for the tilting of the coordinated 2,2′-bipyridine toward two basal borons above the C_2B_3 face. Since the two Pb—N distances are almost equal in the title compound (V), there is no apparent reason for the same kind of tilting of the Pb-bound Lewis base as the one observed for (IV). However, one of the interesting features of the structure is the overall non-planarity of the coordinated 2,2′-bipyridine molecule itself. The dihedral angle between the two C_5N rings within the 2,2′-bipyridine ligand in the title compound is 12·8°, while in the stannacarborane–2,2′-bipyridine complexes, 1-Sn($C_{10}H_8N_2$)-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$ and 1-Sn($C_{10}H_8N_2$)-2-(Me)-3-($SiMe_3$)-2,3-$C_2B_4H_4$, this is 5·6 and 8·8°, respectively (Hosmane, de Meester, Maldar, Potts, Chu & Herber, 1986; Siriwardane, Hosmane & Chu, 1987). The dihedral angles between the planes formed by the C_2B_3 face of the plumbacarborane cage and the C_5N rings of the bipyridine ligand containing N(1) and N(2) donor atoms, are 24·2 and 36·0°, respectively. It is interesting to point out that the dihedral angle of 30·2° between the C_2B_3 face and the calculated overall plane of the 2,2′-bipyridine molecule is significantly larger than that of 1-Pb($C_{10}H_8N_2$)-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$ (IV) (27·5°) and of similar stannacarborane complexes 1-Sn($C_{10}H_8N_2$)-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$ (26·8°) and 1-Sn($C_{10}H_8N_2$)-2-(Me)-3-($SiMe_3$)-2,3-$C_2B_4H_4$ (18·4°) (Hosmane, Lu, Zhu, Siriwardane, Shet & Maguire, 1990; Hosmane, de Meester, Maldar, Potts, Chu & Herber, 1986; Siriwardane, Hosmane & Chu, 1987). The crystal packing diagram (Fig. 3) shows that the intermolecular dipole–dipole type of interactions within the dimeric precursor (II) were broken during the formation of the title compound (V).

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References

HOSMANE, N. S., DE MEESTER, P., MALDAR, N. N., POTTS, S. B., CHU, S. S. C. & HERBER, R. H. (1986). *Organometallics*, **5**, 772–778.

HOSMANE, N. S., LU, K.-J., ZHU, H., SIRIWARDANE, U., SHET, M. S. & MAGUIRE, J. A. (1990). *Organometallics*, **9**, 808–815.

HOSMANE, N. S. & MAGUIRE, J. A. (1988). *Advances in Boron and the Boranes*. In the series *Molecular Structure and Energetics*, edited by J. F. LIEBMAN, A. GREENBERG & R. E. WILLIAMS, Vol. 5, Ch. 14, pp. 297–328. New York: VCH.

HOSMANE, N. S. & MAGUIRE, J. A. (1990). *Adv. Organomet. Chem.* **30**, 99–150.

HOSMANE, N. S., SIRIWARDANE, U., ZHU, H., ZHANG, G. & MAGUIRE, J. A. (1989). *Organometallics*, **8**, 566–568.

SHELDRICK, G. M. (1988). *SHELXTL-Plus*88 *Structure Determination Software Programs*. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

SIRIWARDANE, U., HOSMANE, N. S. & CHU, S. S. C. (1987). *Acta Cryst.* C**43**, 1067–1069.

Acta Cryst. (1990). C**46**, 1394–1396

Structure of Potassium Hydrogen Cyclopropane-1,1-dicarboxylate Hemihydrate

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Abstract. K[$C_5H_5O_4$].1/2H_2O, $M_r = 177{\cdot}2$, monoclinic, $P2_1/a$, $a = 9{\cdot}041\,(1)$, $b = 15{\cdot}634\,(2)$, $c = 9{\cdot}874\,(2)$ Å, $\beta = 93{\cdot}85\,(1)°$, $V = 1392{\cdot}5\,(4)$ Å^3, $Z = 8$, $D_x = 1{\cdot}69$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 65$ cm^{-1}, $F(000) = 720$, $T = 294$ K, $R = 0{\cdot}061$ for 1873 observed independent reflections. The asymmetric unit contains two independent molecules each with an intramolecular hydrogen bond. The potassium ions are both eight coordinated by carboxylate and water oxygens (6 + 2 and 7 + 1).

