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

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Abstract. $Ba^{2+}.C_6H_8O_8^{2-}.H_2O$, $M_r = 363·48$, monoclinic, $P2_1/a$, $a = 10·333$ (5), $b = 10·620$ (1), $c = 10·641$ (6) Å, $\beta = 117·61$ (5)°, $V = 1034·7$ Å^3, $Z = 4$, $D_x = 2·333$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 295·6$ cm^{-1}, $F(000) = 696$, $T = 293$ K, $R = 0·03$ for 1866 observed reflections and 175 parameters refined. $Ca^{2+}.C_6H_8O_8^{2-}.4H_2O$, $M_r = 320·2$, orthorhombic, $Pcan$, $a = 7·349$ (1), $b = 11·632$ (1), $c = 15·118$ (2) Å, $V = 1292·3$ Å^3, $Z = 4$, $D_x = 1·646$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 46·37$ cm^{-1}, $F(000) = 664$, $T = 293$ K, $R = 0·032$ 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 0·29 × 0·14 × 0·14 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, $R_{int} = 0·053$; 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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distribution) = 26·6 (2·2%). Absorption was corrected using the program *DIFABS* (Walker & Stuart, 1983); max., min. transmission 1·642, 0·939. Structure solved by the Patterson method using *SHELXS*86 (Sheldrick, 1985) and least-squares refinement carried out for the positional parameters of all the atoms with anisotropic thermal parameters for the non-H atoms and fixed isotropic thermal parameters (equal to U_{eq} of the connected atom) for the H atoms, using *SHELX*76; $\sum w(\Delta F)^2$ minimized, unit weights; H atoms located from difference Fourier synthesis; $R = 0{\cdot}030$, $wR = 0{\cdot}033$. In the final SFLS cycle, max. shift/e.s.d. 1·371 (H), 0·473 (non-H), average 0·050; on final difference Fourier synthesis max. and min. electron densities 0·65 and −0·71 e Å^{-3}.

Ca salt. Prepared from potassium galactarate and calcium chloride solutions; crystal 0·12 × 0·23 × 0·23 mm; Enraf–Nonius diffractometer; Cu $K\alpha$ radiation; cell dimensions calculated from θ measurements of 39 reflections ($35 < \theta < 61°$). 4174 reflections measured; $2\theta_{max} = 140°$; h −8 to 8, k 0 to 14, l −18 to 18; data merged using *SHELX*76 (Sheldrick, 1976) giving 1193 unique reflections, $R_{int} = 0{\cdot}034$; 429 additional reflections flagged as weak $[I < 3\sigma(I)]$. As an intensity check the 136 reflection was used: average count = 3710 and σ (calculated from the distribution) = 44·9 (1·2%). No absorption correction was made. Structure solved by the Patterson method using *SHELXS*86 (Sheldrick, 1985) and least-squares refinement carried out for the positional parameters of all the atoms, with anisotropic thermal vibration parameters for the non-H atoms and fixed isotropic thermal parameters (equal to U_{eq} of the connected atom) for the H atoms, using *SHELX*76; $\sum w(\Delta F)^2$ minimized with $w^{-1} = \sigma^2 F + 0{\cdot}001228F^2$; H atoms located from difference Patterson syntheses; $R = 0{\cdot}032$, $wR = 0{\cdot}039$. In the final SFLS cycle maximum shift/e.s.d. 0·124, average 0·025; on final difference Fourier synthesis the maximum and minimum electron densities were 0·24 and −0·39 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Figures drawn with *PLUTO*78 (Motherwell & Clegg, 1978).

