Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Sodium dihydrogen tris(cyclopropanecarboxylate)

Kenneth W. Muir,* Alistair Macdonald, Alistair Murray and Allison Macdonald

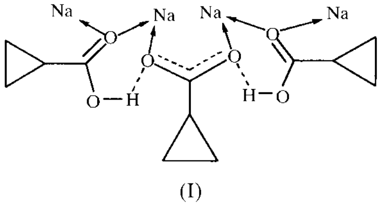
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland
Correspondence e-mail: ken@chem.gla.ac.uk

Received 6 December 1999
Accepted 19 January 2000

The title acid salt, $\mathrm{Na^+\cdot C_4H_5O_2^-\cdot 2C_4H_6O_2}$, contains finite anions in which two cyclopropanoic acid molecules are hydrogen bonded to a cyclopropanoate residue. Each such anion interacts with four different $\mathrm{Na^+}$ cations.

Comment

The title acid salt, (I), was obtained during an attempt to prepare a conventional acid salt of cyclopropanoic acid. Most monocarboxy acids, H*X*, form acid salts of the general type *M*H*X*$_2$, where *M* is any singly charged cation. However, Speakman (1972) noted in his review of the structures of acid salts that more complex compositions are very occasionally found, citing the examples of KH$_2$*X*$_3$ (H*X* = acetic acid) and RbH$_2$*X*$_3$ (H*X* = monochloroacetic acid). Salt (I) belongs to this rare class of acid salts. It appears to be identical to the compound whose cell dimensions were reported by Hwang & Donohue (1971).



(I)

The asymmetric unit of (I) consists of one Na$^+$ cation and an $X\mathrm{H}\cdots X\cdots \mathrm{H}X^-$ anion formed by linking two cyclopropanoic acid molecules, H*X*, to the same cyclopropanoate anion through moderate-to-strong (Jeffrey, 1997) O—H$\cdots$O hydrogen bonds (see Table 2). The geometries of the three independent cyclopropanoic acid residues are consistent with an ordered arrangement of hydrogen bonds; the deprotonated acid contains C11—O bonds of nearly equal length [1.251 (2) and 1.254 (2) Å], whereas the C21—O and C31—O bonds show the difference in length expected if O22 and O32 are protonated [1.214 (2) and 1.305 (2) Å, and 1.189 (2) and 1.325 (2) Å, respectively]. Disorder of the C32–C34 ring obscures some of its structural details, but the other two cyclopropane units show the expected shortening of the distal C—C bonds [1.465 (3) and 1.461 (3) Å] relative to the others [1.491 (3)–1.504 (3) Å; Allen, 1980].

The Na$^+$ ions lie almost exactly on the 2_1 screw axes (Fig. 1). In consequence, the operations of the screw axes generate nearly linear chains of regularly spaced Na$^+$ cations which run parallel to the *b* axis. The distance of 3.402 (2) Å between adjacent Na$^+$ ions in these chains is only 0.014 Å greater than

