

Fig. 2. Stereoscopic view of the *s-fac*-[Co(dien)(NH<sub>3</sub>)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> cation. (Note the relative orientations of the nitro groups about their Co—N axes; it is this feature that destroys the possible C<sub>3</sub> symmetry of this cation.)

Table 3. Deviations (in Å) of atoms from planes

Plane	Atom, with deviation
N(4)—Co—N(5)	C(1), 0.046 (4); C(2), 0.601 (4)
N(5)—Co—N(6)	C(3), -0.203 (4); C(4), 0.382 (4)
O(2A)—N(2)—O(2B)	Co, 0.0153 (4)
O(3A)—N(3)—O(3B)	Co, 0.0228 (4)

The N—O distances average 1.234 (9) Å, agreeing well with those found in *mer*-[Co(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>] (Laing, Baines & Sommerville, 1971) and *fac*-[Co(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>] (Nuber, Siebert, Weidenhammer, Weiss & Ziegler, 1979).

The chloride ion is involved in hydrogen bonding *via* various N—H...Cl interactions.

This work was supported by the National Science Foundation (Grant CHE79-24560 to MRC).

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*Acta Cryst.* (1981). **B37**, 697–699

## Structure of Lithium Hydrogen Acetylenedicarboxylate Monohydrate

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(Received 16 October 1980; accepted 1 December 1980)

**Abstract.** C<sub>4</sub>H<sub>4</sub>LiO<sub>4</sub>·H<sub>2</sub>O, LiHC<sub>4</sub>O<sub>4</sub>·H<sub>2</sub>O, triclinic, *P*1̄, *a* = 6.296 (3), *b* = 6.545 (2), *c* = 7.877 (2) Å, α = 66.87 (2), β = 83.92 (3), γ = 70.82 (3)°, *V* = 281.8 Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>*(flotation) = 1.61 (2), *D<sub>x</sub>* = 1.63 Mg m<sup>-3</sup>, *F*(000) = 140; *R* = 0.034 and *R*' = 0.069 for 1201 reflections. In this compound the hydrogen acetylenedicarboxylate anions form infinite chains *via* intermolecular hydrogen bonds. The O—H...O distance is 2.537 (1) Å, the longest so far observed in the acid salts of acetylenedicarboxylic acid.

**Introduction.** Acid salts of acetylenedicarboxylic acid (H<sub>2</sub>ADC) form polymeric structures with strong hydrogen bonds (Blain, Speakman, Stamp, Golić & Leban, 1973; Leban, Golić & Speakman, 1973; Leban, 1974; Gupta & Mahata, 1976). The O...O distances lie in the range 2.43–2.47 Å. The structures of all alkali-metal acid salts of H<sub>2</sub>ADC except LiHADC

have been reported previously. As a small cation, lithium usually favours very short hydrogen bonds in similar compounds (Follner, 1970; Thomas, 1972; Küppers, 1978). LiHADC crystallizes as the monohydrate from a solution of H<sub>2</sub>ADC and Li<sub>2</sub>CO<sub>3</sub> in the ratio 2:1 at room temperature. A crystal 0.20 × 0.25 × 0.4 mm was used for data collection at 123 K on a Syntex P<sub>2</sub> diffractometer with graphite-monochromated Mo *K*α radiation. With the θ/2θ scan and variable scan speeds (4.86–29.3° min<sup>-1</sup>), 1219 reflections were measured to θ<sub>max</sub> = 27°. Backgrounds were measured at each end of the scan for a total time of 0.8 times the scan time. No absorption correction was applied (μ = 0.16 mm<sup>-1</sup>). The structure determination is based on 1201 reflections with *I* > 3.92σ(*I*). The structure was solved using the Syntex *E-XTL* program system by a combination of direct methods, and Patterson and Fourier methods, in space group *P*1,

Table 1. *Final fractional atomic coordinates* ( $\times 10^4$ ) *and isotropic thermal parameters*

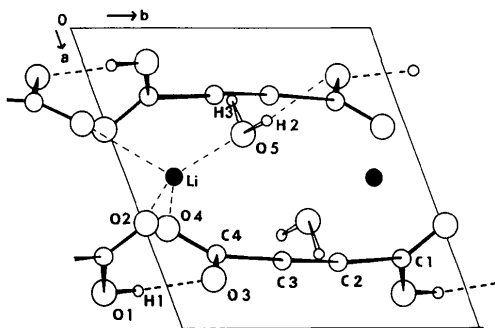
E.s.d.'s are given in parentheses.

	x	y	z	$B_{eq}/B$ ( $\text{\AA}^2$ )*
Li	4923 (4)	1362 (4)	3119 (3)	1.86 (8)
O(1)	8786 (2)	-2132 (2)	-96 (1)	1.28 (4)
O(2)	6573 (1)	75 (1)	1374 (1)	1.38 (4)
O(3)	8352 (2)	1690 (1)	7156 (1)	1.45 (4)
O(4)	6694 (1)	805 (1)	5274 (1)	1.44 (4)
O(5)	3520 (2)	4484 (2)	1605 (1)	1.94 (4)
C(1)	7649 (2)	-1817 (2)	1308 (2)	1.09 (5)
C(2)	7742 (2)	5990 (2)	2848 (2)	1.28 (5)
C(3)	7702 (2)	4210 (2)	4092 (2)	1.24 (5)
C(4)	7571 (2)	2061 (2)	5622 (1)	1.03 (4)
H(1)	8736 (47)	-974 (61)	-938 (47)	7.3 (2.5)
H(2)	3001 (48)	5455 (50)	1926 (37)	4.5 (6)
H(3)	2281 (36)	4541 (37)	1006 (31)	5.1 (4)

\* For nonhydrogen atoms  $B_{eq} = (B_{11} B_{22} B_{33})^{1/3}$ .