Introduction. In a previous spectroscopic study, Fabregue, Cassanas, Delarbre, Maury & Bardet (1988) concluded that, in aqueous solution, the cyclopropane-1,1-dicarboxylic acid salt belongs to the point group C_2 and was, in addition, intramolecu-

0108-2701/90/081394-03$03.00

Table 1. *Fractional atomic coordinates* (O, K, C × 10^4, H × 10^3) *with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (Å^2)

	x	y	z	B_{eq}
O	2659 (6)	−2148 (3)	865 (5)	5·5
K	5952 (1)	392 (1)	8032 (1)	3·5
K′	5092 (2)	2048 (1)	911 (1)	4·1
C(1)	2732 (6)	1921 (3)	4928 (5)	3·1
C(2)	2220 (8)	2813 (4)	5270 (6)	4·1
C(3)	1132 (7)	2117 (5)	5201 (7)	4·3
C(4)	3618 (6)	1450 (3)	6027 (5)	3·2
C(5)	3056 (6)	1758 (3)	3469 (5)	3·2
O(1)	3496 (5)	1593 (3)	7231 (4)	4·6
O(2)	4502 (5)	857 (3)	5639 (4)	4·0
O(3)	4007 (4)	1173 (3)	3255 (4)	3·9
O(4)	2407 (5)	2130 (3)	2554 (4)	4·3
C(1)′	6161 (6)	4922 (4)	8181 (5)	3·4
C(2)′	5607 (9)	5778 (5)	7649 (7)	5·1
C(3)′	6281 (10)	5182 (5)	6709 (7)	5·2
C(4)′	7581 (6)	4928 (4)	9049 (4)	3·4
C(5)′	5028 (6)	4255 (4)	8455 (7)	4·7
O(1)′	8527 (4)	5478 (3)	8942 (4)	4·2
O(2)′	7759 (5)	4328 (3)	9949 (4)	4·4
O(3)′	5389 (6)	3698 (3)	9384 (5)	5·6
O(4)′	3834 (5)	4255 (4)	7797 (6)	7·2
H(*A*)	255 (12)	−247 (6)	163 (7)	14
H(*B*)	218 (9)	−170 (3)	116 (9)	10
H(1)	225 (6)	319 (4)	450 (6)	4
H(2)	256 (7)	303 (4)	616 (7)	6
H(3)	80 (6)	139 (4)	604 (6)	5
H(4)	40 (8)	204 (5)	451 (7)	7
H(5)	453 (8)	89 (5)	461 (8)	8
H(1)′	617 (6)	622 (4)	786 (6)	4
H(2)′	452 (7)	587 (4)	759 (6)	5
H(3)′	728 (7)	528 (4)	650 (6)	4
H(4)′	563 (7)	492 (4)	614 (6)	5
H(5)′	181 (6)	93 (4)	−15 (6)	5

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(2)—C(1)	1·516 (8)	H(*A*)—O	0·92 (8)
C(3)—C(1)	1·520 (9)	H(*B*)—O	0·88 (7)
C(4)—C(1)	1·498 (7)	H(1)—C(2)	0·96 (6)
C(5)—C(1)	1·511 (7)	H(2)—C(2)	0·98 (7)
C(3)—C(2)	1·466 (9)	H(3)—C(3)	0·97 (6)
O(1)—C(4)	1·221 (6)	H(4)—C(3)	0·92 (7)
O(2)—C(4)	1·299 (7)	H(5)—O(2)	1·01 (8)
O(3)—C(5)	1·283 (7)	H(1)′—C(2)	0·87 (6)
O(4)—C(5)	1·235 (6)	H(2)′—C(2)′	0·99 (6)
C(2)′—C(1)′	1·511 (9)	H(3)′—C(3)′	0·96 (6)
C(3)′—C(1)′	1·521 (9)	H(4)′—C(3)′	0·89 (6)
C(4)′—C(1)′	1·495 (7)	H(5)′—O(2)′	0·94 (7)
C(5)′—C(1)′	1·499 (8)		
C(3)′—C(2)′	1·476 (11)	H(5)···O(3)	1·46 (8)
O(1)′—C(4)′	1·223 (7)	H(5)′···O(3)′	1·36 (7)
O(2)′—C(4)′	1·294 (7)		
O(3)′—C(5)′	1·291 (8)		
O(4)′—C(5)′	1·222 (8)		
C(3)—C(1)—C(2)	57·7 (4)	H(*B*)—O—H(*A*)	94 (8)
C(4)—C(1)—C(2)	116·5 (4)	H(1)—C(2)—C(1)	111 (3)
C(4)—C(1)—C(3)	116·1 (5)	H(2)—C(22)—C(1)	116 (4)
C(5)—C(1)—C(2)	116·7 (5)	H(2)—C(2)—H(1)	119 (5)
C(5)—C(1)—C(3)	116·8 (5)	C(3)—C(2)—H(1)	118 (3)
C(5)—C(1)—C(5)	118·7 (5)	C(3)—C(2)—H(2)	118 (4)
C(3)—C(2)—C(1)	61·3 (4)	H(3)—C(3)—C(1)	116 (3)
C(2)—C(3)—C(1)	61·0 (4)	H(3)—C(3)—C(2)	119 (4)
O(1)—C(4)—C(1)	122·5 (5)	H(4)—C(3)—C(1)	119 (5)
O(2)—C(4)—C(1)	116·5 (4)	H(4)—C(3)—C(2)	125 (5)
O(2)—C(4)—O(1)	121·0 (5)	H(4)—C(3)—H(3)	109 (6)
O(3)—C(5)—C(1)	116·9 (4)	H(5)—O(2)—C(4)	108 (4)
O(4)—C(5)—C(1)	119·6 (5)	H(1)′—C(2)′—C(1)′	116 (4)
O(4)—C(5)—O(3)	123·5 (5)	H(2)′—C(2)′—C(1)′	117 (4)
C(3)′—C(1)′—C(2)′	58·3 (5)	H(2)′—C(2)′—H(1)′	117 (5)
C(4)′—C(1)′—C(2)′	116·5 (5)	C(3)′—C(2)′—H(1)′	113 (4)
C(4)′—C(1)′—C(3)′	115·6 (5)	C(3)′—C(2)′—H(2)′	120 (4)
C(5)′—C(1)′—C(2)′	117·7 (5)	H(3)′—C(3)′—C(1)′	112 (4)
C(5)′—C(1)′—C(3)′	116·9 (5)	H(3)′—C(3)′—C(2)′	118 (4)
C(5)′—C(1)′—C(4)′	118·2 (5)	H(4)′—C(3)′—C(1)′	113 (4)
C(3)′—C(2)′—C(1)′	61·2 (4)	H(4)′—C(3)′—C(2)′	114 (4)
C(2)′—C(3)′—C(1)′	60·5 (4)	H(4)′—C(3)′—H(3)′	122 (6)
O(1)′—C(4)′—C(1)′	122·2 (5)	H(5)′—O(2)′—C(4)′	99 (4)
O(2)′—C(4)′—C(1)′	116·9 (5)	O(2)—H(5)···O(3)	155 (6)
O(2)′—C(4)′—O(1)′	120·9 (5)	H(5)···O(3)—C(5)	104 (3)
O(3)′—C(5)′—C(1)′	117·0 (5)	O(2)′—H(5)′···O(3)′	168 (5)
O(4)′—C(5)′—C(1)′	119·6 (6)	H(5)′···O(3)′—C(5)′	97 (3)
O(4)′—C(5)′—O(3)′	123·4 (6)		

