Acta Cryst. (1973). B**29**, 2082

The Crystal Structure of a Potassium Salt of *trans*-Aconitic Acid Containing Two Different Anionic Forms in a 1:1 Ratio

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(*Received* 12 *March* 1973; *accepted* 16 *April* 1973)

The crystal structure of the potassium salt of a 1:1 mixture of dihydrogen *trans*-aconitate and monohydrogen *trans*-aconitate has been studied by X-ray diffraction using three-dimensional data. The crystals are triclinic, space group $P\bar{1}$, with cell dimensions $a=8{\cdot}081$ (2), $b=16{\cdot}487$ (3), $c=7{\cdot}647$ (1) Å, $\alpha=107{\cdot}53$ (1), $\beta=102{\cdot}78$ (1), and $\gamma=93{\cdot}71$ (2)°. The unit cell contains 6 K^+ ions, 4 molecules of H_2O and 2 molecules each of $(HC_6O_6H_3)^{2-}$ and $(H_2C_6O_6H_3)^-$. The formula for the asymmetric unit is $K_3(H_2C_6O_6H_3)(HC_6O_6H_3).2H_2O$. For $Z=2$ the calculated density is 1·774 g cm^{-3} and the measured density is 1·77 g cm^{-3}. The structure was solved by Patterson superposition techniques and refined to a final residual $R=0{\cdot}047$ for 4075 non-zero weight data. All hydrogen atoms were located and refined with isotropic thermal parameters. The $H(C_6O_6H_3)^{2-}$ ion contains a strong intramolecular hydrogen bond while the $(H_2C_6O_6H_3)^-$ ion does not contain this hydrogen bond. In addition the two anionic species have different conformations. The two anionic species are hydrogen bonded to each other through a short (2·50 Å) hydrogen bond and ions of the mono-ionic species are further hydrogen bonded to each other through a 2·53 Å hydrogen bond. The dihydrogen *trans*-aconitate anions are packed such that there is a considerable amount of overlap of the carbon–carbon double bonds, with an interplanar spacing between the planes of the double bond and its substituents of nearest neighbor anions of 3·496 Å, indicating a possibility for solid-state polymerization under appropriate conditions.

Introduction

trans-Aconitate is an isomer of *cis*-aconitate, which is a substrate of the enzyme aconitase and is itself a weak competitive inhibitor of the action of the aconitase (Thomson, Nance, Bush & Szczepanik, 1966). The structure of dipotassium hydrogen *cis*-aconitate has been reported (Glusker, Orehowsky, Casciato & Carrell, 1972) as has the structure of potassium dihydrogen *trans*-aconitate (Dargay, Berman, Carrell & Glusker, 1972). During the course of the preparation of crystals of potassium dihydrogen *trans*-aconitate, crystals were formed which proved to be triclinic but which had the same density as the monoclinic dihydrogen *trans*-aconitate crystals. It appeared as if the crystals contained dipotassium hydrogen *trans*-aconitate with two molecules per asymmetric unit, thus affording a dual determination of the structure of the *trans*-aconitate anion and a comparison with the structure found for the monoclinic dihydrogen *trans*-aconitate.

Experimental

Crystals of the triclinic *trans*-aconitate salt were first prepared by mixing hot alcoholic potassium hydroxide and *trans*-aconitic acid. It was also found that crystals of the same composition could be obtained from solution of *trans*-aconitic acid and potassium hydroxide at *p*H 13. In each case, it was necessary to add a small amount of very dilute hydroquinone solution in order to prevent the apparent polymerization of the *trans* aconitate. Crystals grown under either of the above conditions were found to be triclinic; the crystal data are given in Table 1. For the data collection, a crystal was ground to an ellipsoid of revolution 0·4 × 0·3 mm. Three-dimensional data were collected on a Syntex automated diffractometer with monochromated Mo $K\alpha$ radiation (λMo $K\alpha=0{\cdot}7107$ Å) using a variable rate θ–2θ scan technique. Intensities for 5454 independent reflections were measured out to $\sin\theta/\lambda=0{\cdot}7$ Å^{-1} ($2\theta=65°$). The data were corrected for intensity loss due to radiation damage by means of a curve derived from the loss in intensity of the measured check reflections as a function of time (8% over 163 hours of exposure). The values of $\sigma(F)$ were derived from counting statistics and measured instrumental uncertainties. Of the 5454 reflections measured, 1379 were found to have intensity, I(meas), less than $2{\cdot}33\sigma(I)$. The data were converted to structure amplitudes by application of Lorentz and polarization factors and were later corrected for absorption using the program of Johnson (1963) for an ellipsoid of revolution.

