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# Effects of Cation Interactions on Sugar Anion Conformation in Complexes of Lactobionate and Gluconate with Calcium, Sodium or Potassium

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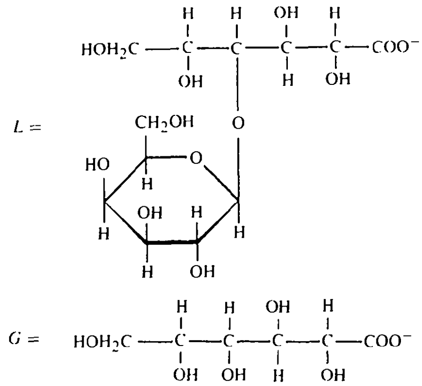
## Abstract

In the investigated compounds, the tetrahydrated calcium chloride salt of lactobionic acid ($Ca^{2+}$.-$Cl^-$.$C_{12}H_{21}O_{12}^-$.$4H_2O$), potassium lactobionate ($K^+$.-$C_{12}H_{21}O_{12}^-$), sodium lactobionate monohydrate ($Na^+$.-$C_{12}H_{21}O_{12}^-$.$H_2O$) and calcium galactonate hydrate ($Ca^{2+}$.$2C_6H_{11}O_7^-$.$5H_2O$), the cations and hydrogen-bonding systems have a strong influence on the geometries and conformations of the carbohydrate anions.

## Comment

As a part of an extensive study of the influence of the cation on the conformation of the lactobionate or gluconate anions in carbohydrate–cation complexes (Lis, 1981, 1984; Jeffrey & Fasiska, 1972; Panagiotopoulos, Jeffrey, La Placa & Hamilton, 1974; Cook & Bugg, 1973), we have determined the crystal and molecular structures of the tetrahydrated calcium chloride salt of lactobionic acid, (1), potassium lactobionate, (2), sodium lactobionate monohydrate, (3), and calcium galactonate hydrate, (4). They are of the type of carbohydrate complex in which interactions between the cation and the carbohydrate anion play an important role in a number of physiological processes (Angyal, 1980; Krestinger & Nelson, 1976; Bugg, 1973). X-ray data of structures containing a lactobionate or a galactonate anion have been available only for the bromide analogue of (1) (Cook & Bugg, 1973).



(1) $Ca^{2+}$.$Cl^-$.*L*.$4H_2O$
(2) $K^+$.*L*
(3) $Na^+$.*L*.$H_2O$
(4) $Ca^{2+}$.2*G*.$5H_2O$

The asymmetric part of the unit cell of (1) comprises one lactobionate and one $Cl^-$ anion, one $Ca^{2+}$ cation and four water molecules. The $Ca^{2+}$ ion binds to three water molecules (O2*W*, O3*W* and O4*W*) and to two lactobionate ions, by O8, O9 and O10 of the first anion and by O7 and O12 of the second symmetry-related anion (Fig. 1). Table 3 presents the intermolecular hydrogen bonding with H···O distances not greater than 2.20 Å. The contacts of the $Cl^-$ ion and O1*W* water molecule with the lactobionate moiety are depicted in Fig. 1.

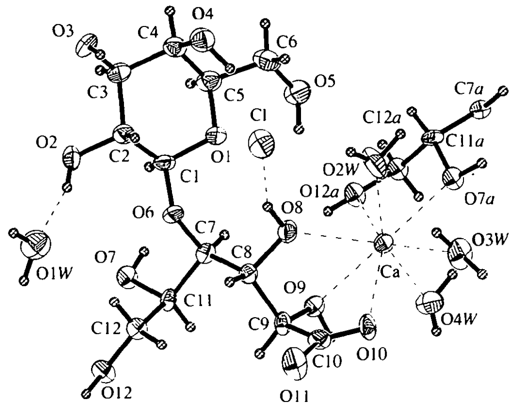



Fig. 1. The environment of the $Ca^{2+}$ cation in (1) showing 50% probability displacement ellipsoids.

Comparison of (1) with the bromide analogue (Cook & Bugg, 1973) shows that the structures are very similar. The bromide analogue crystallizes in the same space group, with similar cell constants. The geometries about the $Ca^{2+}$ ion and the conformations of the

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lactobionate moieties are almost identical (Cambridge Structural Database, 1993).

The environment of the $K^+$ cation in (2) is shown in Fig. 2 and described in detail in Table 2. The asymmetric part of the unit cell of (2) contains one $K^+$ cation and one lactobionate anion. The $K^+$ cation binds to four lactobionate anions, by O5, O8 and O11 to the first anion, by O2*a* and O7*a* to the second, and by O11*b* and O12*c* to the next two symmetry-related anions. For clarity, Fig. 2 show only part of the environment around the $K^+$ cation.

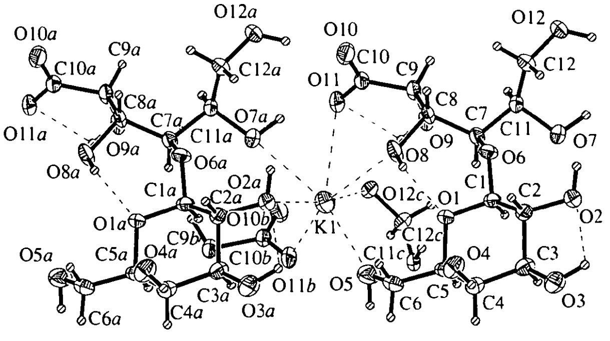


Fig. 2. The environment of the $K^+$ cation in (2), with the intramolecular hydrogen-bonding system in the lactobionate moiety. Displacement ellipsoids are shown at the 50% probability level.

The crystal lattice of (2) shows the characteristic intermolecular hydrogen-bonding system. Three intramolecular hydrogen contacts, O8—H8···O1, O9—H9···O11 and O3—H3···O2, with distances smaller than 2.20 Å, are found (Fig. 2, Table 3).

Fig. 3 shows the lactobionate (3). One lactobionate anion, one $Na^+$ cation and one water molecule constitute the asymmetric part of the unit cell. The $Na^+$ cation binds to three lactobionate anions, by O1, O4, O6 and O9 to the first anion, and by O7*a*, O12*a* and O5*b* to two symmetry-related anions (Fig. 3).