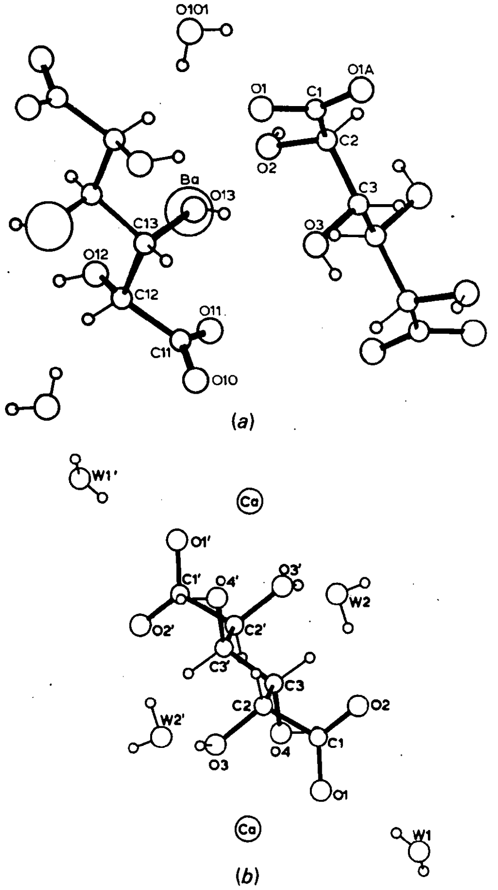

Fig. 1. Perspective views of the molecules of (*a*) Ba galactarate and (*b*) Ca galactarate showing the atom-labelling schemes.

Discussion. Fig. 1 shows the structures with the labelling scheme. Fig. 2 gives packing diagrams of the unit cells viewed along *y* (Ba salt) and along *x* (Ca salt). Atom coordinates and equivalent isotropic temperature factors for both structures are given in Table 1,* and bond lengths and angles in Table 2.

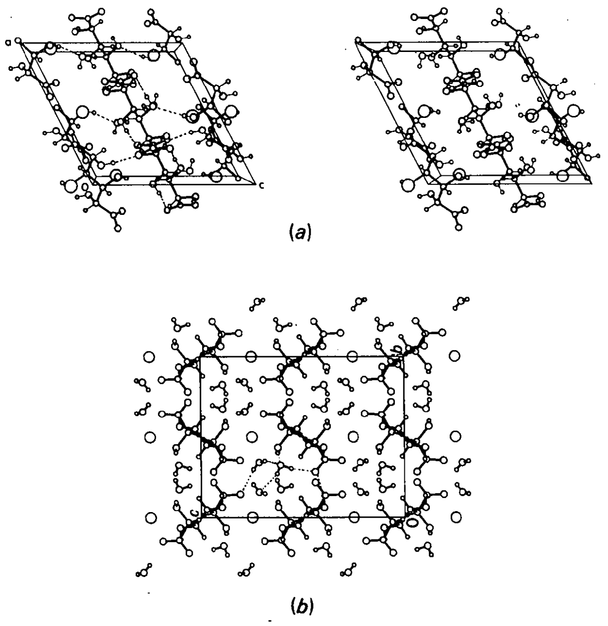

Fig. 2. Unit-cell packing diagrams for (*a*) the Ba salt and (*b*) the Ca salt. The stereo-projection has the *c* axis horizontal and the *a* axis vertical.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, torsion angles and best planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51448 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates with e.s.d.'s* (×10⁴ *for the barium salt;* ×10⁵ *for the calcium salt) and equivalent isotropic U values* (Å² × 10⁴)

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

	x	y	z	$U_{\rm eq}$
Ba	178·2 (3)	1598·3 (3)	1482·8 (4)	251
O1	2555 (5)	2179 (4)	4017 (5)	439
O1*A*	2997 (7)	2354 (5)	6237 (6)	586
O2	1656 (4)	−146 (4)	3749 (5)	368
O3	−560 (4)	1288 (4)	3702 (5)	378
O10	1313 (5)	434 (4)	−129 (6)	484
O11	2462 (4)	2259 (4)	699 (5)	387
O12	−1258 (5)	2901 (4)	−1020 (5)	371
O13	233 (4)	4265 (4)	1612 (5)	329
C1	2523 (6)	1776 (6)	5100 (7)	353
C2	1841 (6)	467 (5)	5018 (7)	300
C3	348 (6)	630 (5)	4982 (7)	297
C11	2244 (6)	1267 (6)	−4 (7)	333
C12	−1818 (6)	4038 (5)	−741 (7)	321
C13	−554 (6)	4880 (5)	273 (6)	311
O101	4315 (9)	−314 (11)	3407 (11)	1383
Ca	5409 (5)	0	25000	216
O1	26274 (16)	14539 (10)	30858 (8)	334
O2	35166 (18)	21829 (12)	43832 (9)	411
O3	22016 (14)	−6605 (9)	37912 (7)	255
O4	−7999 (14)	6459 (11)	39696 (7)	259
*W*1	35804 (17)	34114 (11)	21554 (9)	323
*W*2	45191 (16)	17515 (13)	60874 (9)	331
C1	28908 (20)	13936 (14)	39059 (11)	261
C2	22917 (20)	2929 (14)	43851 (10)	228
C3	3559 (18)	5015 (13)	47262 (9)	218