Table 1. *Crystal data*

Formula: $K_3(H_2C_6O_6H_3)\,(HC_6O_6H_3).2H_2O$	F.W. 498·54
Crystal system: triclinic	
$a=$ 8·081 (2) Å	$\alpha=107{\cdot}53$ (1)°
$b=$ 16·487 (3)	$\beta=102{\cdot}78$ (1)
$c=$ 7·647 (1)	$\lambda=$ 93·71 (2)
$V=937{\cdot}6$ (3) Å^3	$F(000)=508$
$D_m=1{\cdot}77$ g cm^{-1} (flotation in *m*-xylene and iodomethane)	
$D_x=1{\cdot}774$ g cm^{-3}	$Z=2$
λ(Mo $K\alpha$) = 0·7107 Å	μ(Mo $K\alpha$) = 7·4 cm^{-1}
Space group: $P\bar{1}$	

Table 2. *Atomic parameters for* $K_3(H_2C_6O_6H_3)(HC_6O_6H_3).2H_2O$

The positional parameters are expressed as fractions of the cell edges. Anisotropic temperature factors are of the form

$$\exp\left[-(\tfrac{1}{4})\left(B_{11}h^2a^{*2}+\ldots+2B_{12}hka^*b^*+\ldots\right)\right]$$

and isotropic temperature factors are expressed as $\exp(-B\sin^2\theta/\lambda^2)$ with the B values given in Å^2. Estimated standard deviations, determined from the inverted matrix, are listed with respect to the last decimal place given. Labels *a* and *b* are used to denote the $(HC_6O_6H_3)^{2-}$ and $(H_2C_6O_6H_3)^-$ anions respectively.

(*a*) Non-hydrogen atomic parameters (x, y, and $z \times 10^5$)

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K(1)	13169 (8)	20446 (4)	10810 (10)	1·98 (2)	2·95 (2)	2·60 (2)	0·17 (1)	0·44 (1)	1·17 (2)
K(2)	1804 (8)	61240 (4)	20011 (10)	2·24 (2)	2·46 (1)	2·95 (2)	0·19 (1)	0·77 (2)	1·26 (2)
K(3)	27818 (8)	21147 (4)	60969 (10)	2·33 (2)	2·99 (2)	2·27 (2)	0·17 (1)	0·40 (2)	1·02 (2)
O(*W*1)	4458 (27)	80882 (14)	60815 (35)	2·35 (7)	2·71 (8)	4·12 (10)	0·50 (7)	0·78 (8)	0·92 (8)
O(*W*2)	17489 (30)	39136 (16)	54014 (37)	3·22 (8)	5·01 (10)	4·17 (9)	1·44 (8)	1·63 (9)	2·38 (10)
O(1*a*)	25512 (27)	32595 (13)	−3300 (33)	2·26 (8)	3·03 (8)	3·22 (8)	−0·02 (6)	0·07 (7)	1·35 (8)
O(2*a*)	48805 (29)	36583 (16)	−10673 (32)	2·97 (8)	4·33 (10)	2·32 (8)	−0·40 (8)	0·55 (7)	0·88 (8)
O(3*a*)	102082 (28)	45301 (14)	24620 (36)	2·40 (7)	3·76 (8)	4·22 (9)	0·04 (7)	1·13 (8)	2·25 (9)
O(4*a*)	77477 (27)	44867 (13)	4670 (31)	2·92 (8)	2·96 (7)	2·68 (7)	0·00 (6)	0·96 (7)	1·53 (7)
O(5*a*)	69735 (26)	28832 (13)	50492 (32)	2·05 (7)	3·40 (7)	3·32 (7)	0·40 (6)	0·72 (7)	2·20 (8)
O(6*a*)	42076 (25)	29390 (13)	39290 (31)	2·10 (7)	3·05 (7)	3·00 (7)	0·11 (6)	0·76 (7)	1·68 (8)
O(1*b*)	15130 (38)	−24887 (18)	10344 (45)	2·02 (10)	2·32 (9)	3·53 (10)	−0·42 (8)	−0·06 (9)	1·33 (10)
O(2*b*)	38351 (36)	−18266 (17)	33533 (42)	2·26 (9)	2·93 (9)	2·50 (9)	−0·37 (8)	−0·04 (9)	1·56 (9)
O(3*b*)	83259 (36)	1869 (17)	23319 (40)	1·74 (9)	2·32 (9)	5·72 (9)	0·20 (8)	1·46 (8)	0·88 (8)
O(4*b*)	71478 (37)	−11598 (18)	16157 (43)	2·06 (9)	2·21 (9)	4·20 (10)	0·57 (8)	1·27 (9)	1·30 (10)
O(5*b*)	25241 (34)	7959 (17)	28007 (39)	2·26 (9)	2·08 (9)	4·06 (8)	0·40 (7)	0·95 (8)	0·57 (8)
O(6*b*)	9588 (37)	−4984 (18)	17444 (45)	1·84 (10)	2·32 (9)	5·55 (10)	0·43 (8)	1·66 (10)	1·02 (10)
C(1*a*)	39940 (26)	36671 (12)	1598 (33)	2·33 (7)	2·25 (7)	2·54 (9)	0·49 (6)	0·29 (7)	1·16 (8)
C(2*a*)	48486 (27)	41850 (13)	22081 (30)	2·19 (7)	2·04 (7)	2·34 (7)	0·40 (6)	0·68 (6)	0·94 (7)
C(3*a*)	62368 (26)	37314 (14)	30295 (40)	2·15 (7)	1·78 (8)	1·76 (11)	0·13 (6)	0·38 (8)	0·69 (9)
C(4*a*)	78269 (25)	37732 (13)	28171 (35)	2·15 (7)	2·38 (7)	2·43 (9)	0·14 (6)	0·72 (7)	1·21 (8)
C(5*a*)	86461 (26)	43028 (13)	18569 (38)	2·60 (7)	2·07 (8)	2·79 (11)	0·30 (6)	1·35 (8)	1·04 (9)
C(6*a*)	57491 (26)	31437 (13)	40812 (34)	2·03 (7)	2·01 (7)	1·76 (10)	0·18 (6)	0·64 (8)	0·79 (8)
C(1*b*)	27917 (33)	−19590 (16)	16750 (42)	1·75 (8)	1·53 (8)	2·51 (10)	0·44 (7)	0·61 (8)	0·78 (9)
C(2*b*)	33838 (33)	−14084 (17)	6108 (39)	1·60 (8)	1·82 (9)	1·88 (9)	0·20 (7)	0·30 (8)	0·61 (9)
C(3*b*)	38640 (34)	−4680 (17)	17442 (40)	1·73 (9)	1·92 (8)	2·11 (8)	0·44 (7)	0·75 (8)	1·00 (9)
C(4*b*)	54397 (35)	−266 (18)	23747 (44)	1·87 (9)	1·89 (9)	2·76 (10)	0·32 (8)	0·92 (9)	0·76 (9)
C(5*b*)	70675 (35)	−3821 (18)	20802 (43)	1·59 (9)	2·51 (10)	2·48 (10)	0·55 (8)	0·71 (8)	1·08 (10)
C(6*b*)	23856 (35)	188 (18)	21576 (44)	1·73 (9)	2·41 (9)	2·57 (10)	0·50 (8)	0·64 (9)	1·10 (10)