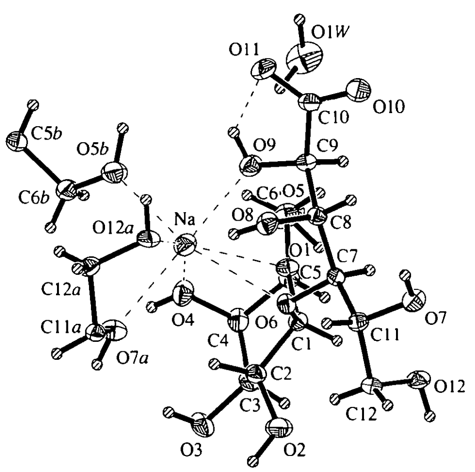


Fig. 3. The environment of the $Na^+$ cation in (3), with one strong intramolecular hydrogen bond in the lactobionate moiety. Displacement ellipsoids are shown at the 50% probability level.

There is one hydrogen contact, O9—H9···O11, with an H···O distance shorter than 2.20 Å (Fig. 3, Table 3). The O1*W* water molecule binds to atom O8 of the lactobionate moiety (hydrogen contact O1*W*—H1*W*···O8, Table 3).

The asymmetric part of the unit cell of (4) contains one galactonate anion, one $Ca^{2+}$ cation and three water molecules (atoms Ca and O3*W* are in special positions in the unit cell). The environment of the $Ca^{2+}$ cation is depicted in Fig. 4. The $Ca^{2+}$ ion binds to two symmetrical gluconate anions (by O2 and O12 in both molecules) and to three water molecules, O3*W*, O1*W* and symmetry-related O1*Wa*. The galactonate anion adopts an almost planar zigzag carbon-chain configuration. Torsion angles are given in Table 4.

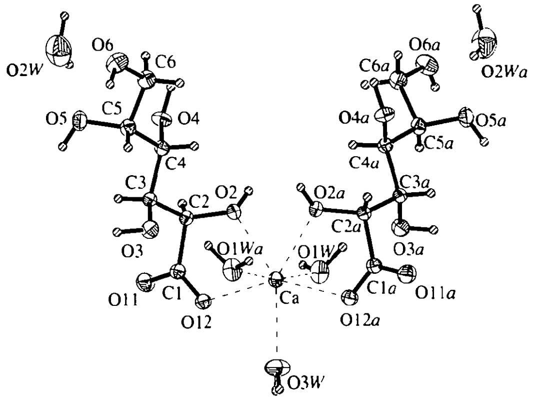


Fig. 4. The environment of the $Ca^{2+}$ cation in (4). Displacement ellipsoids are shown at the 50% probability level.

Analysis of hydrogen contacts shorter than 2.20 Å did not show any intramolecular hydrogen bonds. However, in the crystal lattice of (4), two strong intermolecular hydrogen contacts are seen: O4—H4···O12 and O1*W*—H2*W*1···O3 (Table 3).

The present X-ray analyses of (1)–(4) show that both the nature and environment at the cation strongly influence the geometry and conformation of the carbohydrate anion. The different cations in the crystal lattices of (1)–(3) and their different binding to the carbohydrate anions have a strong influence on conformation of the lactobionate anion (Table 4), in particular on the conformation of the six-membered rings, which are in differently deformed chair forms (Table 5).

## Experimental

Synthesis of (1) was carried out by the reaction of calcium lactobionate and calcium chloride (molar ratio 1:1.2) in a water solution for 2 h at 333 K (Król, 1986). Recrystallization was from water. The sodium and potassium lactobionates, (2) and

(3), were obtained by the neutralization of lactobionic acid by sodium and potassium carbonates, respectively, concentration of the obtained solution to 65% mass fraction and crystallization from a water solution for 12 h at 323 K. Synthesis of the calcium galactonate (4) was carried out by electrochemical oxidation of galactose in the presence of calcium carbonate. Recrystallization was from water for 24 h at 293 K (Frush & Isbell, 1963).

**Compound (1)**

*Crystal data*

$Ca^{2+}.Cl^{-}.C_{12}H_{21}O_{12}^{-}.4H_2O$
$M_r$ = 504.9
Orthorhombic
$P2_12_12_1$
$a$ = 8.2498 (9) Å
$b$ = 15.046 (2) Å
$c$ = 16.450 (1) Å
$V$ = 2041.9 (4) Å$^3$
$Z$ = 4
$D_x$ = 1.643 (2) Mg m$^{-3}$
Cu $K\alpha$ radiation
$\lambda$ = 1.54184 Å
Cell parameters from 25 reflections
$\theta$ = 18.5–25.6°
$\mu$ = 4.61 mm$^{-1}$
$T$ = 293 K
Plate
0.47 × 0.35 × 0.22 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968; Frenz, 1986)
$T_{min}$ = 0.676, $T_{max}$ = 0.997
2136 measured reflections
2024 independent reflections
1861 observed reflections [$I > 3\sigma(I)$]
$R_{int}$ = 0.0331
$\theta_{max}$ = 75°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: 0.4%

*Refinement*

Refinement on $F$
$R$ = 0.0515
$wR$ = 0.0595
$S$ = 0.788
1861 reflections
274 parameters
H atoms: see below
$w = 1/[\sigma^2(F) + 0.01F^2]$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.639 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.401 e Å$^{-3}$
Extinction correction: *SHELXTL/PC* (Sheldrick, 1991)
Extinction coefficient: 0.007 (1)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

**Compound (2)**

*Crystal data*

$K^{+}.C_{12}H_{21}O_{12}^{-}$
$M_r$ = 396.4
Orthorhombic
$P2_12_12_1$
$a$ = 8.7037 (9) Å
$b$ = 8.7037 (9) Å
$c$ = 21.055 (2) Å
$V$ = 1595.0 (5) Å$^3$
$Z$ = 4
$D_x$ = 1.651 (2) Mg m$^{-3}$
Cu $K\alpha$ radiation
$\lambda$ = 1.54184 Å
Cell parameters from 25 reflections
$\theta$ = 20.8–29.5°
$\mu$ = 3.56 mm$^{-1}$
$T$ = 293 K
Bipyramidal trigonal
0.55 × 0.30 × 0.30 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968; Frenz, 1986)
$T_{min}$ = 0.896, $T_{max}$ = 0.999
3613 measured reflections
3289 independent reflections
3283 observed reflections [$I > 3\sigma(I)$]
$R_{int}$ = 0.025
$\theta_{max}$ = 75°
$h = -10 \rightarrow 0$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 60 min
intensity decay: 3.3%

