-z$; (iv) $1-x, -y, 1-z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (vii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$.

Structure determination and refinement. The structure was determined using the direct-methods procedure of the *SHELXS*86 program (Sheldrick, 1985), which revealed all non-H atoms. After refinement involving isotropic temperature factors (with the *SHELX*76 program, Sheldrick, 1976), the H atoms were located from a $\Delta\rho$ synthesis. Refinement was made using the least-squares program *DUPALS* (Lundgren, 1982) in the centrosymmetric space group *C*2/*c*, following a clear indication from intensity statistics of the presence of a center of symmetry. Moreover, refinement within the non-centrosymmetric space group did not converge.

Isotropic extinction corrections models (type I and type II) according to Becker & Coppens (1974*a*,*b*; 1975) were applied. No reflection had a y_{ext} value less than 0·98 ($F_o^2{}_{,\mathrm{obs}} = y_{\mathrm{ext}}.F_o^2{}_{,\mathrm{corr}}$). No extinction correction was included in the final refinement. The function minimized was $\sum w(F_o^2 - F_c^2)$, where $w^{-1} = \sigma^2_{\mathrm{count}}(F_o^2) + (kF_o^2)^2$, with $\sigma^2_{\mathrm{count}}$ based on Poisson counting statistics. The value for k was set empirically to 0·02 on the basis of a weight analysis following the least-squares cycles. Atomic scattering factors for O, C, Li^+ and H, and anomalous-dispersion corrections for O and C were taken from *International Tables for X-ray Crystallography* (1974). In the final refinement, one scale factor, positional parameters for all atoms, anisotropic displacement parameters for non-H atoms and isotropic displacement parameters for H atoms were refined; 161 parameters in all. Maximum shift to e.s.d. ratio in the final cycle of refinement was 0·02.

Discussion. *The structure.* The final positional parameters and equivalent isotropic temperature factors are listed in Table 2.* Interatomic distances and angles are given in Table 3. An illustration of the asymmetric unit showing the labeling of the atoms is given in Fig. 1. The environments around the Li^+ and HCOO^- ions are illustrated in Fig. 2. These also show the various ring systems formed when the asymmetric units link together. Although crystallographically non-equivalent, the C(1) and C(2) formate ions are seen to have rather similar environments. This is also true for the C(3) and C(4) formate ions, the $\mathrm{Li(1)}^+$ and $\mathrm{Li(2)}^+$, and the $\mathrm{Li(3)}^+$ and $\mathrm{Li(4)}^+$ ions, respectively.

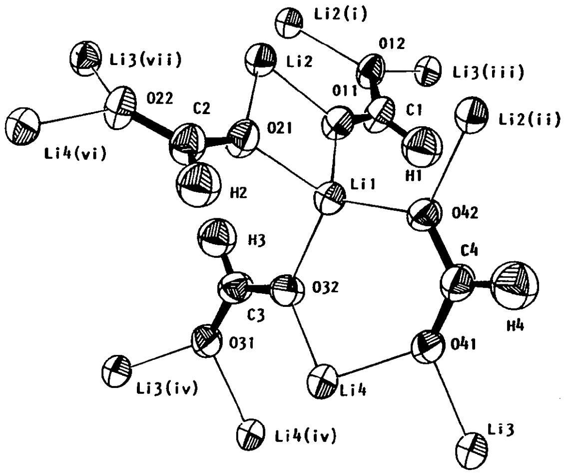

Fig. 1. An *ORTEP* illustration of the asymmetric unit of LiHCOO comprising four HCOO^- and four Li^+ ions. Li^+ ions from surrounding asymmetric units are also shown. The symmetry codes are those listed in Table 3. The thermal ellipsoids are drawn to include 50% probability.

The structure consists of a three-dimensional network, in which all Li^+ ions are tetrahedrally coordinated by four O atoms. The Li^+ ions are linked to each other either *via* one O atom or an O—C—O bridge, thus forming rings of various sizes (see Fig. 2).† For each of the two different four-membered ring systems, symmetry-related rings are linked together by O atoms, as shown in Fig. 3. The resulting ten-membered rings are symmetrically different; the Li(1)—Li(2) ring has a center of symmetry, while the Li(3)—Li(4) ring is formed by translation.

