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Lithium Croconate Dihydrate

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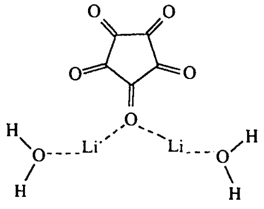
Abstract

The lithium salt of croconic acid (4,5-dihydroxy-4-cyclopentene-1,2,3-trione), or lithium croconate, consists of planes containing almost parallel croconate units interconnected by water molecules and Li^+ ions $(2Li^+.C_5O_5^{2-}.2H_2O)$.

Comment

Despite the interest in the coordinating properties of the croconate ion (Glick, Downs & Dahl, 1964; Glick & Dahl, 1966; Deguenon, Bernardinelli, Tuchagues & Castan, 1990; Castro *et al.*, 1992; Brouca-Cabarrecq & Trombe, 1992*a*,*b*), the structure of the ion has been reported in only a few cases, for example, the ammonium (Baenziger & Hegenbarth, 1964), rubidium hydrogen and ammonium hydrogen salts (Baenziger, Hegenbarth & Williams, 1963; Baenziger & Williams, 1966). These structures contain extended networks of intermolecular hydrogen bonding, enhancing the stability of the crystals. Another motivation for a detailed X-ray investigation of lithium croconate is the possibility of interpreting the solid-state vibrational spectra on the basis of a factor group analysis, for which a knowledge of the crystal structure is mandatory.

The Li^+ ions are tetrahedrally coordinated to two croconate O atoms (O1 and $O3^{i}$) and two water molecules (*OW* and OW^{ii}) with an average O—Li—O angle of 109.4°. It should be noted that in the case of lithium squarate monohydrate, $LiHC_4O_4.H_2O$ (Semmingsen, 1976), tetrahedral coordination is also found, although much more distorted. In fact, it has been shown that tetrahedral coordination is quite usual for the Li^+ ion in a great variety of its salts (Olsher, Izatt, Bradshaw & Dalley, 1991).



(I)

The water molecules are also coordinated to two Li^+ ions and two O atoms belonging to different croconate units, with tetrahedral geometry. It is worth noting that O2 is connected to two different water molecules by hydrogen bonding: $OW\cdots O2 = 2.747\,(2)$, $H1\cdots O2 = 1.81\,(2)$ Å and $OW—H1\cdots O2 = 157.8\,(2)°$; $OW\cdots O2$ $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z) = 2.692\,(2)$, $H2\cdots O2 = 1.95\,(2)$ Å and $OW—H2\cdots O2 = 169.0\,(1)°$; this is accompanied by an appreciable distortion of the H1—*OW*—H2 angle [108.7 (2)°].

The croconate ion in lithium croconate does not show a significant deviation from planarity, or from pentagonal geometry, as was reported for the ammonium salt (Baenziger & Hegenbarth, 1964). The C═O distances are also very much comparable with those observed in other croconates. However, it is worth noting that the C1—O1 distance [1.268 (3) Å] is slightly greater than the C2—O2 [1.245 (2) Å] and C3—O3 [1.235 (2) Å] distances, suggesting a displacement of charge in the C1—O1 bond towards the O atom, as a consequence of its interaction with two Li^+ ions. Consequently, although the O2 atom is interacting with two H atoms, the electrostatic effect originating from the positive charge

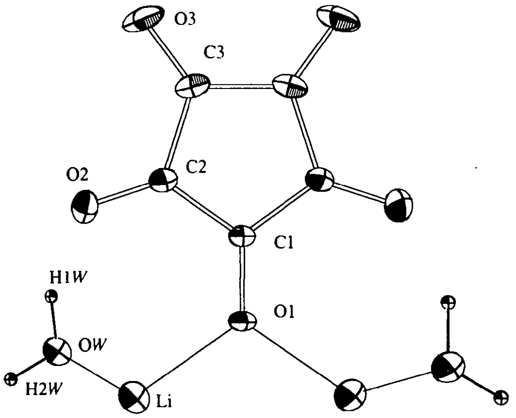


Fig. 1. Perspective view of the title compound showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

of the Li^+ ion seems to be greater than the effect of the hydrogen bonding.