*Refinement*

Refinement on $F$
$R$ = 0.0409
$wR$ = 0.0492
$S$ = 0.823
3283 reflections
248 parameters
H atoms: see below
$w = 1/[\sigma^2(F) + 0.0073F^2]$
$(\Delta/\sigma)_{max}$ = 0.016
$\Delta\rho_{max}$ = 0.805 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.751 e Å$^{-3}$
Extinction correction: *SHELXTL/PC* (Sheldrick, 1991)
Extinction coefficient: 0.012 (2)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

**Compound (3)**

*Crystal data*

$Na^{+}.C_{12}H_{21}O_{12}^{-}.H_2O$
$M_r$ = 398.3
Orthorhombic
$P2_12_12_1$
$a$ = 9.2358 (9) Å
$b$ = 10.4021 (6) Å
$c$ = 16.7994 (5) Å
$V$ = 1613.9 (2) Å$^3$
$Z$ = 4
$D_x$ = 1.639 (2) Mg m$^{-3}$
Cu $K\alpha$ radiation
$\lambda$ = 1.54184 Å
Cell parameters from 25 reflections
$\theta$ = 21.7–28.0°
$\mu$ = 1.49 mm$^{-1}$
$T$ = 293 K
Plate
0.62 × 0.45 × 0.30 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1932 measured reflections
1857 independent reflections
1818 observed reflections [$I > 3\sigma(I)$]
$R_{int}$ = 0.0173
$\theta_{max}$ = 75°
$h = -11 \rightarrow 0$
$k = 0 \rightarrow 13$
$l = -21 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 1.7%

*Refinement*

Refinement on $F$
$R$ = 0.0320
$wR$ = 0.0574
$S$ = 1.358
1818 reflections
237 parameters
H atoms: see below
$w = 1/[\sigma^2(F) + 0.001627F^2]$
$(\Delta/\sigma)_{max}$ = 0.034
$\Delta\rho_{max}$ = 0.322 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.198 e Å$^{-3}$
Extinction correction: *SHELXTL/PC* (Sheldrick, 1991)
Extinction coefficient: 0.007 (2)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

**Compound (4)**

*Crystal data*

$Ca^{2+}.2C_6H_{11}O_7^-.5H_2O$
$M_r = 520.45$
Monoclinic
$C2$
$a = 12.4263$ (7) Å
$b = 7.6563$ (9) Å
$c = 11.094$ (1) Å
$\beta = 102.073$ (6)°
$V = 1032$ (1) Å$^3$
$Z = 2$
$D_x = 1.674$ (2) Mg m$^{-3}$

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 19.0$–$29.0°$
$\mu = 3.49$ mm$^{-1}$
$T = 293$ K
Plate
0.55 × 0.43 × 0.15 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968; Frenz, 1986)
$T_{min} = 0.681$, $T_{max} = 0.999$
1176 measured reflections
1124 independent reflections

1123 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.0118$
$\theta_{max} = 75°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 9$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: none

*Refinement*

Refinement on $F$
$R = 0.0264$
$wR = 0.0425$
$S = 1.765$
1123 reflections
147 parameters
H atoms: see below
$w = 1/[\sigma^2(F) + 0.0005F^2]$