larly hydrogen bonded like the acid itself. By comparison of the infrared spectra of some acid salts of cycloalkane-1,1-diacids (C_3, C_4, C_5) in the crystalline state, Belhekar & Jose (1982) hypothesized that potassium hydrogen cyclopropane-1,1-dicarboxylate [KHC_3] could be hydrogen bonded. The crystal and molecular structure of the cyclopropane-1,1-dicarboxylic acid has been described (Meester, Schenk & MacGillavry, 1971); consequently, it seemed of interest to investigate the crystal structure of the acid salt as part of a systematic study of dicarboxylic acids or their intramolecular hydrogen-bonded acid salts.

Experimental. Colourless transparent crystal, 0·12 × 0·12 × 0·25 mm, obtained by recrystallization from water. Huber 424 + 511 diffractometer, graphite-monochromated Cu $K\alpha$ radiation, ω–2θ scan, room temperature. Lattice parameters refined using 18 reflections in the range $9 \le 2\theta \le 25°$. Standard reflection (021) checked every 50 reflections, no significant deviation. No absorption correction. $2\theta_{\max} = 135°$. Index range h 10/10, k 0/18, l 0/11. 2513 independent reflections, 1873 observed [$I \ge 2·5\sigma(I)$]. Potassium position obtained with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Complete resolution by use of *DIRDIF*81 (Beurskens *et al.*, 1981). Least-squares refinement based on F using *SHELX*76 (Sheldrick, 1976). Scattering factors as given in *International Tables for X-ray Crystallography* (1974).

After the first isotropic refinements, a difference Fourier synthesis showed a residual peak of significant electron density. It was identified as a water molecule and was included in further cycles. H atoms from difference Fourier synthesis. In the last refinement, anisotropic for C, O and K (parameters refined: x, y, z and U_{ij}) and isotropic for H (x, y, z and U), final $R = 0·061$, $wR = 0·068$, weight for every observed structure factor calculated according to $w = 1/[\sigma^2(F) + 0·00092F^2]$. $(\Delta/\sigma)_{\max} = 0·5$; $S = 2·1$; $-0·7 \le \Delta\rho \le 0·5$ e Å^{-3}.

Discussion. Fractional atomic coordinates are given in Table 1.* Bond distances and angles are displayed

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* Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52805 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in Table 2. The molecular structure (Fig. 1) was drawn with *PLUTO*78 (Motherwell & Clegg, 1978).