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s*

(*a*) Barium salt			
C1—O1	1·243 (7)	C11—O10	1·268 (7)
C1—O1*A*	1·237 (8)	C11—O11	1·250 (7)
C1—C2	1·543 (8)	C11—C12	1·528 (7)
C2—O2	1·429 (7)	C12—O12	1·429 (7)
C2—C3	1·535 (7)	C12—C13	1·537 (8)
C3—O3	1·428 (7)	C13—O13	1·429 (7)
C3—C3′	1·528 (10)	C13—C13′	1·527 (10)
O1—C1—O1*A*	124·6 (6)	O10—C11—O11	124·6 (5)
O1—C1—C2	117·7 (6)	O10—C11—C12	115·2 (5)
O1*A*—C1—C2	117·7 (5)	O11—C11—C12	120·1 (5)
C1—C2—C3	109·1 (4)	C11—C12—C13	107·2 (5)
C1—C2—O2	108·7 (5)	C11—C12—O12	109·9 (4)
O2—C2—C3	109·6 (5)	O12—C12—C13	110·1 (4)
C2—C3—C3′	112·4 (5)	C12—C13—C13′	111·9 (5)
C2—C3—O3	106·7 (4)	C12—C13—O13	109·9 (5)
O3—C3—C3′	110·0 (5)	O13—C13—C13′	106·0 (5)
(*b*) Calcium salt			
C1—O1	1·257 (2)	C2—C3	1·533 (2)
C1—O2	1·255 (2)	C3—O4	1·435 (2)
C1—C2	1·536 (2)	C3—C3′	1·523 (3)
C2—O3	1·429 (2)		
O1—C1—O2	125·7 (1)	C1—C2—C3	117·9 (1)
O1—C1—C2	117·9 (1)	C1—C2—O3	111·4 (1)
O2—C1—C2	116·3 (1)	O3—C2—C3	106·9 (1)

Table 3. *Coordination distances* (Å)

			Translation		
		Symmetry	*a*	*b*	*c*
(*a*) Barium					
Ba···O1	2·747 (5)	(i)	0	0	0
Ba···O2	2·857 (4)	(i)	0	0	0
Ba···O3	2·817 (4)	(i)	0	0	0
Ba···O10	2·656 (5)	(ii)	−1	0	0
Ba···O10	2·776 (5)	(−ii)	0	1	0
Ba···O11	2·806 (4)	(i)	0	0	0
Ba···O11	2·929 (5)	(−ii)	0	1	0
Ba···O12	2·747 (5)	(i)	0	0	0
Ba···O13	2·835 (4)	(i)	0	0	0

Symmetry operations: (i) x, y, z; (ii) $0{\cdot}5-x, 0{\cdot}5+y, -z$.

			Translation		
(*b*) Calcium					
Ca···O1	2·449 (1)	(i)	0	0	0
Ca···O3	2·427 (1)	(i)	0	0	0
Ca···O4	2·544 (1)	(i)	0	0	0
Ca···*W*1	2·400 (2)	(iii)	−1	0	0
Ca···O1′	2·449 (1)	(ii)	0	0	0
Ca···O3′	2·427 (1)	(ii)	0	0	0
Ca···O4′	2·544 (1)	(ii)	0	0	0
Ca···*W*1′	2·400 (2)	(iv)	−1	−1	0

Symmetry operations: (i) x, y, z; (ii) $x, -y, 0{\cdot}5-z$; (iii) $0{\cdot}5+x, 0{\cdot}5-y, z$; (iv) $0{\cdot}5+x, 0{\cdot}5+y, 0{\cdot}5-z$.

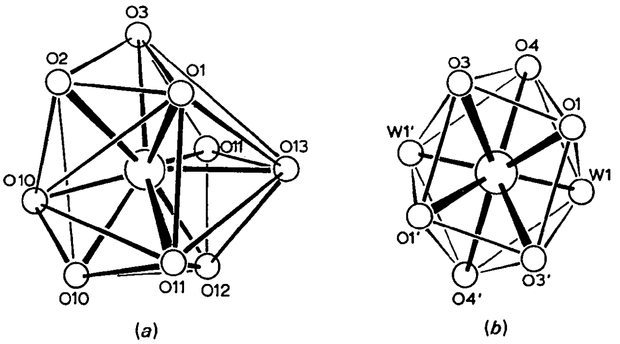

Fig. 3. Perspective diagrams of the coordination of (*a*) the Ba ion and (*b*) the Ca ion.