Structure determination and refinement

Although it was initially thought that the crystals contained 4 K$^+$ ions per asymmetric unit, the Patterson function was consistent with only 3 K$^+$ ions per asymmetric unit. By using vector superposition techniques, the positions of 3 K$^+$ and 12 lighter atoms were found. The subsequent structure factor calculation gave a residual R of 0·36 and the resultant electron density map gave the positions of 14 additional atoms. The resulting residual for this trial structure was 0·27. Two cycles of isotropic full-matrix least-squares refinement reduced the residual to 0·085. A difference map was calculated with only those data for which $\sin\theta/\lambda \le 0{\cdot}5$ and the positions of 13 hydrogen atoms were determined. The structure was further refined first by treating each molecule independently, then by one final cycle of full-matrix least-squares calculations. The final residual R for the 4075 nonzero weight data is 0·047 and the weighted residual R_w is 0·048. No corrections for secondary extinction were made. The quantity minimized in the least-squares treatment is $\sum\omega(kF_o-F_c)^2$ where the weights $\omega=1/\sigma^2(F)$. Those reflections with $I <$ 2·33$\sigma(I)$ were assigned $\omega=0$. The final refined atomic parameters are presented in Table 2.*

Table 2 (*cont.*)

(*b*) Hydrogen atomic parameters (x, y, and $z \times 10^3$)

	x	y	z	B
H(*W*11)	117 (5)	781 (3)	571 (6)	5·3 (11)
H(*W*12)	90 (7)	854 (3)	639 (7)	6·0 (16)
H(*W*21)	252 (5)	377 (3)	513 (7)	5·0 (12)
H(*W*22)	145 (5)	414 (2)	457 (6)	4·7 (10)
H(1*a*)	402 (3)	425 (1)	286 (4)	1·9 (5)
H(2*a*)	534 (3)	471 (2)	217 (4)	2·0 (5)
H(3*a*)	857 (3)	345 (2)	341 (4)	2·6 (6)
H(4*a*)	613 (5)	401 (2)	−46 (6)	6·8 (10)
H(1*b*)	253 (3)	−148 (2)	−47 (4)	2·2 (5)
H(2*b*)	431 (3)	−162 (1)	25 (3)	1·3 (5)
H(3*b*)	556 (3)	59 (2)	311 (4)	2·0 (5)
H(4*b*)	358 (4)	−219 (2)	396 (4)	3·5 (7)
H(5*b*)	6 (4)	−26 (2)	196 (5)	5·5 (9)

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* The structure factor list has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30124. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Computations

The least-squares computations were carried out using a modified version of the program of Gantzel, Sparks, Long & Trueblood (*UCLALS*4) (1969). The data reduction program was written by H. L. C. and the program used to calculate molecular geometry was one written by H. L. C. and A. Caron.

The program *ORTEP* of Johnson (1965) was used in preparing some of the diagrams and all remaining computations were made using X-RAY 70 (Stewart, Kundell & Baldwin, 1970).

Scattering factors for K^+, carbon, and oxygen are those found in *International Tables for X-ray Crystallography* (1962) and those for hydrogen were from Stewart, Davidson & Simpson (1965). The corrections for anomalous scattering for potassium ($\Delta f' = 0{\cdot}179$, $\Delta f'' = 0{\cdot}250$) of Cromer & Liberman (1970) were used in the calculation of structure factors.

Discussion

The overall relationship of the anions and cations in the crystal is illustrated in Fig. 1. The near-neighbor distances about the potassium ions are presented in Table 3 and the distances pertaining to the hydrogen bonding in the crystal are given in Table 4. Throughout the remaining discussion, the dihydrogen *trans*-aconitate found in this study will be referred to as H_2A^- while the hydrogen *trans*-aconitate will be referred to as HA^{2-}. The dihydrogen *trans*-aconitate anion in the structure reported by Dargay *et al.* (1972) will be referred to as KH_2 *trans* A and the anion of dipotassium hydrogen *cis*-aconitate reported by Glusker *et al.* (1971) will be referred to as K_2H *cis* A.

