Monohydrate Sodium and Hexaaqua-magnesium *p*-Chloro-*trans*-cinnamates

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Abstract

The crystal structures of sodium 4-chloro-(E)-3-phenylpropenoate monohydrate, $2Na^+.2C_9H_6ClO_2^-.2H_2O$, and hexaaquamagnesium bis[4-chloro-(E)-3-phenylpropenoate], $[Mg(H_2O)_6]^{2+}.2C_9H_6ClO_2^-$, are layered. They consist of hydrophilic sheets of coordinated cations which sandwich bilayers of organic anions. In addition to electrostatic forces, the structures are held together by van der Waals and hydrogen-bonding interactions.

Comment

The structures were determined as part of an investigation into the packing and reactivity of substituted cinnamate anions within the interlayer region of layered double hydroxides (LDH's). The solid-state chemistry of the cinnamic acids is well known (Schmidt, 1971). LDH's are materials consisting of positively charged metal oxide/hydroxide layers separated by intercalated anions and water molecules (Jones & Chibwe, 1990). Based on knowledge gained from studies of other organic salts (Kariuki & Jones, 1992), it was anticipated that the structures of the cinnamates would be layered and hence provide some insight into the arrangement of the anions in the LDH (Valim, Kariuki, King & Jones, 1992).

The asymmetric unit of the sodium salt, (I), consists of two anions, two cations and two molecules of water of crystallization (Fig. 1). The cations occupy two distinct types of sites. One site (Na1) is coordinated by six O atoms (three from water molecules and three from carboxylate groups) in the form of a distorted octahedron. The second type of site (Na2) is coordinated

by three water and four carboxylate O atoms which form a distorted monocapped octahedron. In the crystal structure, the octahedra link to create infinite sheets which are separated by organic bilayers (Fig. 2). In the anions the $—(CH)_2—CO_2^-$ group is planar. The angles between the plane of this group and the phenyl ring are 18.0 (1)° for anion C1–C9 and 20.8 (1)° for C10–C18.

(I) $2Na^+.2H_2O$ ($n = 2$)
(II) $Mg(H_2O)_6^{2+}$ ($n = 2$)
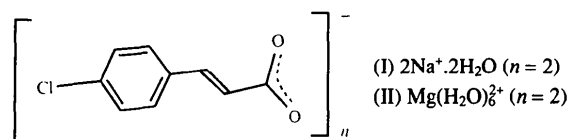
The asymmetric unit of the magnesium salt, (II), is composed of one anion, one cation and three molecules of water of hydration. The cations occupy centres of symmetry and each is coordinated by six molecules of water in the form of an octahedron. The octahedra are present as discrete units and are linked to the anions by a network of hydrogen bonds (Fig. 3). The dihedral angle between the planar $—(CH)_2—CO_2^-$ group and the phenyl ring is 40.9 (1)°.
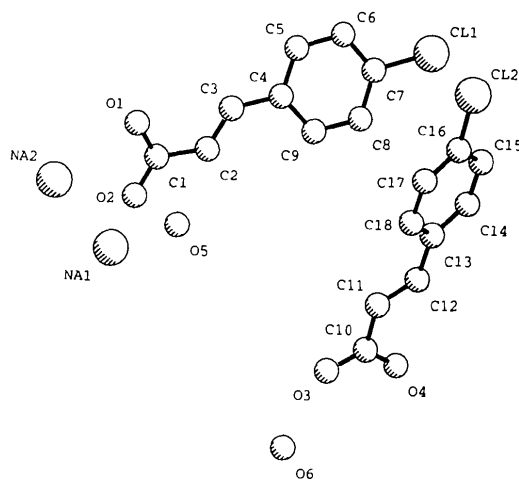

Fig. 1. The asymmetric unit of the sodium salt showing the numbering scheme. H atoms have been omitted for clarity.
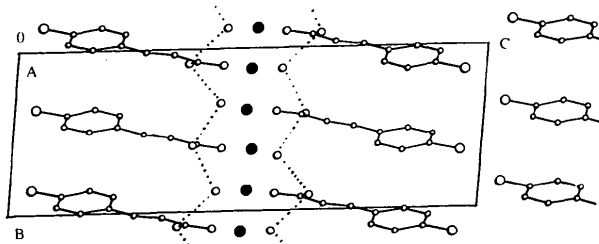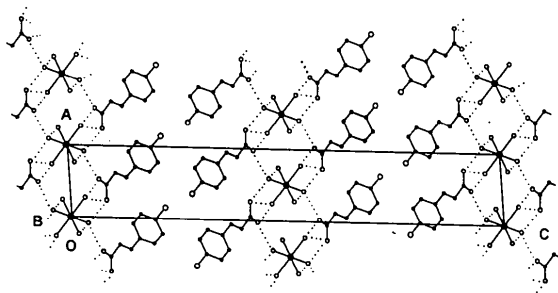

Fig. 2. The structure of the sodium salt viewed down the *a* axis. H atoms have been omitted for clarity and the filled circles are Na^+. The dotted lines represent hydrogen bonds.