The structure is seen to consist of infinite chains of croconate groups and Li^+ ions extending along the *b* axis, in planes almost perpendicular to the *ac* and *bc* planes [89.8 (9) and 85.1 (2)°, respectively] and at an angle of 11.34 (5)° with the *ab* plane. The distance between the centres of adjacent layers in the stack is one-half of the *c* cell edge [*ca* 3.30 (5) Å]. The croconate groups form bonded chains by means of Li^+—O1 and Li^+—$O3^i$ interactions, with an angle O1—Li^+—$O3^i$ of 119.4 (2)° (see Table 2). These chains are transversely linked along the *c* axis *via* the water molecules and Li^+ ions, where the O*W*—Li^+—OW^{ii} angle is 113.2 (2)°. Another chain is generated by the symmetry operation $\frac{1}{2} + x$, $\frac{1}{2} + y$, z. The former and latter chains are bonded *via* hydrogen bonds formed by the water molecule and lithium coordination sphere.

It is worth mentioning the relatively short distances between the consecutive planes that suggests a π–π interaction involving the oxocarbon units in the stack, as previously suggested for potassium squarate monohydrate (Macintyre & Werkema, 1964).

Experimental

The title compound was synthesized from the metathetical reaction between barium croconate and lithium sulfate. Barium croconate was obtained according to the procedure of Fatiadi, Isbell & Sager (1963). The salt was recrystallized twice from deionized water. Single crystals suitable for X-ray crystallographic work were obtained by slow isothermic evaporation of the solvent. The density D_m was measured by flotation.

Crystal data

$2Li^+.C_5O_5^{2-}.2H_2O$
$M_r = 189.97$
Monoclinic
$C2/c$
$a = 15.1058\ (6)$ Å
$b = 7.5393\ (2)$ Å
$c = 6.6094\ (3)$ Å
$\beta = 106.200\ (3)°$
$V = 722.79\ (5)$ Å^3
$Z = 4$
$D_x = 1.745$ Mg m^{-3}
$D_m = 1.75$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 19.3$–$25.5°$
$\mu = 0.152$ mm^{-1}
$T = 293$ K
Prismatic
0.70 × 0.60 × 0.50 mm
Yellow

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.958$, $T_{max} = 1.000$
925 measured reflections
829 independent reflections

776 observed reflections [$F > 6\sigma(F)$]
$R_{int} = 0.035$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 19$
$k = -9 \rightarrow 0$
$l = -8 \rightarrow 8$
3 standard reflections frequency: 120 min intensity decay: 1.4%

Refinement

Refinement on F
$R = 0.0472$
$wR = 0.0513$
$S = 0.884$
776 reflections
72 parameters
H atoms refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.13$

$\Delta\rho_{max} = 0.381$ e Å^{-3}
$\Delta\rho_{min} = -0.456$ e Å^{-3}
Extinction correction: $(1 + gI_c)$ applied to F_c
Extinction coefficient: $g = 9.27\ (1) \times 10^{-5}$
Atomic scattering factors from *MolEN* (Fair, 1990)

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

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

	x	y	z	U_{eq}
Li	0.1126 (2)	0.5483 (4)	0.3087 (5)	0.0291 (7)
O1	0	0.3992 (2)	1/4	0.0270 (4)
O2	0.16230 (8)	0.1717 (2)	0.3235 (2)	0.0333 (3)
O3	0.10066 (9)	−0.1986 (2)	0.2932 (2)	0.0359 (3)
C1	0	0.2310 (3)	1/4	0.0194 (5)
C2	0.0812 (1)	0.1194 (2)	0.2871 (2)	0.0212 (4)
C3	0.0507 (1)	−0.0663 (2)	0.2724 (2)	0.0234 (4)
O*W*	0.18381 (7)	0.4744 (2)	0.1108 (2)	0.0274 (3)

Table 2. *Selected geometric parameters* (Å, °)

Li—O1	1.984 (3)	O2—C2	1.245 (2)
Li—O*W*	1.990 (4)	O3—C3	1.235 (2)
Li—$O3^i$	1.917 (3)	C1—C2	1.451 (2)
Li—OW^{ii}	1.994 (3)	C2—C3	1.469 (2)
O1—C1	1.268 (3)		
C1—O1—Li	124.5 (1)	$O3^i$—Li—O1	119.4 (2)
O1—C1—C2	125.44 (9)	$O3^i$—Li—O*W*	107.6 (2)
O2—C2—C1	126.1 (2)	$O3^i$—Li—OW^{ii}	98.9 (2)
O2—C2—C3	126.1 (1)	O1—Li—O*W*	107.7 (1)
C1—C2—C3	107.9 (1)	O1—Li—OW^{ii}	109.9 (2)
O3—C3—C2	126.3 (2)	O*W*—Li—OW^{ii}	113.2 (2)

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

Owing to the twofold axis residing on O1 and C1, one formula unit is obtained from two asymmetric units. H atoms were located from $\Delta\rho$ maps and were refined with a common fixed isotropic displacement parameter. All calculations were performed on a DEC 3000 AXP computer.