Each of the three potassium ions is coordinated to seven oxygen atoms with K···O distances ranging from 2·678 to 2·986 Å. The geometry of the arrangement of the oxygen atoms around the potassium ions is different for each of the potassium ions and is such that it defies description in terms of standard packing geometry.

The HA^{2-} anion is associated with seven different potassium ions and forms a bidentate chelate through O(1) and O(6) with K(1) (at x,y,z) to form the seven-membered ring K(1)–O(1)–C(1)–C(2)–C(3)–C(6)–O(6) in the same manner as found in KH_2 *trans* A anion (Dargay *et al.*, 1972). All the oxygen atoms of the HA^{2-} anion are coordinated to at least one K^+ cation

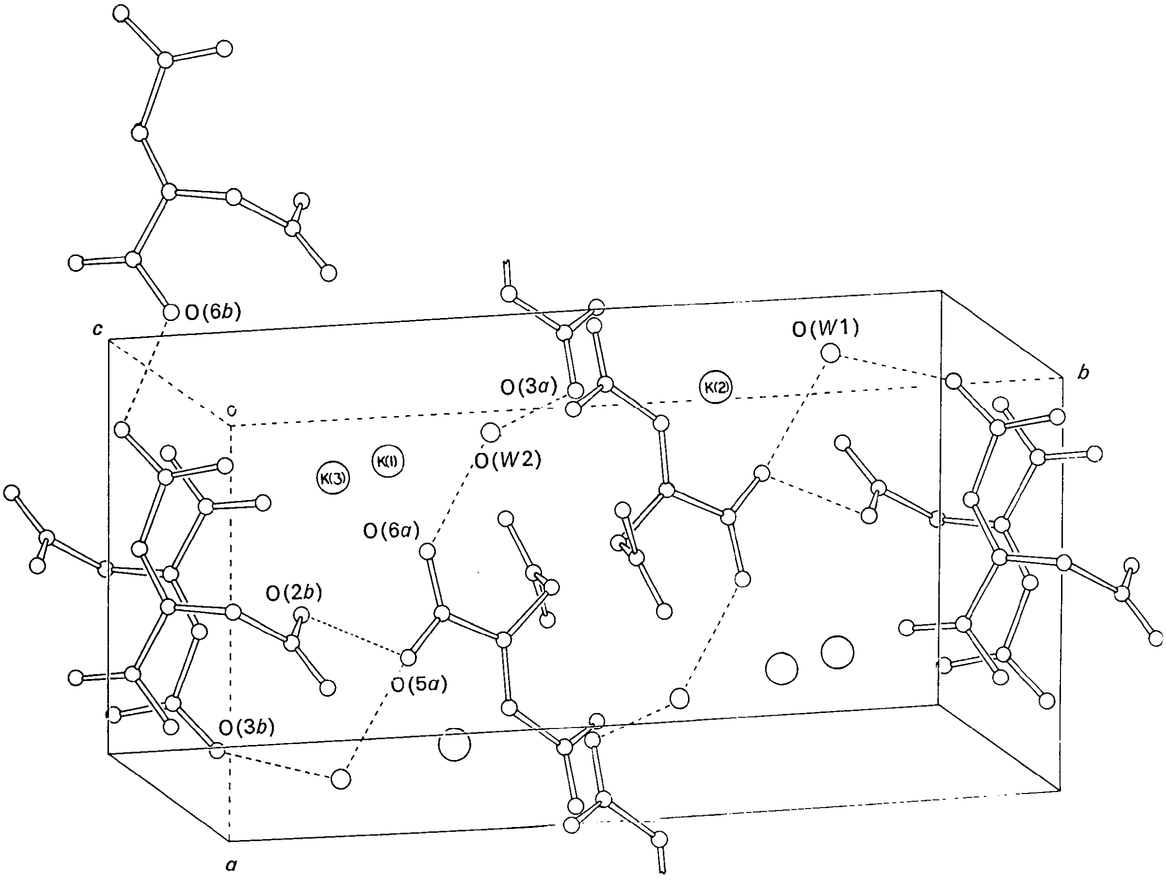

Fig. 1. Crystal packing of $K_3(H_2C_6O_6H_3)(HC_6O_6H_3).2H_2O$ as viewed with **c*** perpendicular to the page. The hydrogen bonding is denoted by the dashed lines.

Table 3. *Some interatomic distances around the potassium ions*

(*a*) $K^+\cdots O$ distances (e.s.d. = 0·002 Å)

K(1)···O(*W*1)	2·901 Å	$-x$	$1-y$	$1-z$
K(1)···O(1*a*)	2·773	x	y	z
K(1)···O(6*a*)	2·785	x	y	z
K(1)···O(1*b*)	2·771	$-x$	$-y$	$-z$
K(1)···O(4*b*)	2·734	$1-x$	$-y$	$-z$
K(1)···O(5*b*)	2·873	x	y	z
K(1)···O(6*b*)	2·979	$-x$	$-y$	$-z$
K(2)···O(*W*2)	2·798	$-x$	$1-y$	$1-z$
K(2)···O(1*a*)	2·714	$-x$	$1-y$	$-z$
K(2)···O(3*a*)	2·756	$-1+x$	y	z
K(2)···O(4*a*)	2·986	$-1+x$	y	z
K(2)···O(4*a*)	2·803	$1-x$	$1-y$	$-z$
K(2)···O(5*a*)	2·839	$1-x$	$1-y$	$1-z$
K(2)···O(1*b*)	2·826	x	$1+y$	z
K(3)···O(*W*1)	2·708	$-x$	$1-y$	$1-z$
K(3)···O(1*a*)	2·869	x	y	$1+z$
K(3)···O(2*a*)	2·923	x	y	$1+z$
K(3)···O(6*a*)	2·816	x	y	z
K(3)···O(2*b*)	2·768	$1-x$	$-y$	$1-z$
K(3)···O(4*b*)	2·678	$1-x$	$-y$	$1-z$
K(3)···O(5*b*)	2·745	x	y	z

