

Sodium 1-carboxycyclopropane-
1-carboxylate cyclopropane-1,1-di-
carboxylic acid monohydrateKenneth W. Muir,* Alistair MacDonald and Alan
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Received 8 October 2004

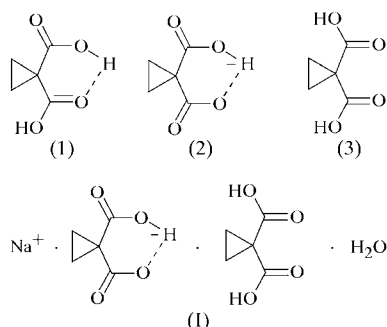
Accepted 25 October 2004

Online 11 November 2004

In the title type B_2 acid salt, $\text{Na}(\text{LH})(\text{LH}_2)\cdot\text{H}_2\text{O}$ [$\text{LH}_2 = \text{C}_2\text{H}_4\text{C}(\text{CO}_2\text{H})_2$] or $\text{Na}^+\cdot\text{C}_5\text{H}_5\text{O}_4^- \cdot \text{C}_5\text{H}_6\text{O}_4\cdot\text{H}_2\text{O}$, the vertices of a distorted octahedron centred on each Na^+ cation are defined by six O atoms, one from a water molecule, one from an internally hydrogen-bonded LH^- anion and four from three neutral LH_2 acid molecules. Chains of edge-sharing O_6 octahedra are stabilized by hydrogen bonds, which interconnect the donor H_2O and LH_2 molecules and LH^- anions. In particular, the LH_2 molecule donates H atoms to LH^- and H_2O and forgoes the internal hydrogen bond which stabilizes the free acid and all of its characterized salts.

Comment

The cyclopropane-1,1-dicarboxylic acid molecule, (1), hereinafter LH_2 , where L is $\text{C}_2\text{H}_4\text{C}(\text{CO}_2)_2$, contains an internal $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond (see scheme) and, in consequence, its monoanion LH^- , (2), is a very weak acid (Meester *et al.*, 1971). The LH^- anions of the related acid salt $\text{K}(\text{LH})\cdot 0.5\text{H}_2\text{O}$ are also stabilized by internal $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Dubourg *et al.*, 1990). We now report that our attempt to prepare the analogous sodium salt $\text{Na}(\text{LH})\cdot 0.5\text{H}_2\text{O}$ has instead produced the title compound, $\text{Na}(\text{LH})(\text{LH}_2)\cdot\text{H}_2\text{O}$, (I).



Crystals of (I) are built up from Na^+ cations, LH^- anions, molecules of the neutral acid and water. The LH^- anions

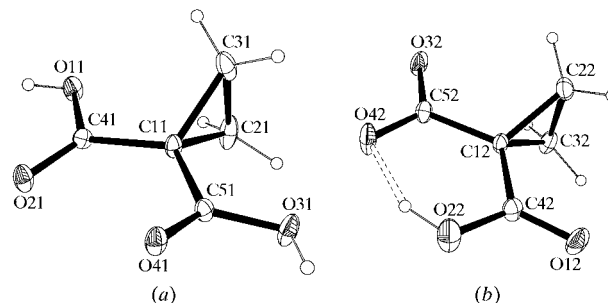


Figure 1

Views of (a) the LH_2 molecule and (b) the LH^- anion of (I). Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii.

(Fig. 1b) contain an internal $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond with an $\text{O}\cdots\text{O}$ distance of 2.429 (3) Å, which is even shorter than the corresponding bond in the free acid (2.563 Å). The internal $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds in the LH_2 molecule (Meester *et al.*, 1971) and in the LH^- anions of (I) and $\text{K}(\text{LH})\cdot 0.5\text{H}_2\text{O}$ (Dubourg *et al.*, 1990) all have ordered H atoms conventionally bonded to one of the O atoms. This contrasts with $[\text{Co}(\text{H}_2\text{O})_6](\text{LH})_2$, where the anions straddle crystallographic mirror planes so that the acidic H atom is either equidistant from the two O atoms or is disordered (Schwarz *et al.*, 1998).

The LH_2 molecules of (I) (Fig. 1a) have near C_{2v} symmetry but adopt a conformation, (3), which precludes internal hydrogen bonding [$\text{O}21\cdots\text{O}41 = 2.834$ (3) Å]. The geometries of the LH_2 molecule and LH^- anion (Table 1) show typical features (see, for example, Meester *et al.*, 1971; Dubourg *et al.*, 1990; Muir *et al.*, 2000; Schwarz *et al.*, 1998). First, pairs of C—O bond lengths differ by > 0.08 Å in CO_2H groups and by < 0.02 (5) Å in CO_2^- groups. Secondly, an electronic effect of the carboxyl substituents shortens the distal $\text{C}2n-\text{C}3n$ ($n = 1$ or 2) ring bonds by 0.05–0.07 Å relative to the other C—C bonds in the cyclopropane rings. Finally, each carboxyl group nearly coincides with the plane normal to $\text{C}2n-\text{C}3n$ passing through $\text{C}1n$; the $\text{C}51$ carboxyl group is an exception, as can be seen by comparing the $\text{C}41-\text{C}11-\text{C}51-\text{O}41$ torsion angle with the others in Table 1.