Data collection: *CAD-4-EXPRESS* (Nonius, 1993). Cell refinement: *CAD-4-EXPRESS*. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *SIR*92 (Burla *et al.*, 1992). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1272). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(3-methyl-1,3-thiazolinylidene)gold(I) Trifluoromethanesulfonate

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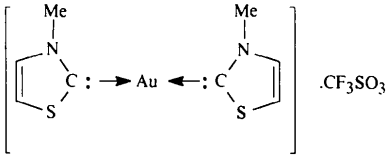
Abstract

The structure of $[Au(C_4H_5NS)_2]CF_3SO_3$ displays essentially linear cationic gold(I) units [C11—Au—C21 175.8 (7)°]. These linear cations are aggregated through alternating Au···Au interactions [3.1926 (11) and 3.4830 (10) Å] to form chains of Au atoms parallel to the *c* axis.

Comment

Recent studies have shown that some gold(I) compounds aggregate through second-order Au···Au bonding to form dimers (Schmidbaur, Weidenhiller, Steigelmann & Mueller, 1990), tetramers (Bates & Waters, 1985) or even polymers (Ahrland, Aurivillius, Dreisch, Noren & Oskarsson, 1992). It is believed that correlation and relativistic effects (Pyykkö & Zhao, 1991) are involved in this novel type of interaction ('aurophilicity').

The structure of chloro(trimethylphosphine)gold(I) (Angermaier, Zeller & Schmidbaur, 1994) shows aggregation of monomeric units to form helical chains, in contrast to the structure of chloro(triethylphosphine)gold(I) (Tiekink, 1989), which shows no significant Au···Au interactions. This confirms that steric hindrance influences secondary Au bonding.



(I)

The structure of (I) shows two planar 3-methylthiazolinylidene ligands [dihedral angle between the planes is 10.0 (3)°] coordinating a gold(I) centre, with the two methyl groups on the same side of the C11—Au—C21 bonds. The Au—C bond lengths [Au—C11 2.01 (2) and Au—C21 2.06 (2) Å] correspond to those found for bis(1,2-dihydropyridylidene)gold(I) trifluoromethanesulfonate dihydrate [2.02 (2) Å; Raubenheimer, Toerien *et al.*, 1994] and (pentafluorobenzene)(3,4-dimethylthiazolinylidene)gold(I) [1.96 (9) Å; Raubenheimer, Scott, Roos & Otte, 1990]. The N—$C_{carbene}$ bond lengths [N1—C11 1.34 (2) and N2—C21 1.28 (3) Å] agree with those found for bis(1-benzylimidazolinylidene)gold(I) chloride [1.33 (1) Å; Bovio, Burini & Pietroni, 1993] and reveal a high degree of multiple-bond character, as analogous C—N distances of 1.31–1.34 Å have been shown to correspond to a bond order of approximately 1.7 (Cotton & Lukehart, 1972).

Two different Au interactions determine the arrangement of the complex molecules in the lattice. The shorter Au···Au interactions [Fig. 1; Au···Au^i 3.1926 (11) Å; symmetry code: (i) $1-x, y, \frac{1}{2}-z$] result in the formation of dimeric units, similar to those formed by bis(4-methylthiazolinylidene)gold(I) tetrachlorozincate (Kruger, Olivier, Otte & Raubenheimer, 1996), with the S atoms turned towards each other. This interaction is longer than that found for (4-methylthiazolyl)(4-methylthiazolinylidene)gold(I) (Raubenheimer, Scott *et al.*, 1994), where extensive intermolecular hydrogen bonding enhances the secondary Au bonding. The methyl groups in the dimeric units of (I) are directed away from each other and therefore do not affect the Au···Au interaction in terms of steric hindrance. The resulting C11—Au···Au^i—$C11^i$ dihedral angle of 110.9 (6)° agrees with the findings of Patheneni & De-