(*b*) $K^+\cdots K^+$ distances

K(1)···K(2)	4·431	$-x$	$1-y$	$-z$
K(1)···K(3)	4·264	x	y	$-1+z$
K(1)···K(3)	3·720	x	y	z
K(2)···K(2)	3·978	$-x$	$1-y$	$-z$
K(2)···K(3)	4·021	$-x$	$1-y$	$1-z$

and O(1*a*) is coordinated to three potassium cations. Each H_2A^- ion is coordinated to 6 potassium ions. This anionic species forms bidentate chelates through O(1) and O(6) with K(1) at $-x, -y, -z$ and through O(2) and O(4) with K(4) at $1-x, -y, 1-z$. With K(1) a seven-membered ring is formed similar to that formed in the HA^{2-} anion, while with K(3), an eight-membered ring, K(3)–O(2)–C(1)–C(2)–C(3)–C(4)–C(5)–O(4) is formed. The atom O(3*b*) is the only oxygen atom in the crystal which is not coordinated to a potassium ion.

The HA^{2-} anion contains an intramolecular hydrogen bond between O(2)–H(4) and O(4) with an O···O separation of 2·456 (3) Å. A similar short intramolecular hydrogen bond was found in KH_2 *trans* A (Dargay *et al.*, 1972) where the O(2)···O(4) distance is 2·53 Å. There is also a strong intramolecular hydrogen bond in K_2H *cis* A (Glusker *et al.*, 1971) with an O···O distance of 2·425 (2) Å. In the latter case, it was concluded that the hydrogen bond is probably symmetrical since the experimental distances were O(4)–H(4) = 1·13 (7) and H(4)···O(6) = 1·30 (7) Å. In the present study, however, it is quite apparent, from both the difference map and least-squares refinement, that the hydrogen bond is not symmetric. The O(2)–H(4) bond length is 1·06 (3) Å and the H(4)···O(4) distance is 1·40 (3) Å and there is no indication that the hydrogen is disordered.

In addition to the short intramolecular hydrogen bond found in the HA^{2-} anion, the anion is involved in four other hydrogen bonds; in each case the oxygen atom of the anion is the receptor atom. Three of these hydrogen bonds occur with water molecules, these being O(3*a*)···O(*W*2$^{\text{iv}}$) at 2·817 Å, O(5*a*)···O(*W*1$^{\text{iii}}$) at 2·839 Å, and O(6*a*)···O(*W*2$^{\text{i}}$) at 2·848 Å. The fourth intermolecular hydrogen bond is O(5*a*)···H–O(2*b*$^{\text{ii}}$) at 2·538 Å.

The H_2A^- anion does not contain an intramolecular hydrogen bond between O(2) and O(4). Each anion of this species does, however, participate in four intermolecular hydrogen bonds, only one of which is with a water molecule, this being O(*W*1$^{\text{iii}}$). The O(*W*1$^{\text{iii}}$)···O(3*b*) distance is 2·751 Å. O(3*b*) is also the receptor of a hydrogen bond, that from O(6*b*)–H(5*b*) of another anion of the same species. The O(6*b*$^{\text{v}}$)···O(3*b*) distance is 2·536 Å. There is a hydrogen bond O(6*b*)–H(5*b*)···O(3*b*$^{\text{iv}}$) so that the H_2A^- anions form an infinite chain parallel to the *a* axis. There is also the hydrogen bond

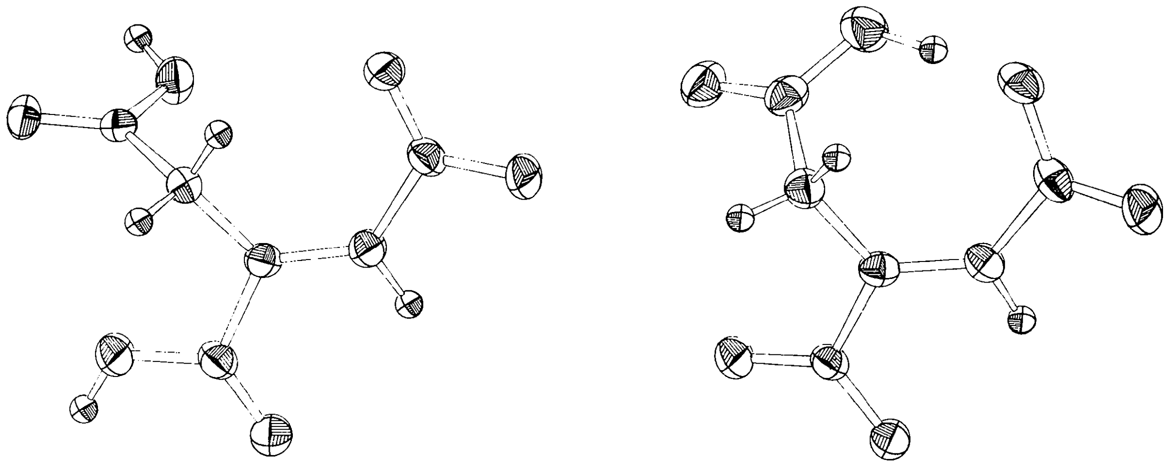
(*a*) (*b*)

Fig. 2. Thermal ellipsoid plot (*ORTEP*) for (*a*) $(H_2C_6O_6H_3)^-$ and (*b*) $(HC_6O_6H_3)^{2-}$. The ellipsoids have been drawn at 50% probability. The hydrogen atoms are represented by spheres with $B = 1·0$ Å^2.