The crystal structure of (I) is built from kinked chains of identical NaO_6 octahedra (Table 1 and Fig. 2a), which are axially elongated along the $\text{O}21\cdots\text{Na}1\cdots\text{O}1\text{W}$ direction and linked *via* edges which pass through crystallographic inversion centres. Atom $\text{Na}1$ shares octahedral edges with atoms $\text{Na}1^i$ and $\text{Na}1^{iii}$, themselves related directly by translation along the a axis which thus defines the direction of the chains [symmetry codes: (i) $1-x, 1-y, 2-z$; (iii) $-x, 1-y, 2-z$].

Atom $\text{Na}1$ bonds to three different LH_2 molecules, one water molecule and one LH^- anion. In consequence, the LH_2 molecule participates in four $\text{Na}-\text{O}$ bonds (Fig. 2b), with atom $\text{O}2^i$ bonded to both atoms $\text{Na}1$ and $\text{Na}1^i$, and atom $\text{O}41^i$ shared between atoms $\text{Na}1$ and $\text{Na}1^{iii}$. The LH^- anion is attached to only one cation, through atom $\text{O}42$, which is part of the ionized carboxyl group. Similarly, the water atom $\text{O}1\text{W}$

bonds to only one Na⁺ cation. Each acid molecule is also the donor in two O—H···O hydrogen bonds (Table 2), namely a very strong bond [O···O = 2.478 (3) Å] to the LH⁻ anion and a weaker one [O···O = 2.642 (3) Å] to a water molecule. Atom O22 accepts a hydrogen bond from atom O1W. The resulting arrangement surrounds atoms Na1 and Na1ⁱⁱⁱ by a roughly planar belt containing an (LH₂–LH⁻–H₂O)₂ ring in which the individual molecules and anions are joined by hydrogen bonds. Not shown in Fig. 2(b) are the O1W–H···O12 hydrogen bonds which link together the chains of octahedra.

The crystal architecture of (I) uses all five available O–H groups as hydrogen-bond donors, two of these bonds being very short (O···O < 2.50 Å). In each independent O–H···O bond, the two O atoms are unrelated by crystallographic symmetry. Compound (I) is therefore a B₂ acid salt in the classification of Speakman (1972).

It is tempting to ascribe the different stoichiometries of the sodium and potassium acid salts of cyclopropane-1,1-dicarboxylic acid to the different ionic radii of K⁺ and Na⁺. However, in the case of malonic acid, L'H₂, where L' is

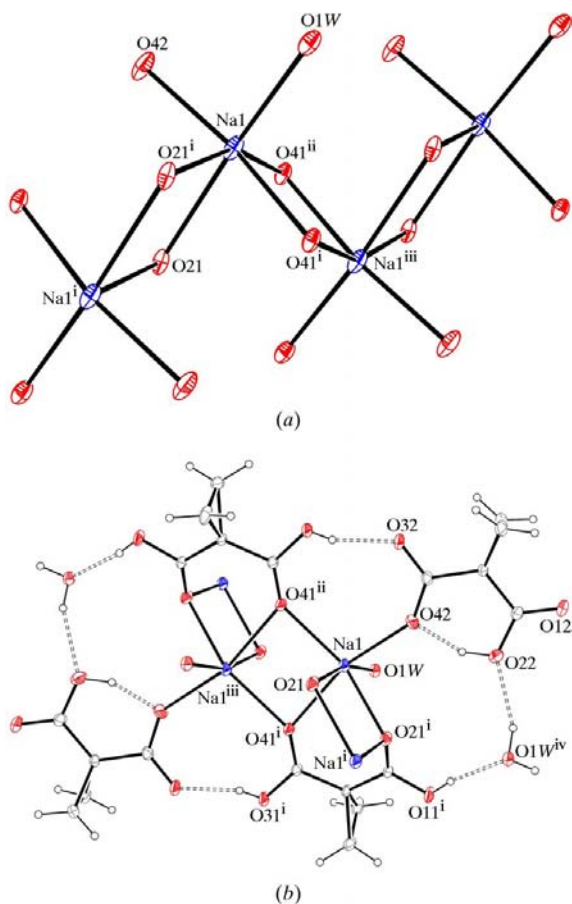


Figure 2
(a) Part of the infinite chain of linked NaO₆ octahedra. (b) The hydrogen-bonded (LH₂–LH⁻–H₂O)₂ belt around atoms Na1 and Na1ⁱⁱⁱ. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) 1 – x, 1 – y, 2 – z; (ii) x – 1, y, z; (iii) –x, 1 – y, 2 – z; (iv) 1 + x, y, z.]