$(\Delta/\sigma)_{max} = 0.012$
$\Delta\rho_{max} = 0.226$ e Å$^{-3}$
$\Delta\rho_{min} = -0.267$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for (1)–(4)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| (1) | | | | |
| Ca | 0.2237 (1) | 0.6328 (1) | 0.7718 (1) | 0.0273 (3) |
| Cl | 0.2707 (3) | 0.5777 (1) | 0.4833 (1) | 0.0483 (4) |
| O1 | 0.6392 (5) | 0.5445 (3) | 0.5754 (2) | 0.0307 (8) |
| O2 | 0.7401 (6) | 0.3412 (3) | 0.4652 (3) | 0.0380 (8) |
| O3 | 0.8033 (5) | 0.4767 (3) | 0.3452 (2) | 0.035 (1) |
| O4 | 0.6392 (6) | 0.6241 (3) | 0.4154 (3) | 0.0383 (8) |
| O5 | 0.7321 (6) | 0.6975 (4) | 0.6599 (3) | 0.046 (1) |
| O6 | 0.5317 (5) | 0.4061 (3) | 0.5904 (2) | 0.0283 (8) |
| O7 | 0.7053 (4) | 0.2924 (3) | 0.7010 (3) | 0.0327 (9) |
| O8 | 0.3028 (5) | 0.5238 (3) | 0.6628 (2) | 0.0323 (8) |
| O9 | 0.3219 (4) | 0.4842 (3) | 0.8163 (2) | 0.0290 (8) |
| O10 | 0.0127 (5) | 0.5189 (3) | 0.7801 (3) | 0.038 (1) |
| O11 | −0.0256 (5) | 0.3860 (3) | 0.7218 (4) | 0.050 (1) |
| O12 | 0.4891 (4) | 0.1586 (3) | 0.7107 (3) | 0.033 (1) |
| O1*W* | 0.5314 (7) | 0.1963 (4) | 0.4540 (3) | 0.060 (1) |
| O2*W* | 0.2193 (10) | 0.7023 (4) | 0.6379 (3) | 0.070 (2) |
| O3*W* | −0.0272 (5) | 0.7102 (3) | 0.7781 (3) | 0.047 (1) |
| O4*W* | 0.2245 (6) | 0.6333 (3) | 0.9217 (3) | 0.046 (1) |
| C1 | 0.6693 (6) | 0.4531 (4) | 0.5634 (3) | 0.027 (1) |
| C2 | 0.6860 (6) | 0.4300 (4) | 0.4734 (3) | 0.029 (1) |
| C3 | 0.8067 (7) | 0.4914 (4) | 0.4314 (3) | 0.030 (1) |
| C4 | 0.7807 (8) | 0.5886 (4) | 0.4530 (4) | 0.035 (1) |
| C5 | 0.7724 (8) | 0.5968 (4) | 0.5465 (4) | 0.035 (1) |
| C6 | 0.7408 (11) | 0.6908 (5) | 0.5740 (4) | 0.045 (2) |
| C7 | 0.5006 (6) | 0.4072 (4) | 0.6771 (3) | 0.026 (1) |
| C8 | 0.3203 (6) | 0.4322 (4) | 0.6816 (3) | 0.027 (1) |
| C9 | 0.2417 (6) | 0.4229 (4) | 0.7646 (3) | 0.026 (1) |
| C10 | 0.0609 (6) | 0.4456 (4) | 0.7557 (4) | 0.030 (1) |
| C11 | 0.5380 (6) | 0.3146 (4) | 0.7123 (3) | 0.026 (1) |
| C12 | 0.4433 (6) | 0.2412 (4) | 0.6731 (4) | 0.029 (1) |
| (2) | | | | |
| K1 | 0.4415 (1) | 0.7126 (1) | 0.6754 (1) | 0.0403 (2) |
| O1 | 0.0161 (2) | 0.6538 (2) | 0.5758 (1) | 0.0283 (4) |
| O2 | −0.4002 (2) | 0.7113 (2) | 0.5629 (1) | 0.0343 (4) |
| O3 | −0.3575 (2) | 0.4414 (2) | 0.4924 (1) | 0.0400 (4) |
| O4 | −0.0396 (2) | 0.4910 (2) | 0.4611 (1) | 0.0370 (4) |
| O5 | 0.2836 (2) | 0.4773 (2) | 0.6119 (1) | 0.0540 (5) |
| O6 | −0.1206 (2) | 0.8657 (2) | 0.6011 (1) | 0.0260 (4) |
| O7 | −0.3165 (2) | 0.9232 (2) | 0.7050 (1) | 0.0433 (5) |
| O8 | 0.1984 (2) | 0.8734 (2) | 0.6365 (1) | 0.0377 (4) |
| O9 | 0.1288 (2) | 0.9805 (2) | 0.7679 (1) | 0.0353 (4) |
| O10 | 0.3609 (2) | 1.1893 (2) | 0.6568 (1) | 0.0390 (4) |
| O11 | 0.4142 (2) | 1.0377 (2) | 0.7396 (1) | 0.0357 (4) |
| O12 | −0.3350 (2) | 1.2559 (2) | 0.6808 (1) | 0.0410 (5) |
| C1 | −0.1323 (2) | 0.7074 (2) | 0.5954 (1) | 0.0253 (4) |
| C2 | −0.2496 (2) | 0.6655 (2) | 0.5444 (1) | 0.0253 (4) |
| C3 | −0.2502 (2) | 0.4913 (2) | 0.5388 (1) | 0.0283 (4) |