Fig. 3. The structure of the magnesium salt viewed along the b axis.

Experimental

Compound (I)

Crystal data

$2Na^+.2C_9H_6ClO_2^-.2H_2O$
$M_r = 445.19$
Triclinic
$P\bar{1}$
$a = 6.2368\ (10)$ Å
$b = 7.3286\ (10)$ Å
$c = 21.438\ (3)$ Å
$\alpha = 95.834\ (10)°$
$\beta = 97.413\ (10)°$
$\gamma = 89.533\ (10)°$
$V = 966.6\ (2)$ Å^3
$Z = 2$
$D_x = 1.530$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25
reflections
$\theta = 9–14°$
$\mu = 0.414$ mm^{-1}
$T = 293\ (2)$ K
Transparent plates
$0.38 \times 0.27 \times 0.04$ mm
Colourless
Crystal source: slow
evaporation of aqueous
solution at 295 K

Data collection

Enraf–Nonius CAD-4
  diffractometer
$2\theta/\omega$ scans
Absorption correction:
  none
3506 measured reflections
3406 independent reflections
2145 observed reflections
  $[I > 2\sigma(I)]$
$R_{int} = 0.0277$

$\theta_{max} = 24.97°$
$h = -7 \to 7$
$k = -8 \to 8$
$l = 0 \to 25$
3 standard reflections
  monitored every 100
  reflections
  frequency: 120 min
  intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0420$
$wR(F^2) = 0.1110$
$S = 1.203$
3401 reflections
281 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.014$

$\Delta\rho_{max} = 0.239$ e Å^{-3}
$\Delta\rho_{min} = -0.298$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from International Tables
  for Crystallography (1992,
  Vol. C, Tables 4.2.6.8 and
  6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)

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

	x	y	z	U_{eq}
Na1	0.7332 (2)	0.12534 (15)	0.49639 (5)	0.0321 (3)
Na2	0.7458 (2)	-0.3759 (2)	0.50818 (5)	0.0380 (3)
Cl1	0.1550 (2)	0.14896 (13)	0.95384 (4)	0.0548 (3)
Cl2	0.2984 (2)	0.64764 (14)	0.95561 (4)	0.0607 (3)
O1	0.9014 (3)	-0.0872 (3)	0.63755 (10)	0.0423 (6)
O2	0.6146 (3)	-0.1035 (3)	0.56334 (9)	0.0346 (5)
O3	-0.3977 (3)	0.3854 (3)	0.55571 (9)	0.0376 (5)
O4	-0.6546 (3)	0.4047 (3)	0.61872 (10)	0.0406 (5)
O5	0.0992 (4)	-0.3342 (4)	0.56463 (11)	0.0373 (5)
O6	-0.0924 (4)	0.8763 (4)	0.43808 (11)	0.0376 (5)
C1	0.6986 (5)	-0.0784 (4)	0.62045 (13)	0.0296 (6)
C2	0.5575 (5)	-0.0335 (4)	0.67026 (13)	0.0320 (7)
C3	0.6339 (5)	-0.0140 (4)	0.73091 (14)	0.0329 (7)
C4	0.5143 (5)	0.0306 (4)	0.78450 (13)	0.0306 (6)
C5	0.6132 (5)	0.0067 (4)	0.84531 (14)	0.0360 (7)
C6	0.5054 (5)	0.0453 (4)	0.89752 (14)	0.0388 (8)
C7	0.2972 (5)	0.1103 (4)	0.88922 (14)	0.0372 (7)
C8	0.1965 (5)	0.1404 (4)	0.82969 (15)	0.0400 (8)
C9	0.3053 (5)	0.0999 (4)	0.77795 (14)	0.0373 (7)
C10	-0.4585 (5)	0.4110 (4)	0.60989 (14)	0.0321 (7)
C11	-0.2918 (5)	0.4557 (4)	0.66490 (14)	0.0344 (7)
C12	-0.3358 (5)	0.4844 (4)	0.72345 (14)	0.0349 (7)
C13	-0.1822 (5)	0.5314 (4)	0.78015 (13)	0.0327 (7)
C14	-0.2380 (5)	0.5056 (4)	0.83970 (15)	0.0403 (8)
C15	-0.0933 (5)	0.5440 (4)	0.89366 (15)	0.0423 (8)
C16	0.1096 (5)	0.6103 (4)	0.88853 (15)	0.0393 (7)
C17	0.1672 (5)	0.6432 (4)	0.83076 (14)	0.0416 (8)
C18	0.0224 (5)	0.6043 (4)	0.77696 (14)	0.0415 (8)