CH₂(CO₂)₂, a similar difference is the result of a solvent isotope effect: the salts Na(L'H) and Na(L'H)(LH₂) can be produced by identical procedures, but using D₂O as the solvent gives partially deuterated Na(L'H)(L'H₂), whereas H₂O gives Na(L'H) (Kalsbeek, 1992).

Experimental

Crystals of (I) were obtained from an aqueous solution containing sodium hydroxide and cyclopropane-1,1-dicarboxylic acid in a 1:2 molar ratio. The IR spectrum contains broad bands at 2480 and 1905 cm⁻¹ attributable to unsymmetrical O–H···O hydrogen bonds.

Crystal data

Na ⁺ ·C ₅ H ₅ O ₄ ⁻ ·C ₅ H ₆ O ₄ ·H ₂ O	Z = 2
M _r = 300.19	D _x = 1.593 Mg m ⁻³
Triclinic, P1̄	Mo Kα radiation
a = 5.2910 (13) Å	Cell parameters from 22 reflections
b = 10.118 (3) Å	θ = 18.8–20.7°
c = 12.895 (5) Å	μ = 0.17 mm ⁻¹
α = 109.44 (3)°	T = 293 (2) K
β = 98.64 (2)°	Needle, white
γ = 99.57 (2)°	0.48 × 0.22 × 0.16 mm
V = 626.0 (4) Å ³	

Data collection

Enraf–Nonius CAD-4 diffractometer	θ _{max} = 28.0°
Non-profiled ω scans	h = –6 → 1
3932 measured reflections	k = –13 → 13
2985 independent reflections	l = –17 → 17
1654 reflections with I > 2σ(I)	3 standard reflections
R _{int} = 0.047	frequency: 120 min
	intensity decay: 1%

Table 1
Selected geometric parameters (Å, °).

Na1–O42	2.261 (2)	O41–C51	1.207 (3)
Na1–O21 ⁱ	2.325 (2)	C11–C21	1.513 (4)
Na1–O41 ⁱ	2.370 (2)	C11–C31	1.525 (4)
Na1–O41 ⁱⁱ	2.384 (2)	C21–C31	1.464 (5)
Na1–O1W	2.526 (3)	O12–C42	1.215 (3)
Na1–O21	2.533 (2)	O22–C42	1.298 (4)
Na1–Na1 ⁱⁱⁱ	3.245 (2)	O32–C52	1.233 (3)
Na1–Na1 ⁱ	3.769 (3)	O42–C52	1.258 (3)
O11–C41	1.320 (3)	C12–C32	1.518 (4)
O21–C41	1.204 (3)	C12–C22	1.520 (4)
O31–C51	1.301 (3)	C22–C32	1.451 (5)
C51–C11–C41–O21	–1.4 (4)	C52–C12–C42–O22	–3.1 (4)
C41–C11–C51–O41	–23.0 (4)	C42–C12–C52–O42	1.9 (4)

Symmetry codes: (i) 1 – x, 1 – y, 2 – z; (ii) x – 1, y, z; (iii) –x, 1 – y, 2 – z.

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

D–H···A	D–H	H···A	D···A	D–H···A
O22–H22···O42	0.93 (6)	1.56 (6)	2.429 (3)	154 (5)
O1W–H2W···O12 ^v	0.86 (4)	1.90 (4)	2.737 (3)	162 (4)
O1W–H1W···O22 ⁱⁱ	0.85 (4)	1.98 (4)	2.777 (4)	155 (3)
O11–H11···O1W ⁱⁱⁱ	0.77 (5)	1.88 (5)	2.642 (3)	170 (5)
O31–H31···O32 ^{iv}	0.72 (6)	1.80 (6)	2.478 (3)	155 (6)

Symmetry codes: (ii) x – 1, y, z; (iii) –x, 1 – y, 2 – z; (iv) 1 + x, y, z; (v) 1 – x, –y, 2 – z.

Refinement

Refinement on F^2
 $R(F) = 0.051$
 $wR(F^2) = 0.150$
 $S = 0.99$
 2985 reflections
 202 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$

H atoms were initially located in difference maps. In the final refinement, the positions of the methylene H atoms were determined by the HFIX instruction in *SHELXL97* (Sheldrick, 1997) and they were then treated as riding on their parent C atoms, with C–H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The positional and isotropic displacement parameters of H atoms attached to O atoms were freely refined.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors thank the EPSRC, UK, and the University of Glasgow for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1070). Services for accessing these data are described at the back of the journal.

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