The HCOO^- *ions.* The environments around the HCOO^- ions are shown in Figs. 1 and 2. The four crystallographically independent HCOO^- ions are linked *via* the Li^+ ions in four-, six-, eight- and

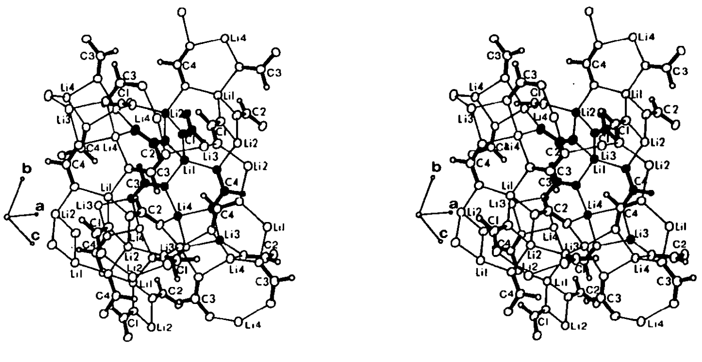

Fig. 2. A stereoscopic illustration of the molecular packing, showing the different rings formed by symmetry in the three-dimensional network. The atoms of the original asymmetric unit, referred to in Table 2, are blackened.

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* Lists of structure factors, anisotropic displacement parameters, O—Li—O angles and C—O—Li angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51347 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Four-membered planar rings: [—Li(1)—O(21)—Li(2)—O(11)— and —Li(3)—O(41)—Li(4)—$\mathrm{O(31^{iv})}$—]; six-membered rings: [—Li(1)—O(42)—C(4)—O(41)—Li(4)—O(32)— and —Li(2)—O(21)—C(2)—O(22)—$\mathrm{Li(3^{vii})}$—$\mathrm{O(2^{i})}$—]; eight-membered rings: [—Li(4)—O(32)—C(3)—O(31)—$\mathrm{Li(4^{iv})}$—$\mathrm{O(32^{iv})}$—$\mathrm{C(3^{iv})}$—$\mathrm{O(31^{iv})}$— and —Li(2)—O(11)—C(1)—O(12)—$\mathrm{Li(2^{viii})}$—$\mathrm{O(11^{viii})}$—$\mathrm{C(1^{viii})}$—$\mathrm{O(12^{viii})}$]; and ten-membered rings: [—O(42)—$\mathrm{Li(1)}\!<\!\begin{smallmatrix}\mathrm{O(21)}\\ \mathrm{O(11)}\end{smallmatrix}\!>\!\mathrm{Li(2)}$—$\mathrm{O(42^{ii})}$—$\mathrm{Li(1^{ii})}\!<\!\begin{smallmatrix}\mathrm{O(21^{ii})}\\ \mathrm{O(11^{ii})}\end{smallmatrix}\!>\!\mathrm{Li(2^{ii})}$— and $\mathrm{Li(3^{ix})}\!<\!\begin{smallmatrix}\mathrm{O(41^{ix})}\\ \mathrm{O(31^{x})}\end{smallmatrix}\!>\!\mathrm{Li(4^{ix})}$—$\mathrm{O(22^{v})}$—$\mathrm{Li(3)}\!<\!\begin{smallmatrix}\mathrm{O(41)}\\ \mathrm{O(31^{iv})}\end{smallmatrix}\!>\!\mathrm{Li(4)}$—O(22)—]. Symmetry codes (i)–(vii) refer to those given in Table 3; the other symmetry codes are: (viii) = $1-x$, $1+y$, $\frac{1}{2}-z$, (ix) = $1-x$, y, $\frac{3}{2}-z$ and (x) = x, $-y$, $\frac{1}{2}+z$.

ten-membered rings, as discussed above. The $HCOO^-$ ions are planar with four coordinated Li^+ ions lying roughly in the same plane, thus forming planes perpendicular to the unit-cell axes. Dihedral angles between the Li—O—Li and the respective $HCOO^-$ ion plane lie in the range 11·8–30·8° with a mean value of 17·7°. Dihedral angles between the Li—O—Li planes involving the same $HCOO^-$ ion vary between 0·8 and 46·6° with a mean of 27·6°.