O(2*b*)-H(2*b*)···O(5*a*^{ii}) of 2·538 Å which is the only hydrogen bond formed between the two different anionic species present in the crystal.

There is some overlap of the carbon–carbon double bond systems of the H_2A^- anions. The interplanar separation of the anions at x,y,z and $1-x,-y,-z$ is 3·496 Å [the planes are defined by atoms C(2), C(3), C(4), C(5) and C(6)]. The C(4)···C(3) distance between anions is 3·630 Å and the C(4)···C(4) distance is 3·572 Å. The fact that these double bonds are so close to each other in the first situation listed might account for the tendency for polymerization to occur. The interplanar distance between the H_2A^- anions at x,y,z and $1-x,-y,1-z$ is 3·896 Å.

The thermal motion of the two anions is illustrated in Fig. 2 and the bond distances and angles are presented in Fig. 3. The bond lengths are also presented in Table 5 along with the values reported for KH_2 *trans* A (Dargay *et al.*, 1972) and K_2H *cis* A (Glusker *et al.*, 1971).

The primary difference in the two anions is that H(5), which is present on O(6) in H_2A^-, is not present in the HA^{2-} anion. It is interesting to note that H(5) in KH_2 *trans* A is bonded to O(5) so that the relative configuration of the H_2A^- ion is different from the anion in KH_2 *trans* A with respect to the C(6)–C(3) bond. The H_2A^- and HA^{2-} anions found in this study have a different conformation at the C(2)–C(3) bond

Table 4. *Hydrogen bonds in* $K_3(H_2C_6O_6H_3)\,(HC_6O_6H_3).2H_2O$

Donor (*D*)	Acceptor (*A*)	Symmetry position	$O_D\cdots O_A$ (Å)	O_D–H (Å)	H···O_A	H–$O_D\cdots O_A$	O_D–H···O_A
O(2*a*)-H(4*a*)	O(4*a*)	i	2·456 (2)	1·06 (3)	1·40 (3) Å	2 (2)°	176 (4)°
O(2*b*)-H(4*b*)	O(5*a*)	ii	2·538 (2)	0·90 (2)	1·64 (2)	2 (2)	177 (3)
O(6*b*)-H(5*b*)	O(3*b*)	iv	2·536 (2)	0·87 (3)	1·67 (2)	1 (2)	179 (4)
O(*W*1)-H(*W*11)	O(5*a*)	iii	2·839 (2)	0·81 (3)	2·03 (3)	3 (3)	176 (4)
O(*W*1)-H(*W*12)	O(3*b*)	iii	2·751 (2)	0·75 (4)	2·02 (4)	11 (3)	164 (4)
O(*W*2)-H(*W*21)	O(6*a*)	i	2·848 (2)	0·74 (3)	2·14 (3)	14 (2)	167 (3)
O(*W*2)-H(*W*22)	O(3*a*)	iv	2·817 (3)	0·83 (3)	2·00 (4)	9 (2)	161 (3)