| C4 | −0.0898 (2) | 0.4340 (2) | 0.5214 (1) | 0.0310 (4) |
| C5 | 0.0236 (2) | 0.4889 (2) | 0.5719 (1) | 0.0287 (4) |
| C6 | 0.1895 (3) | 0.4456 (2) | 0.5593 (1) | 0.0390 (5) |
| C7 | −0.0675 (2) | 0.9175 (2) | 0.6625 (1) | 0.0243 (4) |
| C8 | 0.0907 (2) | 0.9904 (2) | 0.6533 (1) | 0.0253 (4) |
| C9 | 0.1530 (2) | 1.0700 (2) | 0.7129 (1) | 0.0270 (4) |
| C10 | 0.3237 (2) | 1.1038 (2) | 0.7026 (1) | 0.0273 (4) |
| C11 | −0.1894 (2) | 1.0203 (2) | 0.6914 (1) | 0.0260 (4) |
| C12 | −0.2367 (2) | 1.1514 (2) | 0.6488 (1) | 0.0337 (4) |
| (3) | | | | |
| Na | 0.1930 (1) | 0.0463 (1) | 0.9810 (1) | 0.0257 (3) |
| O1 | −0.0439 (2) | −0.0214 (2) | 1.0370 (1) | 0.0210 (4) |
| O2 | 0.1250 (3) | −0.2288 (2) | 1.1839 (1) | 0.0337 (4) |
| O3 | 0.1747 (2) | 0.0274 (2) | 1.2503 (1) | 0.0310 (5) |
| O4 | 0.1284 (2) | 0.1643 (2) | 1.1025 (1) | 0.0293 (4) |
| O5 | −0.2368 (3) | 0.2726 (2) | 1.0847 (1) | 0.0377 (4) |
| O6 | 0.0779 (2) | −0.2046 (2) | 1.0135 (1) | 0.0193 (4) |
| O7 | −0.0804 (2) | −0.5064 (2) | 0.9418 (1) | 0.0260 (4) |
| O8 | 0.1653 (2) | −0.2692 (2) | 0.8558 (1) | 0.0250 (4) |
| O9 | 0.0484 (2) | −0.0197 (2) | 0.8662 (1) | 0.0277 (4) |
| O10 | −0.1353 (3) | −0.2144 (2) | 0.7239 (1) | 0.0387 (4) |
| O11 | 0.0249 (2) | −0.0540 (2) | 0.7138 (1) | 0.0337 (4) |
| O12 | −0.1341 (2) | −0.4297 (2) | 1.0950 (1) | 0.0250 (4) |
| O1*W* | −0.2239 (3) | 0.1572 (3) | 0.8071 (1) | 0.0520 (6) |
| C1 | 0.0044 (2) | −0.1373 (2) | 1.0738 (1) | 0.0180 (4) |
| C2 | 0.1114 (2) | −0.1125 (2) | 1.1411 (1) | 0.0207 (4) |
| C3 | 0.0610 (3) | −0.0034 (3) | 1.1955 (1) | 0.0233 (4) |
| C4 | 0.0122 (3) | 0.1137 (2) | 1.1486 (1) | 0.0237 (4) |
| C5 | −0.1056 (3) | 0.0689 (2) | 1.0913 (1) | 0.0213 (4) |
| C6 | −0.1704 (3) | 0.1743 (3) | 1.0392 (1) | 0.0263 (4) |
| C7 | −0.0123 (2) | −0.2839 (2) | 0.9633 (1) | 0.0180 (4) |
| C8 | 0.0160 (3) | −0.2547 (2) | 0.8752 (1) | 0.0187 (4) |
| C9 | −0.0411 (3) | −0.1251 (2) | 0.8443 (1) | 0.0200 (4) |
| C10 | −0.0523 (3) | −0.1316 (2) | 0.7524 (1) | 0.0237 (4) |
| C11 | 0.0207 (3) | −0.4257 (2) | 0.9818 (1) | 0.0193 (4) |
| C12 | 0.0108 (3) | −0.4583 (2) | 1.0699 (1) | 0.0213 (4) |
| (4) | | | | |
| Ca | 1/2 | 0.7611 | 1/2 | 0.0202 (4) |
| O11 | 0.1374 (1) | 0.7559 (3) | 0.3607 (2) | 0.0276 (4) |
| O12 | 0.3150 (1) | 0.8323 (3) | 0.4017 (2) | 0.0218 (4) |
| O2 | 0.3806 (1) | 0.5094 (3) | 0.4586 (1) | 0.0213 (4) |
| O3 | 0.3297 (2) | 0.5759 (3) | 0.1926 (1) | 0.0266 (4) |
| O4 | 0.2516 (1) | 0.1696 (3) | 0.3200 (2) | 0.0241 (4) |
| O5 | 0.2102 (1) | 0.1765 (3) | 0.0554 (2) | 0.0280 (4) |
| O6 | 0.3947 (2) | 0.0202 (4) | 0.0179 (2) | 0.0336 (4) |
| O1*W* | 0.4680 (1) | 0.7295 (4) | 0.6992 (2) | 0.0327 (4) |
| O2*W* | 0.0765 (2) | −0.0818 (5) | 0.1127 (2) | 0.0616 (6) |
| O3*W* | 1/2 | 1.0723 (5) | 1/2 | 0.0383 (7) |
| C1 | 0.2393 (2) | 0.7213 (4) | 0.3820 (2) | 0.0185 (4) |
| C2 | 0.2722 (2) | 0.5284 (4) | 0.3845 (2) | 0.0171 (4) |
| C3 | 0.2677 (2) | 0.4618 (4) | 0.2535 (2) | 0.0176 (4) |