Table 2. Selected geometric parameters (Å, °) for (I)

Na1—O2^i	2.370 (2)	O1—C1	1.273 (3)
Na1—O3^{ii}	2.381 (2)	O2—C1	1.264 (3)
Na1—O6^{iii}	2.435 (3)	O3—C10	1.263 (4)
Na1—O5^i	2.436 (3)	O4—C10	1.264 (4)
Na1—O6^{iv}	2.487 (3)	C1—C2	1.480 (4)
Na1—O2	2.491 (2)	C2—C3	1.320 (4)
Na2—O3^{iii}	2.350 (2)	C3—C4	1.457 (4)
Na2—O5^{ii}	2.380 (3)	C10—C11	1.480 (4)
Na2—O2	2.408 (2)	C11—C12	1.315 (4)
Na2—O3^v	2.410 (2)	C12—C13	1.461 (4)
Na2—O4^v	2.693 (2)	O5$\cdots$O1^{vii}	2.670 (4)
Na2—O5^{vi}	2.751 (3)	O5$\cdots$O4^{iii}	2.703 (4)
Na2—O6^{iii}	2.771 (3)	O6$\cdots$O4^{viii}	2.695 (4)
C11—C7	1.738 (3)	O6$\cdots$O1^{iv}	2.734 (4)
C12—C16	1.737 (3)		
O2^i—Na1—O3^{ii}	87.01 (8)	O2—C1—O1	123.1 (3)
O2^i—Na1—O6^{iii}	98.61 (8)	O2—C1—C2	119.2 (2)
O2^i—Na1—O5^i	98.77 (8)	O1—C1—C2	117.7 (3)
O3^{ii}—Na1—O5^i	88.48 (9)	C3—C2—C1	122.1 (3)
O6^{iii}—Na1—O5^i	87.28 (10)	C2—C3—C4	127.8 (3)
O2^i—Na1—O6^{iv}	175.37 (10)	C9—C4—C3	122.7 (3)
O2^i—Na1—O2	88.55 (7)	C5—C4—C3	119.3 (3)
O5^i—Na1—O2	171.90 (9)	C6—C7—C11	119.7 (2)
O3^{iii}—Na2—O2	103.38 (8)	C8—C7—C11	119.3 (2)
O5^{ii}—Na2—O2	92.21 (9)	O4—C10—O3	122.9 (3)
O5^{ii}—Na2—O3^v	172.82 (9)	O4—C10—C11	119.0 (3)
O2—Na2—O3^v	85.50 (8)	O3—C10—C11	118.0 (3)
O3^v—Na2—O4^v	51.20 (7)	C12—C11—C10	123.4 (3)
O2—Na2—O5^{vi}	174.19 (8)	C11—C12—C13	126.9 (3)
O4^v—Na2—O5^{vi}	59.53 (7)	C14—C13—C12	120.2 (3)
O3^{iii}—Na2—O6^{iii}	172.77 (9)	C18—C13—C12	121.8 (3)
O2—Na2—O6^{iii}	82.59 (8)	C17—C16—C12	119.2 (3)
O4^v—Na2—O6^{iii}	59.07 (7)	C15—C16—C12	119.6 (2)

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 + x, y, z$; (iii) $1 + x, y - 1, z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $-x, -y, 1 - z$; (vi) $1 - x, -1 - y, 1 - z$; (vii) $x - 1, y, z$; (viii) $-1 - x, 1 - y, 1 - z$.

Compound (II)

Crystal data

$[Mg(H_2O)_6]2(C_9H_6ClO_2)$
$M_r = 247.79$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å

Monoclinic
$P2_1/n$
$a = 5.7790$ (10) Å
$b = 5.300$ (3) Å
$c = 35.811$ (5) Å
$\beta = 95.06$ (2)°
$V = 1092.5$ (7) Å^3
$Z = 4$
$D_x = 1.507$ Mg m^{-3}

Cell parameters from 25
    reflections
$\theta = 6\text{--}13°$
$\mu = 0.379$ mm^{-1}
$T = 293$ (2) K
Transparent plates
$0.50 \times 0.42 \times 0.13$ mm
Colourless
Crystal source: slow
    evaporation of aqueous
    solution at 295 K

Data collection

Enraf–Nonius CAD-4
    diffractometer
$2\theta/\omega$ scans
Absorption correction:
    none
1955 measured reflections
1923 independent reflections
1566 observed reflections
    $[I > 2\sigma(I)]$
$R_{int} = 0.0127$