Symmetry code

i	x	y	z
ii	$1-x$	$-y$	$1-z$
iii	$1-x$	$1-y$	$1-z$
iv	$-1+x$	y	z

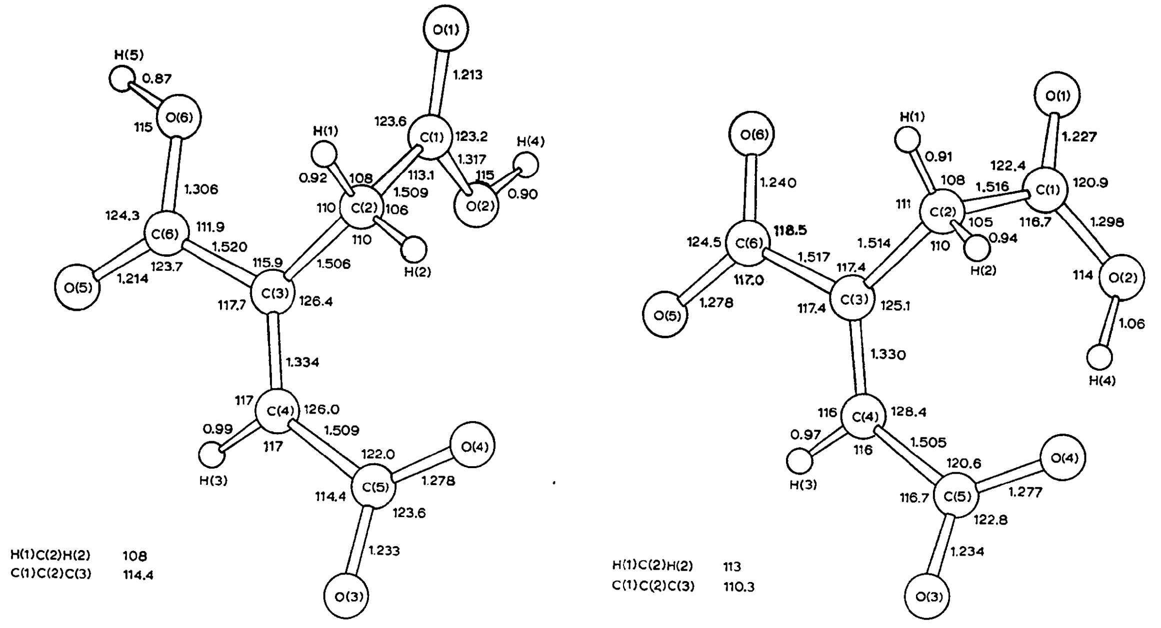

Fig. 3. Bond distances and angles for the two anions of $K_3(H_2C_6O_6H_3)\,(HC_6O_6H_3).2H_2O$. (*a*) $(H_2C_6O_6H_3)^-$. (*b*) $(HC_6O_6H_3)^{2-}$. The estimated standard deviations for the distances and angles are:

C–C; C–O	0·003 Å	C–C–C; C–C–O; O–C–O	0·2°
C–H; O–H	0·02	C–C–H; C–O–H	1·0
		H–C–H	2·0

Table 5. *Bond lengths* (Å) *for* H_2A^-, HA^{2-}, KH_2 *trans* A *and* K_2H *cis* A

	H_2A^-	HA^{2-}	KH_2*trans*A*	K_2H*cis*A†
C(1)–O(1)	1·213 (3)	1·227 (3)	1·204 (2)	1·241 (2)
C(1)–O(2)	1·317 (3)	1·298 (3)	1·312 (2)	1·258 (2)
C(5)–O(3)	1·278 (2)	1·234 (3)	1·257 (2)	1·235 (2)
C(5)–O(4)	1·233 (3)	1·277 (3)	1·252 (2)	1·291 (2)
C(6)–O(5)	1·214 (3)	1·278 (3)	1·310 (2)	1·230 (2)
C(6)–O(6)	1·306 (2)	1·240 (2)	1·211 (2)	1·287 (2)
C(1)–C(2)	1·508 (3)	1·516 (4)	1·516 (2)	1·535 (2)
C(2)–C(3)	1·506 (3)	1·514 (3)	1·508 (2)	1·498 (2)
C(3)–C(4)	1·334 (3)	1·330 (3)	1·336 (2)	1·345 (2)
C(3)–C(6)	1·520 (3)	1·517 (3)	1·505 (2)	1·519 (2)
C(4)–C(5)	1·509 (3)	1·505 (3)	1·493 (2)	1·485 (2)

* Dargay, Berman, Carrell & Glusker (1972). KH_2*trans*A is the same anionic species as H_2A^- of this work. This structure refined to $R=0·043$.

† Glusker, Orehowsky, Casciato & Carrell (1971). The *cis*-aconitate anion has been numbered in a fashion consistent with this work. The carboxyl at C(1) is ionized and the symmetric hydrogen bond occurs between O(4) and O(6). This structure refined to $R=0·025$.

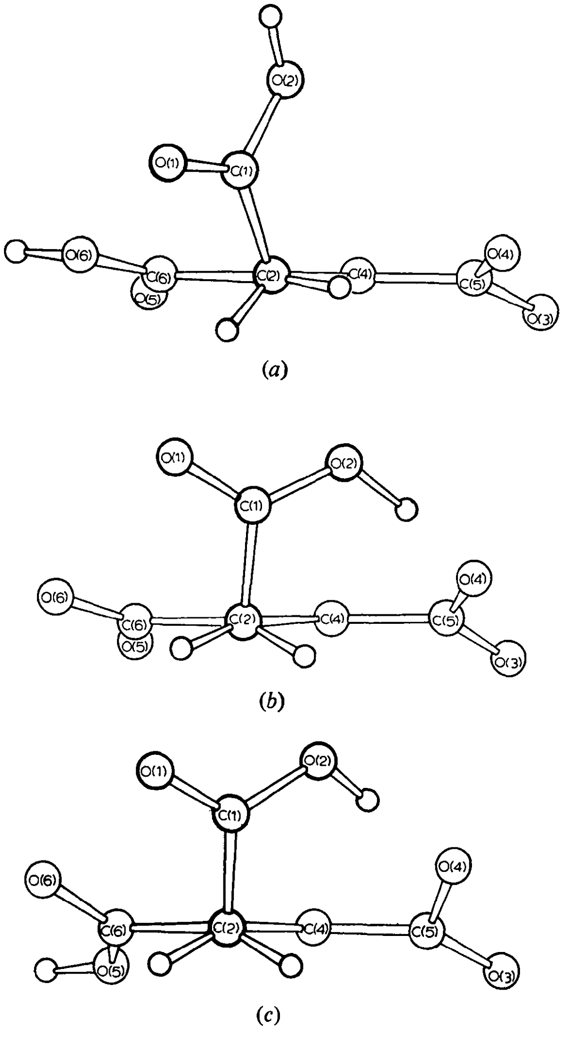

Fig. 4. Views down the C(2)–C(3) bond for (*a*) $(H_2C_6O_6H_3)^-$, (*b*) $(HC_6O_6H_3)^{2-}$ and (*c*) KH_2*trans*A.