The asymmetric unit consists of two $C_3H_4(CO_2H)$-(CO_2^-) ions, one H_2O molecule and two K^+ ions. All corresponding values of the two independent molecules are equal within the limits of accuracy [exception: angle O(2)—H(5)···O(3) = 155 (6)° and O(2)′—H(5)′···O(3)′ = 168 (5)°].

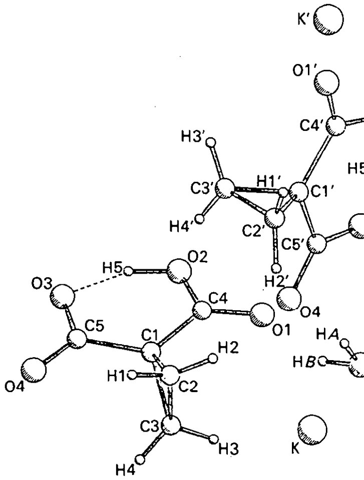

Fig. 1. Perspective view of the asymmetric unit with atomic numbering scheme. Hydrogen bonds are represented by broken lines.

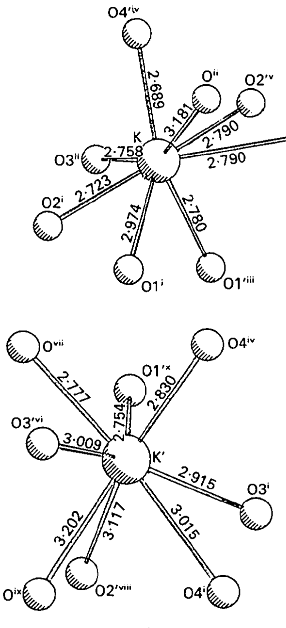

Fig. 2. Environment of the K^+ ions and contact distances less than 3·250 Å. Symmetry transformations: (i) x, y, z; (ii) $1-x, -y, 1-z$; (iii) $0·5+x, 0·5-y, z$; (iv) $-0·5+x, 0·5-y, z$; (v) $1·5-x, 0·5+y, 2-z$; (vi) $x, y, 1+z$; (vii) $1-x, -y, -z$; (viii) $0·5+x, 0·5-y, 1+z$; (ix) $0·5-x, -0·5+y, -z$; (x) $1·5-x, 0·5+y, 1-z$.

In the cyclopropane ring, the mean values of bond lengths (1·50 Å) and angles (60·2°) were close to those already reported (Long, Maddox & Trueblood, 1969). As for the acid itself, the cyclopropane group is nearly perpendicular to the best plane through the chelated ring and the 'back' ring bond (1·47 Å) is shorter than that linking the C atom to the carboxyl groups.

The environment of the K^+ ions is shown in Fig. 2. In the asymmetric unit, there are two crystallographically different K^+ ions: K is coordinated by eight O atoms, one of them belonging to a water molecule while K′ is coordinated by six O atoms of the carboxyl groups and with two O atoms of H_2O molecules.

Each dicarboxylate ion of the asymmetric unit has a very short intramolecular hydrogen bond, $R(\mathrm{O}\cdots\mathrm{O}) = 2·41$ Å, with an O—H length of 0·98 Å and an O···H distance of 1·41 Å. The mean value of the angle O—H···O is 161°. The length of the hydrogen bond and the bond lengths and angles of the chelated ring are close to the corresponding parameters in potassium hydrogen chloromaleate (Ellison & Levy, 1965). The shortest O(3)—H(5) length imposes such a strain that the chelated ring is only approximately planar [torsion angles C(3)—C(1)—C(4)—C(2) = −7 (1), C(4)—C(1)—C(5)—O(3) = −4 (1)°]. These results agree well with the fact that KHC_3 could be a type A_2 acid salt in Speakman's classification. Infrared analysis will be performed to determine whether the hydrogen bond is 'effectively' or 'statistically' centered.

References

Belhekar, A. A. & Jose, C. I. (1982). *J. Chem. Soc. Faraday Trans.* **78**, 201–204.

Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Gould, R. O., van den Hark, T. H., Prick, P. A., Noordik, J. H., Beurskens, G. & Parthasarathi, V. (1981). *DIRDIF*81. *An Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors.* Crystallography Laboratory, Toernooiveld, Nijmegen, The Netherlands.

Ellison, R. D. & Levy, H. A. (1965). *Acta Cryst.* **19**, 260–268.

Fabregue, E., Cassanas, G., Delarbre, J. L., Maury, L. & Bardet, L. (1988). *Spectrochim. Acta*, **44** (7), 669–676.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Long, R. E., Maddox, H. & Trueblood, K. N. (1969). *Acta Cryst.* **B25**, 2983–2094.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Meester, M. A. M., Schenk, H. & MacGillavry, C. H. (1971). *Acta Cryst.* **B27**, 630–634.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.