The overall structure of LiHCOO is very different from that of $LiHCOO.H_2O$. The nearest environments of the $HCOO^-$ ions also differ: each O atom binds to two Li^+ ions in the anhydrous structure while in the monohydrate one of the O atoms binds to one Li^+ ion and accepts a 2·714 (2) Å O···O hydrogen bond from the water molecule (Tellgren *et al.*, 1974). The C—O bond lengths in the two structures agree, however: 1·243 (2) and 1·247 (2) Å in the monohydrate, and 1·232 (2)–1·245 (2) Å in the anhydrous structure.

A number of other formate structures have been studied by X-ray and/or neutron diffraction; see Table 4. In the NaHCOO structure, each formate O atom binds to four Na^+ ions, two lying roughly in the formate plane, the other two forming an O—Na^+ bond approximately perpendicular to the formate plane. Both C—O distances are 1·2560 (3) Å. In KHCOO, each O atom binds to four cations, all lying out of the formate plane. The C—O bond distances are here 1·2426 (7) Å. In $Mg(HCOO)_2.2H_2O$, there are two crystallographically non-equivalent $HCOO^-$ ions; each O binds to one Mg^{2+} ion and accepts one H bond from a water molecule. The C—O bond lengths (at 293 K) are in the range 1·241 (2)–1·254 (2) Å. The O atoms of the $HCOO^-$ ions in the alkaline earth structures listed above all bind to one or two cations; the C—O bond lengths lie between 1·232 (2) and 1·27 (1) Å. In short, for all the different formate environments present in the structures discussed here, the C—O distance varies between 1·23 and 1·27 Å. For the strongly H-bonded $H(HCOO)_2^-$ ion in $KH(HCOO)_2$ (O···O is 2·437 Å at 120 K; Hermansson, Tellgren & Lehmann, 1983), the C—O bond lengths involving the O atoms participating in the H bond are both 1·276 (1) Å at 120 K and 1·260 (2) Å at 295 K. These C—O bond lengths can be compared with the typical C—OH carbonyl bond length of ≃ 1·31 Å and carboxylate C$\overset{...}{—}$O bond length of ≃ 1·25 Å (see Borthwick, 1980).

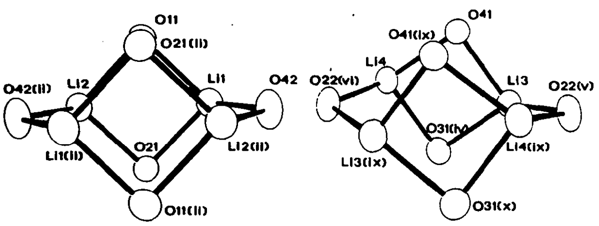

Fig. 3. Schematic representation of the two different ten-membered rings. Symmetry codes (i)–(vii) refer to those given in Table 3; the other symmetry codes are: (viii) = $1-x$, $1+y$, $\frac{1}{2}-z$, (ix) = $1-x$, y, $\frac{3}{2}-z$ and (x) = x, $-y$, $\frac{1}{2}+z$.

Table 4. *C—O distances (Å) for the* $HCOO^-$ *ion in different crystalline environments; the third column gives the nearest neighbors around each formate* O *atom*

Structure	C—O	O neighbors	Reference
LiHCOO	1·232(2)–1·245 (2)	2 Li^+	This work
NaHCOO	1·2560 (3)	4 Na^+	Fuess, Bats, Dannöhl, Meyer & Schweig (1982)
KHCOO	1·226 (1) (120K) 1·217 (1) (295 K)	3 K^+	Bats & Fuess (1980)
	1·235 (1) (120 K) 1·229 (1) (295 K)	4 K^+	
α-$Ca(HCOO)_2$	1·245 (1)–1·266 (1) (100 K) 1·232 (2)–1·261 (2) (296 K)	2 Ca^{2+}	Burger, Fuess & Mason (1977)
α-$Sr(HCOO)_2$	1·24 (1)–1·27 (1)	2 Sr^{2+}	Watanabe & Matsui (1978)
$Ba(HCOO)_2$	1·24 (1)–1·26 (1)	2 Ba^{2+}	Watanabe & Matsui (1978)
$LiNa(HCOO)_2.H_2O$	1·251	3 Na^+	Furmanova, Andrianov & Dobrzhanskii (1986)
	1·245	Li^+, H_2O	
	1·258	3 Na^+	
	1·241	2 Li^+	
$Mg(HCOO)_2.2H_2O$	1·254 (2)–1·265 (2) (130 K) 1·241 (2)–1·254 (2) (293 K)	Mg^{2+}, H_2O	de With, Harkema & van Hummel (1976)

The Li^+ *ions*. The coordination number for Li^+ in stoichiometric compounds varies between four and six, the former being the most common. In the present structure, all Li^+ ions display similarly distorted tetrahedral coordination. The Li^+ ions participate in different ring systems, as discussed above. The four-membered rings are responsible for distortion of the tetrahedral coordination spheres around the Li^+ ions, where one O—Li—O angle around each lithium ion is approximately 90°.