Barium galactarate

The asymmetric unit consists of a Ba ion and two separate half galactarate ions. The latter are connected through different centres of symmetry to symmetry-related half-molecules. Examination of the lengths of corresponding bonds in the two half-molecules shows that all are almost identical, with the exception of the carboxyl O atoms to their C atoms. Differences in the C—O bond lengths of the carboxyl groups are probably caused by differences in their coordination to the Ba ion.

Ba^{2+} *coordination.* Each Ba^{2+} ion is coordinated to nine O atoms, with the O—Ba distances within the range 2·65 (1)–2·95 (1) with an average = 2·80 Å (Table 3). The carboxyl O atoms (O1, O10 and O11) are coordinated, the latter two acting as bridges between symmetry-related Ba ions and hence appearing twice in each coordination shell. The remaining places are taken by the four hydroxyl O atoms, as shown in Fig. 3. Ninefold coordination in a tricapped trigonal prism form occurs in other structures containing Ba^{2+}, as in barium glucose 6-phosphate heptahydrate (Katti, Seshadri & Viswamitra, 1982) and references quoted therein. The galactarate coordination is unusual in that the O atom of the water molecule is one of the only two not involved in the coordination, in contrast to the barium glucose 6-phosphate heptahydrate structure, where seven atoms of the nine in the coordination sphere are from water molecules. The carboxyl O atom (O1*A*) not taking part in the coordination has a shorter C—O bond length [1·237 (8) Å] as compared with the average value of 1·254 (7) Å for the other three.

Hydrogen bonding. The single water molecule is prominent in the hydrogen-bond network, accepting two bonds (from equivalent hydroxyl groups of the two half-molecules) and donating a hydrogen bond (bifurcated) to a hydroxyl group and a symmetry-related water molecule. The latter values are weaker with H···O distances of 2·340 and 2·465 Å compared with the average of 1·840 Å for the other four.

Calcium galactarate

The asymmetric unit consists of one half of a Ca^{2+} ion (on a twofold rotation axis), one half of a galactarate ion (related to the other half by a centre of symmetry) and two water molecules. This contrasts with the structure of the Ba salt which has two distinct half-molecules of the galactarate ion, a unique Ba^{2+} ion and one water molecule per asymmetric unit. Bond lengths and angles have normal values for carbohydrates (Foces-Foces, Cano & Garcia-Blanco, 1981).

Ca^{2+} *coordination.* Each Ca^{2+} ion is coordinated to eight O atoms, with the Ca—O distances in the range 2·40 (1)–2·54 (1) with an average = 2·46 Å (Table 3*b*). The four O atoms listed are symmetry related (twofold rotation axis) to the other four, producing a characteristic square-antiprism arrangement around the Ca^{2+} ion, with near-normal Ca—O distances for this type of coordination as established by Einspahr & Bugg (1981).

Hydrogen bonding. All hydroxyl H atoms take part in the hydrogen-bonding scheme with the second water molecule (not involved in the calcium coordination) being a receptor for two H bonds and a donor for two.

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Bis(*n*-propylammonium) Tetrachloroplumbate

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Abstract. $[NH_3(C_3H_7)]_2[PbCl_4]$, $M_r = 469$, orthorhombic, *Pnma*, $a = 7·815$ (1), $b = 25·034$ (3), $c = 7·954$ (1) Å, $V = 1556$ Å^3, $Z = 4$, $D_x = 2·0$ g cm^{-3}, D_m not measured, λ (Cu $K\alpha$) = 1·54178 Å, $\mu = 271$ cm^{-1}, $F(000) = 880$, room temperature ($\simeq$295 K), 1228 non-equivalent diffractometer data up to $(\sin\theta)/\lambda = 0·6$ Å^{-1}, final $R(F) = 0·079$, $wR(F) = 0·091$. This compound crystallizes in a perovskite-type layer structure. The Cl octahedra centred by Pb atoms form infinite two-dimensional layers which are sandwiched between the propylammonium chains. The results show a net deformation of Cl octahedra.

Introduction. The perovskite-type layer compounds, with the general formula $[NH_3(C_nH_{2n+1})]_2[MCl_4]$, where *M* is a metal, show a two-dimensional structure.

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