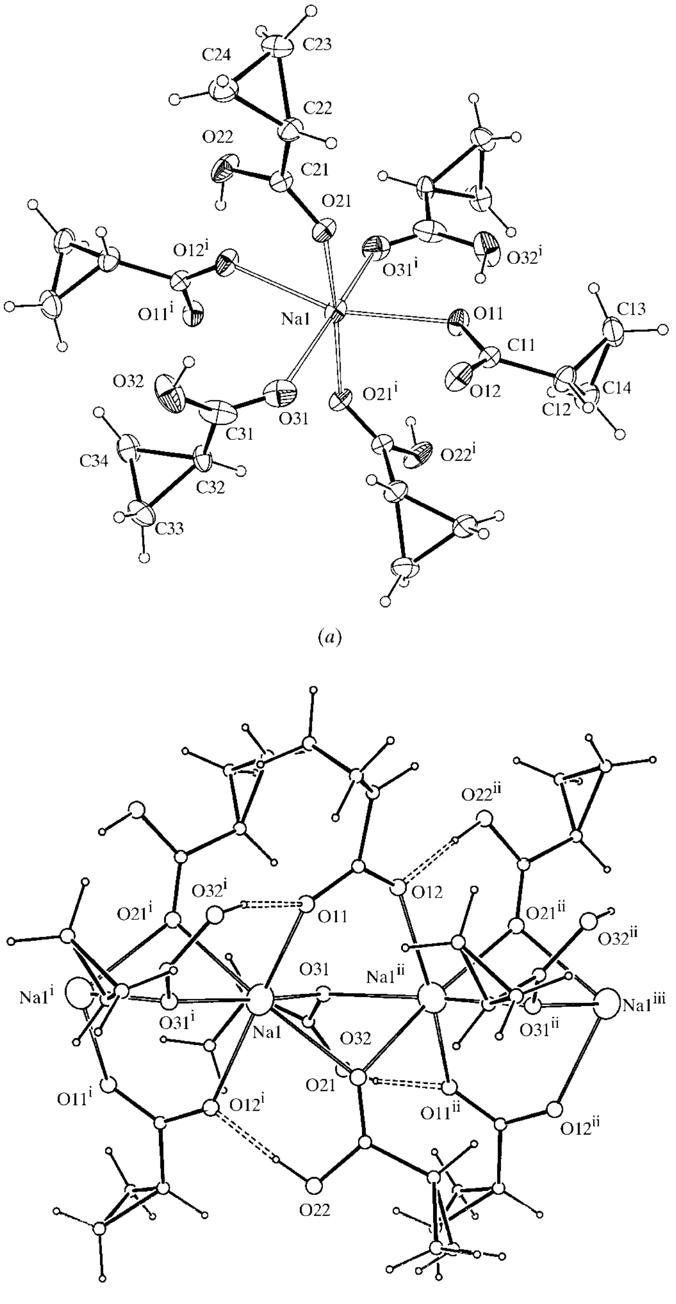


Figure 1
(*a*) A view of the coordination of the Na$^+$ ion showing 20% probability displacement ellipsoids and the atom labelling. Only one component of the disordered C32–C34 ring is displayed. (*b*) A view of one complete anion, formed by the O11$\cdots$HO32^i and O12$\cdots$HO22^{ii} hydrogen bonds, and of the four Na$^+$ cations to which it bonds. These cations are part of a chain running parallel to the *b* axis. [Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $x, -1+y, z$.]

b/2. Each Na^+ ion is surrounded by a distorted octahedron of O atoms (Table 1). Adjacent octahedra are linked through the O21$\cdots$O31 edge and also through the η^2-bridging carboxy group containing O11 and O12. Each Na^+ ion is bonded to three different XH$\cdots X \cdots$HX^- anions and each XH$\cdots X \cdots$HX^- anion donates six electron pairs to four different Na^+ ions. This highly stable arrangement uses all lone pairs on the unprotonated O atoms O11, O12, O21 and O31, and the hydrogen-bond-donor properties of the O22 and O32 hydroxy groups for inter-residue bonding.

Since Speakman's (1972) review, two MH_2X_3 structures have been fully described and both contain the finite XH$\cdots X \cdots$HX^- anions also found in (I). The cation in $KH_2(CH_3CO_2)_3$ (Efremov *et al.*, 1986) is eight-coordinate. $NaH_2(CH_3CO_2)_3$ more closely resembles (I), with the finite XH$\cdots X \cdots$HX^- anions stabilizing a chain of octahedrally coordinated Na^+ cations related by a 4_1 screw axis; the Na—O distances [2.316 (4)–2.580 (4) Å] are less regular than those in (I) and the O$\cdots$O distances in the hydrogen bonds [2.509 (4) and 2.503 (4) Å] are somewhat shorter (Perrotti & Tazzoli, 1981). Interestingly, acetic acid also forms a regular sodium salt, $Na(CH_3CO_2)$, which crystallizes as a trihydrate (Doxsee & Stevens, 1990) and in two anhydrous forms (Hsu & Nordman, 1983), and a regular acid salt $NaHX_2$ (Barrow *et al.*, 1975); all of these have been structurally characterized. Although an analysis of potassium dihydrogen tris(*o*-chlorobenzoate) was successful (Golic & Speakman, 1975), no structural details have been published.