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The Structures of Barium D-Galactarate Monohydrate and Calcium D-Galactarate Tetrahydrate

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Abstract. $Ba^{2+}.C_6H_8O_8^{2-}.H_2O$, $M_r = 363{\cdot}48$, monoclinic, $P2_1/a$, $a = 10{\cdot}333\,(5)$, $b = 10{\cdot}620\,(1)$, $c = 10{\cdot}641\,(6)$ Å, $\beta = 117{\cdot}61\,(5)°$, $V = 1034{\cdot}7$ Å^3, $Z = 4$, $D_x = 2{\cdot}333$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 295{\cdot}6$ cm^{-1}, $F(000) = 696$, $T = 293$ K, $R = 0{\cdot}03$ for 1866 observed reflections and 175 parameters refined. $Ca^{2+}.C_6H_8O_8^{2-}.4H_2O$, $M_r = 320{\cdot}2$, orthorhombic, $Pcan$, $a = 7{\cdot}349\,(1)$, $b = 11{\cdot}632\,(1)$, $c = 15{\cdot}118\,(2)$ Å, $V = 1292{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}646$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 46{\cdot}37$ cm^{-1}, $F(000) = 664$, $T = 293$ K, $R = 0{\cdot}032$ for 1156 observed reflections and 111 parameters refined. The galactarate ion is centrosymmetrical in both structures, although the Ba salt contains independent half-ions. The Ba ion is nine-coordinated (tricapped trigonal prism) and the Ca ion is eight-coordinated (square antiprism). Ca—O and Ba—O distances are in the ranges 2·400 (1) to 2·544 (1) and 2·656 (5) to 2·929 (5) Å respectively.

Introduction. Chelation of divalent cations (particularly calcium) by carbohydrates in the solid state and in aqueous solution is of considerable interest in the biological field (Morris, Rees & Robinson, 1980). A specific example of this is the binding of calcium ions by the polysaccharide hydrocolloids alginate and pectin, in the course of which gels are obtained. In both cases it has been suggested that, at the molecular level, polysaccharide-chain conformations are such that suitable coordination sites are provided by two chains leading to cooperative calcium binding in so-called 'egg boxes' (Belton, Morris & Tanner, 1985). Specific binding of barium and strontium also occurs and leads to similar gel formation but there appears to be no specific binding for smaller cations such as magnesium.

Although suitable coordination sites for divalent cations involving carbohydrate hydroxyl and carboxyl groups have been identified by model building, there are still few experimental data on the coordination of divalent cations by carboxylated carbohydrates.

The present study concerns the molecular structures of crystalline salts of calcium and barium galactarates. This is part of a systematic investigation of the crystalline salts of D-glucaric and -galactaric acids as models for potential binding of divalent cations by polysaccharides containing carboxyl groups. One structure, a re-determination of the structure of calcium D-glucarate, has already been published (Burden, Mackie & Sheldrick, 1985).

Experimental. Ba salt. Prepared from potassium galactarate and barium chloride solutions; crystal $0{\cdot}29 \times 0{\cdot}14 \times 0{\cdot}14$ mm; Enraf–Nonius CAD-4F diffractometer; Cu $K\alpha$ radiation; cell dimensions calculated from θ measurements of 36 reflections ($28 < \theta < 64°$). 3690 reflections measured; $2\theta_{\max} = 120°$; h −12 to 12, k −12 to 12, l 0 to 12; data merged using *SHELX76* (Sheldrick, 1976) giving 1868 unique reflections, $R_{\mathrm{int}} = 0{\cdot}053$; 309 additional reflections flagged as weak [$I < 3\sigma(I)$]. As an intensity check the $\bar{6}04$ reflection was used: average count 1205 and σ (calculated from the

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