| | | | | |
|---|---|---|---|---|
| C4 | 0.3158 (2) | 0.2759 (4) | 0.2566 (2) | 0.0183 (4) |
| C5 | 0.3189 (2) | 0.2054 (4) | 0.1285 (2) | 0.0202 (4) |
| C6 | 0.3831 (2) | 0.0364 (4) | 0.1376 (2) | 0.0263 (4) |

Table 2. *Selected bond lengths (Å) and angles (°) for (1)–(4)*

| | | | |
|---|---|---|---|
| (1) | | | |
| Ca—O7$^{i}$ | 2.512 (5) | O8—Ca—O2*W* | 68.9 (2) |
| Ca—O8 | 2.516 (4) | O8—Ca—O3*W* | 125.2 (2) |
| Ca—O9 | 2.488 (5) | O8—Ca—O4*W* | 135.6 (2) |
| Ca—O10 | 2.447 (5) | O9—Ca—O10 | 65.5 (1) |
| Ca—O12$^{i}$ | 2.418 (3) | O9—Ca—O12$^{i}$ | 77.9 (1) |
| Ca—O2*W* | 2.438 (5) | O9—Ca—O2*W* | 131.0 (2) |
| Ca—O3*W* | 2.377 (4) | O9—Ca—O3*W* | 135.3 (2) |
| Ca—O4*W* | 2.466 (5) | O9—Ca—O4*W* | 73.0 (1) |
| O7$^{i}$—Ca—O8 | 133.6 (1) | O10—Ca—O12$^{i}$ | 143.4 (2) |
| O7$^{i}$—Ca—O9 | 136.9 (1) | O10—Ca—O2*W* | 109.9 (2) |
| O7$^{i}$—Ca—O10 | 145.7 (2) | O10—Ca—O3*W* | 73.8 (2) |
| O7$^{i}$—Ca—O12$^{i}$ | 66.2 (1) | O10—Ca—O4*W* | 87.0 (2) |
| O7$^{i}$—Ca—O2*W* | 75.8 (2) | O12$^{i}$—Ca—O2*W* | 93.1 (2) |
| O7$^{i}$—Ca—O3*W* | 74.2 (2) | O12$^{i}$—Ca—O3*W* | 140.3 (2) |
| O7$^{i}$—Ca—O4*W* | 79.5 (2) | O12$^{i}$—Ca—O4*W* | 83.0 (2) |
| O8—Ca—O9 | 62.6 (1) | O2*W*—Ca—O3*W* | 79.4 (2) |
| O8—Ca—O10 | 76.6 (1) | O2*W*—Ca—O4*W* | 154.4 (2) |
| O8—Ca—O12$^{i}$ | 86.3 (1) | O3*W*—Ca—O4*W* | 87.6 (2) |
| (2) | | | |
| K1—O2$^{ii}$ | 2.740 (2) | O5—K1—O8 | 81.3 (1) |
| K1—O5 | 2.806 (2) | O5—K1—O11 | 145.6 (1) |
| K1—O7$^{ii}$ | 2.861 (2) | O5—K1—O11$^{iii}$ | 97.7 (1) |
| K1—O8 | 2.666 (2) | O5—K1—O12$^{iv}$ | 113.4 (1) |
| K1—O11 | 3.145 (2) | O7$^{ii}$—K1—O8 | 108.4 (1) |
| K1—O11$^{iii}$ | 2.664 (2) | O7$^{ii}$—K1—O11 | 52.1 (1) |
| K1—O12$^{iv}$ | 3.189 (2) | O7$^{ii}$—K1—O11$^{iii}$ | 82.7 (1) |
| O2$^{ii}$—K1—O5 | 80.3 (1) | O7$^{ii}$—K1—O12$^{iv}$ | 86.1 (1) |
| O2$^{ii}$—K1—O7$^{ii}$ | 79.7 (1) | O8—K1—O11 | 66.4 (1) |
| O2$^{ii}$—K1—O8 | 97.8 (1) | O8—K1—O11$^{iii}$ | 151.7 (1) |
| O2$^{ii}$—K1—O11 | 114.4 (1) | O8—K1—O12$^{iv}$ | 89.9 (1) |
| O2$^{ii}$—K1—O11$^{iii}$ | 110.0 (1) | O11—K1—O11$^{iii}$ | 105.1 (1) |
| O2$^{ii}$—K1—O12$^{iv}$ | 165.3 (1) | O11—K1—O12$^{iv}$ | 57.6 (1) |
| O5—K1—O7$^{ii}$ | 158.8 (1) | O11$^{iii}$—K1—O12$^{iv}$ | 64.3 (1) |
| (3) | | | |
| Na—O1 | 2.484 (2) | O4—Na—O5$^{vi}$ | 93.4 (1) |
| Na—O4 | 2.455 (2) | O4—Na—O6 | 101.9 (1) |
| Na—O5$^{vi}$ | 2.278 (2) | O5$^{vi}$—Na—O6 | 161.7 (1) |
| Na—O6 | 2.871 (2) | O5$^{vi}$—Na—O9 | 90.3 (1) |
| Na—O7$^{v}$ | 2.498 (2) | O5$^{vi}$—Na—O12$^{v}$ | 88.3 (1) |
| Na—O9 | 2.444 (2) | O6—Na—O9 | 72.1 (1) |
| Na—O12$^{v}$ | 2.377 (2) | O6—Na—O12$^{v}$ | 83.5 (1) |
| O4—Na—O9 | 131.6 (1) | O9—Na—O12$^{v}$ | 78.5 (1) |
| O4—Na—O12$^{v}$ | 149.9 (1) | O1—Na—O7$^{v}$ | 119.6 (1) |
| O1—Na—O4 | 67.2 (1) | O4—Na—O7$^{v}$ | 81.6 (1) |
| O1—Na—O5$^{vi}$ | 132.0 (1) | O5—Na—O7$^{v}$ | 98.7 (1) |
| O1—Na—O6 | 49.0 (1) | O6—Na—O7$^{v}$ | 93.5 (1) |
| O1—Na—O9 | 74.8 (1) | O7$^{v}$—Na—O9 | 145.2 (1) |
| O1—Na—O12$^{v}$ | 130.6 (1) | O7$^{v}$—Na—O12$^{v}$ | 68.4 (1) |
| (4) | | | |
| Ca—O12 | 2.392 (1) | O12$^{vii}$—Ca—O2$^{vii}$ | 66.5 (1) |
| Ca—O12$^{vii}$ | 2.392 (1) | O12$^{vii}$—Ca—O1*W* | 86.0 (1) |
| Ca—O2 | 2.417 (2) | O12$^{vii}$—Ca—O1*W*$^{vii}$ | 96.7 (1) |
| Ca—O2$^{vii}$ | 2.417 (2) | O12$^{vii}$—Ca—O3*W* | 76.8 (1) |
| Ca—O1*W* | 2.338 (2) | O2—Ca—O2$^{vii}$ | 74.3 (1) |
| Ca—O1*W*$^{vii}$ | 2.338 (2) | O2—Ca—O1*W* | 83.0 (1) |
| Ca—O3*W* | 2.383 (4) | O2—Ca—O1*W*$^{vii}$ | 87.5 (1) |
| O12—Ca—O12$^{vii}$ | 153.7 (1) | O2—Ca—O3*W* | 142.9 (1) |
| O12—Ca—O2 | 66.5 (1) | O2$^{vii}$—Ca—O1*W* | 87.5 (1) |
| O12—Ca—O2$^{vii}$ | 139.6 (1) | O2$^{vii}$—Ca—O1*W*$^{vii}$ | 83.0 (1) |
| O12—Ca—O1*W* | 96.7 (1) | O2$^{vii}$—Ca—O3*W* | 142.9 (1) |
| O12—Ca—O1*W*$^{vii}$ | 86.0 (1) | O1*W*—Ca—O1*W*$^{vii}$ | 168.1 (1) |
| O12—Ca—O3*W* | 76.8 (1) | O1*W*—Ca—O3*W* | 95.9 (1) |
| O12$^{vii}$—Ca—O2 | 139.6 (1) | O1*W*$^{vii}$—Ca—O3*W* | 95.9 (1) |

Symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $x+1, y, z$; (iii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (v) $\frac{1}{2}+x, -\frac{1}{2}-y, 2-z$; (vi) $\frac{1}{2}+x, \frac{1}{2}-y, 2-z$; (vii) $1-x, y, 1-z$.