$\theta_{max} = 24.98°$
$h = -6 \rightarrow 6$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 42$
3 standard reflections
    monitored every 100
    reflections
    frequency: 180 min
    intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0310$
$wR(F^2) = 0.0903$
$S = 1.180$
1920 reflections
172 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.4528P]$
    where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.016$
$\Delta\rho_{max} = 0.192$ e Å^{-3}
$\Delta\rho_{min} = -0.241$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
    from *International Tables*
    for Crystallography (1992,
    Vol. C, Tables 4.2.6.8 and
    6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

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

	x	y	z	U_{eq}
Mg1	0	1/2	0	0.0254 (2)
Cl1	0.15111 (10)	0.00444 (11)	0.21921 (2)	0.0523 (2)
O1	-0.7609 (2)	1.0442 (3)	0.08599 (4)	0.0357 (3)
O2	-0.4738 (2)	1.2931 (3)	0.07147 (4)	0.0403 (4)
O3	0.2729 (2)	0.6395 (3)	0.03617 (4)	0.0338 (3)
O4	-0.0837 (2)	0.2423 (2)	0.03976 (4)	0.0309 (3)
O5	0.2375 (3)	0.2373 (3)	-0.01637 (4)	0.0388 (4)
C1	-0.5496 (3)	1.1040 (3)	0.08800 (5)	0.0284 (4)
C2	-0.3785 (3)	0.9429 (4)	0.11007 (5)	0.0327 (4)
C3	-0.4392 (3)	0.7761 (4)	0.13469 (5)	0.0342 (4)
C4	-0.2863 (3)	0.5975 (4)	0.15603 (5)	0.0332 (4)
C5	-0.3527 (3)	0.4943 (4)	0.18909 (6)	0.0402 (5)
C6	-0.2179 (4)	0.3156 (4)	0.20900 (6)	0.0427 (5)
C7	-0.0160 (3)	0.2370 (4)	0.19526 (5)	0.0371 (5)
C8	0.0562 (4)	0.3349 (4)	0.16263 (6)	0.0399 (5)
C9	-0.0794 (3)	0.5144 (4)	0.14326 (5)	0.0375 (5)

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

Mg1—O4^i	2.0608 (14)	C1—C2	1.481 (3)
Mg1—O4	2.0610 (14)	C2—C3	1.317 (3)
Mg1—O5	2.0755 (15)	C3—C4	1.464 (3)
Mg1—O5^i	2.0756 (15)	O3$\cdots$O2^{ii}	2.605 (2)
Mg1—O3	2.0860 (13)	O3$\cdots$O1^{iii}	2.808 (2)
Mg1—O3^i	2.0860 (13)	O4$\cdots$O2^{iv}	2.626 (2)
Cl1—C7	1.744 (2)	O4$\cdots$O1^{ii}	2.604 (2)
O1—C1	1.257 (2)	O5$\cdots$O4^v	2.796 (2)
O2—C1	1.262 (2)		

O4—Mg1—O5	87.25 (7)	C3—C2—C1	122.6 (2)
O4—Mg1—O3	90.96 (6)	C2—C3—C4	126.8 (2)
O5—Mg1—O3	86.01 (6)	C5—C4—C3	120.0 (2)
O1—C1—O2	123.3 (2)	C9—C4—C3	122.1 (2)
O1—C1—C2	119.0 (2)	C6—C7—Cl1	119.4 (2)
O2—C1—C2	117.7 (2)	C8—C7—Cl1	119.2 (2)

Symmetry codes: (i) $-x, 1 - y, -z$; (ii) $1 + x, y - 1, z$; (iii) $1 + x, y, z$; (iv) $x, y - 1, z$; (v) $-x, -y, -z$.

All non-H atoms were assigned anisotropic displacement parameters. The positions of the anion H atoms were fixed geometrically and the difference Fourier synthesis map revealed the locations of the water H atoms. Data collection and cell refinement: Enraf–Nonius CAD-4 software. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1992). Molecular graphics: *DTMM* (Crabbe & Appleyard, 1991). Software used to prepare material for publication: *SHELXL92*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1117). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Linear Oligo(ferrocenylsilane)

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Abstract

The title compound 1,1′-bis(ferrocenyldimethylsilyl)-ferrocene, [{C$_5$H$_5$-Fe-C$_5$H$_4$-Si(Me$_2$)-C$_5$H$_4$}$_2$Fe] {or bis-[1,3(η^5)-cyclopentadienyl][μ-1(η^5):2(η^5)-dimethylsilanediyldicyclopentadienyl][μ-2(η^5):3(η^5)-dimethylsilanedi-