Experimental

Crystals were obtained from an aqueous solution of cyclopropanoic acid and sodium hydroxide in a 2:1 molar ratio. Analysis found: C 50.8, H 6.05%; calculated for $C_{12}H_{17}NaO_6$: C 51.4, H 6.07%. IR (KBr discs): 3439, 3081, 3022, 2860, 2480, 1905, 1692, 1522, 1430, 1362, 1294, 1228 cm^{-1}.

Crystal data

$Na^+ \cdot C_4H_5O_2^- \cdot 2C_4H_6O_2$
$M_r = 280.25$
Monoclinic, $P2_1/n$
$a = 12.3629\ (7)$ Å
$b = 6.7768\ (4)$ Å
$c = 16.9374\ (12)$ Å
$\beta = 101.151\ (6)^\circ$
$V = 1392.24\ (15)$ Å^3
$Z = 4$
$D_x = 1.337$ Mg m^{-3}
D_m measured by flotation in heptane/1,2-dichloroethane
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 18.3$–23.8°
$\mu = 0.132$ mm^{-1}
$T = 294\ (2)$ K
Needle, colourless
0.49 × 0.21 × 0.11 mm

Table 1
Selected geometric parameters (Å, °).

Na1—O12^i	2.3429 (14)	Na1—O21^i	2.3972 (13)
Na1—O11	2.3590 (14)	Na1—O31	2.5162 (18)
Na1—O21	2.3939 (13)	Na1—O31^i	2.534 (2)
O12^i—Na1—O11	160.70 (6)	O31—Na1—O31^i	169.29 (6)
O21—Na1—O21^i	171.08 (5)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
4477 measured reflections
3357 independent reflections
2175 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 27^\circ$
$h = -15 \rightarrow 2$
$k = -8 \rightarrow 1$
$l = -23 \rightarrow 21$
3 standard reflections every 184 reflections frequency: 120 min intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.042$
$wR(F^2) = 0.125$
$S = 1.017$
3357 reflections
207 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 0.352P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
O22—H2$\cdots$O12^i	0.93 (3)	1.62 (3)	2.5475 (18)	171 (3)
O32—H3$\cdots$O11^{ii}	0.86 (3)	1.72 (3)	2.567 (2)	167 (3)

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

The carboxy H atoms, H2 and H3, were located in a ΔF synthesis and then refined freely. Other H atoms were positioned using stereochemical criteria and were then constrained to ride on their parent C atoms. The C32–C34 cyclopropane ring is disordered over two sites with equal probability and the parameters of the disordered atoms are therefore subject to some systematic error.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WINGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1395). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (1980). *Acta Cryst.* B**36**, 81–96.
Barrow, M. J., Currie, M., Muir, K. W., Speakman, J. C. & White, D. N. J. (1975). *J. Chem. Soc. Perkin Trans.* 2, pp. 15–18.
Doxsee, K. M. & Stevens, R. C. (1990). *J. Incl. Phenom.* **9**, 327–330.
Efremov, V. A., Endeladze, N. O., Chubinidze, A. D. & Trunov, V. K. (1986). *Dokl. Akad. Nauk SSSR*, **286**, 352–355.
Enraf–Nonius (1992). *CAD*-4 *EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Golic, L. & Speakman, J. C. (1975). *Izv. Jug. Cent. Kristallogr. Ser. A*, **10**, 72.
Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.
Hsu, L.-Y. & Nordman, C. E. (1983). *Acta Cryst.* C**39**, 690–694.
Hwang, K. J. & Donohue, J. (1971). *Am. Crystallogr. Assoc. Abstr. Pap.* (Winter), p. 35.
Jeffrey, G. A. (1997). In *An Introduction to Hydrogen Bonding*. New York: Oxford University Press.
Perrotti, A. & Tazzoli, V. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1768–1769.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Speakman, J. C. (1972). *Struct. Bonding* (*Berlin*), **12**, 141–199.