Table 3. *Hydrogen-bonding geometry (Å, °) for (1)–(4)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| (1) | | | | |
| O12—H12···O3$^{i}$ | 0.97 (2) | 1.74 (2) | 2.709 (6) | 179.3 (15) |
| O7—H7···O11$^{ii}$ | 0.96 (2) | 1.80 (2) | 2.651 (6) | 145.8 (15) |
| O2—H2···O1*W* | 0.96 (2) | 1.86 (2) | 2.784 (8) | 160.0 (15) |
| O3—H3···O10$^{iii}$ | 0.94 (2) | 1.89 (2) | 2.819 (6) | 171.7 (15) |
| O2*W*—H1*W*2···O4$^{iv}$ | 0.96 (2) | 1.98 (2) | 2.833 (8) | 146.6 (15) |
| O9—H9···Cl$^{v}$ | 0.97 (2) | 2.05 (2) | 2.999 (4) | 164.7 (15) |
| O5—H5···O12$^{vi}$ | 0.95 (2) | 2.13 (2) | 2.864 (7) | 133.2 (15) |
| O8—H8···Cl | 0.99 (2) | 2.16 (2) | 3.073 (4) | 153.8 (15) |
| (2) | | | | |
| O8—H8···O1 | 1.02 (1) | 1.78 (1) | 2.794 (3) | 174.7 (8) |
| O5—H5···O10$^{vii}$ | 0.92 (1) | 1.86 (1) | 2.762 (3) | 166.3 (8) |
| O7—H7···O11$^{viii}$ | 0.88 (1) | 1.86 (1) | 2.649 (3) | 149.1 (8) |
| O9—H9···O12$^{ix}$ | 0.97 (1) | 1.97 (1) | 2.865 (3) | 151.9 (8) |
| O2—H2···O4$^{iv}$ | 0.95 (1) | 2.04 (1) | 2.905 (3) | 151.2 (8) |
| O9—H9···O11 | 0.97 (1) | 2.10 (1) | 2.603 (3) | 110.5 (8) |
| O3—H3···O2 | 0.93 (1) | 2.15 (1) | 2.804 (3) | 126.2 (8) |
| (3) | | | | |
| O5—H5···O10$^{x}$ | 1.00 (1) | 1.75 (1) | 2.689 (3) | 153.9 (8) |
| O7—H7···O11$^{ix}$ | 0.95 (1) | 1.78 (1) | 2.709 (2) | 165.3 (8) |
| O12—H12···O3$^{xi}$ | 0.88 (1) | 1.80 (1) | 2.663 (2) | 169.6 (8) |
| O4—H4···O1*W*$^{xii}$ | 0.95 (1) | 1.81 (1) | 2.760 (3) | 176.2 (8) |
| O2—H2···O10$^{xiii}$ | 0.93 (1) | 1.87 (1) | 2.766 (3) | 160.5 (8) |
| O1*W*—H1*W*···O8$^{xiv}$ | 0.96 (1) | 1.98 (1) | 2.893 (3) | 158.2 (8) |
| O9—H9···O11 | 0.85 (1) | 1.99 (1) | 2.594 (2) | 127.6 (8) |
| O8—H8···O12$^{xiii}$ | 0.93 (1) | 2.00 (1) | 2.898 (3) | 163.3 (8) |
| O3—H3···O11$^{xv}$ | 0.86 (1) | 2.07 (1) | 2.855 (3) | 150.8 (8) |
| (4) | | | | |
| O4—H4···O12$^{vii}$ | 0.95 (1) | 1.88 (1) | 2.795 (3) | 163.0 (8) |
| O1*W*—H2*W*1···O3$^{xvi}$ | 0.96 (1) | 1.99 (1) | 2.807 (3) | 141.2 (8) |

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$; (ii) $1+x, y, z$; (iii) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$; (v) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (vi) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (vii) $x, y-1, z$; (viii) $x-1, y, z$; (ix) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (x) $-\frac{1}{2}-x, -y, \frac{1}{2}+z$; (xi) $-x, y-\frac{1}{2}, \frac{5}{2}-z$; (xii) $\frac{1}{2}+x, \frac{1}{2}-y, 2-z$; (xiii) $\frac{1}{2}+x, -\frac{1}{2}-y, 2-z$; (xiv) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (xv) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (xvi) $1-x, y, 1-z$.

Table 4. *Selected torsion angles (°) for (1)–(4)*

| | (1) | (2) | (3) |
|---|---|---|---|
| O1—C1—O6—C7 | −68.3 (5) | −87.1 (2) | −86.0 (2) |
| O1—C1—C2—O2 | 171.2 (4) | 177.8 (2) | 166.8 (2) |
| O1—C1—C2—C3 | 50.8 (6) | 61.0 (2) | 45.2 (2) |
| O1—C5—C4—O4 | 63.3 (6) | 64.9 (2) | 56.1 (2) |
| O1—C5—C4—C3 | −60.4 (6) | −57.3 (2) | −63.2 (2) |
| O1—C5—C6—O5 | 60.6 (7) | 68.5 (2) | 180.0 (2) |
| O2—C2—C1—O6 | −72.2 (5) | −65.9 (2) | −77.9 (2) |
| O2—C2—C3—O3 | 67.3 (6) | 60.5 (2) | 68.9 (2) |
| O2—C2—C3—C4 | −166.9 (5) | −177.9 (2) | −166.8 (2) |
| O3—C3—C2—C1 | −171.9 (4) | 179.6 (2) | −171.9 (2) |
| O3—C3—C4—O4 | 52.1 (6) | 60.4 (2) | 61.3 (3) |
| O3—C3—C4—C5 | 175.5 (5) | −180.0 (2) | 178.7 (2) |
| O4—C4—C3—C2 | −72.6 (6) | −62.1 (2) | −61.5 (2) |
| O4—C4—C5—C6 | −54.3 (7) | −55.5 (2) | −61.5 (2) |
| O5—C6—C5—C4 | 179.5 (5) | −170.5 (2) | −60.5 (3) |
| O6—C1—O1—C5 | −178.0 (4) | 176.3 (2) | −172.3 (2) |
| O6—C1—C2—C3 | 167.5 (4) | 177.3 (2) | 160.5 (2) |
| O6—C7—C8—O8 | −73.8 (5) | −68.3 (2) | 55.6 (2) |
| O6—C7—C8—C9 | 169.5 (4) | 172.4 (2) | −71.9 (2) |
| O6—C7—C11—O7 | 61.9 (5) | 68.0 (2) | 171.8 (2) |
| O6—C7—C11—C12 | −57.2 (6) | −54.0 (2) | 52.3 (2) |
| O7—C11—C7—C8 | 175.7 (4) | −170.7 (2) | −66.8 (2) |
| O7—C11—C12—O12 | 57.9 (5) | 68.8 (2) | −61.5 (2) |
| O8—C8—C7—C11 | 168.8 (4) | 169.9 (2) | −64.5 (2) |
| O8—C8—C9—O9 | −56.0 (5) | −77.0 (2) | −49.8 (2) |
| O8—C8—C9—C10 | 63.7 (5) | 46.3 (2) | 71.7 (2) |
| O9—C9—C8—C7 | 63.5 (6) | 43.6 (2) | 78.2 (2) |
| O9—C9—C10—O10 | 12.6 (7) | −176.6 (2) | −175.4 (2) |
| O9—C9—C10—O11 | −168.6 (5) | 6.2 (2) | 5.6 (3) |
| O10—C10—C9—C8 | −103.8 (6) | 60.1 (2) | 60.9 (3) |
| O11—C10—C9—C8 | 75.1 (6) | −117.1 (2) | −118.1 (2) |
| O12—C12—C11—C7 | 179.8 (4) | −172.1 (2) | 59.7 (2) |
| C1—O1—C5—C4 | 67.6 (6) | 62.6 (2) | 64.9 (2) |