Table 2. *Bond distances* ( $\text{\AA}$ ) *and angles* ( $^\circ$ ) *with e.s.d.'s in parentheses*

C(1)—O(1)	1.301 (2)	Li—O(2)	1.926 (2)
C(1)—O(2)	1.220 (2)	Li—O(4)	1.976 (2)
C(4)—O(3)	1.256 (1)	Li—O(4')	1.979 (3)
C(4)—O(4)	1.250 (2)	Li—O(5)	1.871 (3)
C(1)—C(2)	1.458 (2)	O(1)—H(1)	0.78 (4)
C(2)—C(3)	1.198 (2)	O(5)—H(2)	0.73 (3)
C(3)—C(4)	1.470 (2)	O(5)—H(3)	0.94 (2)
O(1)···O(3)	2.537 (1)	O(3)···O(5)	2.889 (1)
O(1)—C(1)—O(2)	125.4 (1)	C(1)—C(2)—C(3)	176.5 (1)
O(1)—C(1)—C(2)	112.8 (1)	C(2)—C(3)—C(4)	178.1 (1)
O(2)—C(1)—C(2)	121.8 (1)	O(1)—H(1)···O(3)	175 (3)
O(3)—C(4)—O(4)	126.8 (1)	O(5)—H(2)···O(3)	177 (3)
O(3)—C(4)—C(3)	115.9 (1)	C(1)—O(1)—H(1)	114 (3)
O(4)—C(4)—C(3)	117.3 (1)	C(4)—O(3)···H(1)	123 (1)
O(2)—Li—O(5)	102.3 (1)	O(4)—Li—O(2)	115.6 (2)
O(4)—Li—O(5)	116.8 (1)	O(4')—Li—O(2)	107.9 (2)
O(4')—Li—O(5)	124.4 (1)	O(4')—Li—O(4)	90.4 (1)

Fig. 1. Projection of the unit-cell contents along *c*.

because of difficulties in placing the anion correctly with respect to the origin of the unit cell. After all nonhydrogen atoms were located a difference Fourier map showed the positions of the three H atoms. They were included in the refinement which converged at  $R = 0.034$  and  $R' [=(\sum w\Delta^2/\sum wF_o^2)^{1/2}] = 0.069$ . All atoms, except the H atoms of the water molecule, were treated anisotropically.

Atomic coordinates are listed in Table 1. Bond distances and bond angles are given in Table 2. Fig. 1 shows a projection of the unit-cell contents along *c*.\*

**Discussion.** The hydrogen acetylenedicarboxylate ion forms infinite chains running approximately in the [011] direction. Within the chain the anions are connected by strong hydrogen bonds. The distance O(1)···O(3) is 2.537 (1)  $\text{\AA}$ . The hydrogen bond is clearly asymmetric and is directed to the possible position of the lone electron pair at O(3). The thermal ellipsoid of the bridging H atom is greatly extended along the bond direction, as in similar studies. The length of the hydrogen bond agrees very well with the spectroscopic results. The IR spectrum of LiHADC.H<sub>2</sub>O is of Hadži's (1965) (i) type, with an absorption maximum at approximately 1500  $\text{cm}^{-1}$  (C band). The 'out of plane' mode is observed at 980  $\text{cm}^{-1}$ .

The hydrogen bond is not of the 'very short' type, as was expected. LiHADC.H<sub>2</sub>O is therefore unique among the acid acetylenedicarboxylates, structurally characterized so far, with Na, K, Rb and Cs as counterions. (Both the Na and Cs salts are monohydrates.)

This might be explained by the unfavourable packing requirements of the stiff acetylenic backbone together with the presence of rather strong polar forces in the Li coordination sphere.

The C—C bond distances in the anion are normal. The C—O bond lengths differentiate in accord with their participation in O···H and O···Li bonds. The dihedral angle between the two carboxylic planes is 62.2°, close to the value in the K and Rb salts. Coplanar ions are present in NaHADC.H<sub>2</sub>O and CsHADC.H<sub>2</sub>O.

The Li ion and the water molecule are situated between pairs of anionic chains. The Li coordination is fairly close to tetrahedral. The O—Li—O bond angles vary between 90.4 and 124.4°. The water molecule forms only one hydrogen bond. The distance O(5)···O(3) is 2.889 (1)  $\text{\AA}$ .

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35825 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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