| | | | |
|---|---|---|---|
| C1—O1—C5—C6 | −171.1 (5) | −172.8 (2) | −171.5 (2) |
| C1—O6—C7—C8 | 131.1 (4) | 113.2 (2) | 128.7 (2) |
| C1—O6—C7—C11 | −108.3 (5) | −120.5 (2) | −110.0 (2) |
| C1—C2—C3—C4 | −46.1 (6) | −58.8 (2) | −47.5 (2) |
| C2—C1—O1—C5 | −62.7 (6) | −64.9 (2) | −55.4 (2) |
| C2—C1—O6—C7 | 172.2 (4) | 155.1 (2) | 154.0 (2) |
| C2—C3—C4—C5 | 50.8 (6) | 57.5 (2) | 55.9 (2) |
| C3—C4—C5—C6 | −178.0 (5) | −177.7 (2) | 179.2 (2) |
| C7—C8—C9—C10 | −176.8 (4) | 166.8 (2) | −160.4 (2) |
| C8—C7—C11—C12 | 56.6 (6) | 67.4 (2) | 173.7 (2) |
| C9—C8—C7—C11 | 52.0 (6) | 50.5 (2) | 168.0 (2) |

(4)

| | | | |
|---|---|---|---|
| O11—C1—C2—O2 | −155.3 (2) | O4—C4—C3—C2 | 58.8 (3) |
| O11—C1—C2—C3 | 82.9 (3) | O4—C4—C5—O5 | 53.5 (3) |
| O12—C1—C2—O2 | 24.4 (3) | O4—C4—C5—C6 | −68.5 (3) |
| O12—C1—C2—C3 | −97.5 (3) | O5—C5—C4—C3 | −67.2 (3) |
| O2—C2—C3—O3 | −68.8 (3) | O5—C5—C6—O6 | 61.8 (3) |
| O2—C2—C3—C4 | 51.6 (3) | O6—C6—C5—C4 | −174.5 (2) |
| O3—C3—C2—C1 | 51.9 (3) | C1—C2—C3—C4 | 172.2 (2) |
| O3—C3—C4—O4 | 179.1 (2) | C2—C3—C4—C5 | −177.1 (2) |
| O3—C3—C4—C5 | −56.9 (3) | C3—C4—C5—C6 | 170.8 (2) |

Table 5. *Asymmetry parameters (Duax & Norton, 1975) of six-membered rings in (1)–(3)*

| | (1) | (2) | (3) |
|---|---|---|---|
| $\Delta C_s$(O1) | 6.8 (3) | 2.6 (2) | 12.7 (2) |
| $\Delta C_s$(C1) | 15.2 (3) | 3.1 (2) | 12.4 (2) |
| $\Delta C_s$(C2) | 8.5 (3) | 5.4 (2) | 1.7 (2) |
| $\Delta C_2$(O1—C1) | 15.6 (3) | 1.6 (2) | 17.8 (2) |
| $\Delta C_2$(C1—C2) | 16.7 (3) | 5.6 (2) | 8.5 (2) |
| $\Delta C_2$(C2—C3) | 1.6 (3) | 5.9 (2) | 9.4 (2) |

Data collection and cell refinement were performed using CAD-4 software (Schagen, Straver, van Meurs & Williams, 1989; Frenz, 1986). For all compounds, anisotropic displacement parameters were applied for all non-H atoms. H atoms were found in a difference Fourier map and refined as riding: isotropically for (2) and (4), and with fixed isotropic displacement parameters for (1) and (3). The absolute structures of (1)–(4) were determined by three methods: the Hamilton test (Hamilton, 1965), the Rogers $\eta$-test (Rogers, 1981), both using *SHELXTL/PC* (Sheldrick, 1991), and calculation of the Flack parameter $x$ (Flack, 1983) using *SHELXL*93 (Sheldrick, 1993). Results for (1): $\eta$ = 1.04 (4), $\eta_{inv}$ = −1.03 (4); $N$ = 1587, $R_{ratio}$ = 1.006, $\alpha < 10^{-6}$; $x$ = 0.06 (4). For (2): $\eta$ = 1.01 (2), $\eta_{inv}$ = −1.00 (2); $N$ = 3035, $R_{ratio}$ = 1.688, $\alpha < 10^{-9}$; $x$ = 0.02 (1). For (3): $\eta$ = 1.4 (3), $\eta_{inv}$ = 1.4 (3); $N$ = 1581, $R_{ratio}$ = 1.0015, $\alpha = 2.5 \times 10^{-2}$; $x$ = 0.08 (16). For (4): $\eta$ = 1.23 (4), $\eta_{inv}$ = −1.19 (4); $N$ = 976, $R_{ratio}$ = 1.398, $\alpha < 10^{-9}$; $x$ = 0.01 (1). Structure solution and refinement were performed using *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1260). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# *m*-Anisidinium Dihydrogenmonoarsenate

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## Abstract

In the structure of $(1,3\text{-}CH_3O\text{–}C_6H_4\text{–}NH_3)^+.H_2AsO_4^-$, the $H_2AsO_4^-$ and $(1,3\text{-}CH_3O\text{–}C_6H_4\text{–}NH_3)^+$ entities alternate in layers perpendicular to the $a$ axis. These organic and inorganic layers are held together in the crystal by N—H···O hydrogen bonds. The $H_2AsO_4^-$ groups are connected by hydrogen bonds to form pairs, with internal short As···As distances of 4.5 Å.

## Comment

The structure and numbering scheme of the title compound, (I), are shown in Figs. 1 and 2. The As···As distance of 4.5 Å between pairs of $H_2AsO_4^-$ tetrahedra is significantly shorter than that observed in ethylenediammonium monohydro-