(Fig. 4) and the C(1)–O(2) bond. For the H_2A^- anion, the torsion angle C(1)C(2)C(3)/C(2)C(3)C(4) is 110·3° and for the HA^{2-} anion this angle has a value of 82·7°. It should be remembered that the HA^{2-} anion contains the intramolecular hydrogen bond while the H_2A^- anion does not have this hydrogen bond. The anion in KH_2 *trans* A (Dargay *et al.*, 1972) also contains an intramolecular hydrogen bond and the corresponding conformation angle is 89·4°. The torsion angle H(4)O(2)C(1)/O(2)C(1)C(2) is 174° (H_2A^-), which has no intramolecular hydrogen bond, or 2° (HA^{2-}), which has the intramolecular hydrogen bond. It is apparent from this study and that of Dargay *et al.*, (1972) that the conformation about the C(2)–C(3) bond is independent of the ionization state of the anion and is dependent upon the environment of the anion.

The bond lengths for the two anions of this study, H_2A^- and HA^{2-}, are compared in Table 5 with those found in KH_2 *trans* A (Dargay *et al.*, 1972) and with those for K_2H *cis* A (Glusker *et al.*, 1971). In this study, the average value for the carbon–carbon single bond is $1·512 \pm 0·005$ Å with values ranging from 1·505 to 1·520 Å. For KH_2 *trans* A the average value is $1·506 \pm 0·008$ Å ranging from 1·493 to 1·516 Å and for K_2H *cis* A the average value is $1·509 \pm 0·020$ Å with values ranging from 1·485 to 1·535 Å. The values found for the carbon–carbon double bond are 1·330 (3) and 1·334 (3) Å in H_2A^- and HA^{2-} respectively, 1·336 (2) Å for KH_2 *trans* A and 1·345 (2) Å for K_2H *cis* A.

A notable feature of the two anionic species found in this study is that the C–O bond lengths in the carboxylate groups are unequal. In three carboxylate groups in the two anionic species, one C–O bond length is ~0·04 Å longer than the other C–O bond. For H_2A^- the C(5)–O(3) bond length is 1·278 (2) Å and the C(5)–O(4) bond length is 1·233 (3) Å while for the HA^{2-} anion the C(5)–O(3) and C(5)–O(4) bond lengths are 1·234 (3) and 1·277 (3) Å and the C(6)–O(5) and C(6)–O(6) distances 1·278 (3) and 1·240 (2) Å. The average difference in these bond lengths is 0·042 Å which represents a Δ/σ value of ~13, a difference which is significant. One explanation of this inequality of C–O bond lengths appears to be in the fact that in all three carboxylate groups in question, the oxygen atom in the longer C–O bond is also involved in a relatively strong hydrogen bond with a carboxyl hydrogen. In KH_2 *trans* A, there is one ionized carboxyl group, but in that group the two C–O bond lengths are the same, 1·256 and 1·252 Å, and this carboxylate group is involved in an intramolecular hydrogen bond [O(2)–H(4)···O(4)] of 2·53 Å. In addition, the other oxygen atom of this carboxylate group, O(3), is the acceptor of a strong intermolecular hydrogen bond from O(5)–H(5), the O(5)···O(3) distance being 2·52 Å. In the case of the ionized groups in this study, the strong hydrogen bonds which are formed with only one of the oxygen atoms of each carboxylate group is apparently responsible for the localization of the unpaired electron, thus the carboxylate group is interme-

Table 6. *Deviations of atoms from least-squares planes through selected portions of the anions*

The H_2A^- and HA^{2-} notations refer to the $H_2(C_6O_6H_3)^-$ and $H(C_6O_6H_3)^{2-}$ anions respectively. The atoms through which the plane was calculated for the pair are denoted by an asterisk. All deviations are in Å.

	H_2A^-		HA^{2-}	H_2A^-		HA^{2-}	H_2A^-		HA^{2-}	H_2A^-		HA^{2-}
O(1)	1·310		2·154	0·004	*	0·003	−0·099		0·078	0·699		1·383
O(2)	2·334		2·085	0·003	*	−0·002	1·418		0·605	2·031		1·733
O(3)	−0·372		−0·544	0·620		−1·354	−0·001	*	0·002	0·064		0·167
O(4)	0·294		0·552	1·580		−0·094	−0·001	*	0·002	0·351		0·716
O(5)	−0·189		−0·305	−3·381		−3·403	−0·164		−0·044	0·000	*	0·002
O(6)	0·204		0·302	−2·606		−2·105	−0·452		−0·562	0·000	*	0·002
C(1)	1·265		1·525	−0·011	*	0·007	0·199		−0·115	0·858		1·011
C(2)	−0·018		0·083	0·003	*	−0·002	−0·792		−1·168	−0·268		−0·285
C(3)	0·006	*	0·002	−1·019		−1·365	−0·342		−0·517	0·000	*	0·001
C(4)	0·010	*	0·003	−0·772		−1·787	−0·001	*	0·002	0·208		0·326
C(5)	−0·008	*	−0·003	0·589		−1·021	0·004	*	−0·006	0·218		0·401
C(6)	−0·007	*	−0·002	−2·467		−2·353	−0·309		−0·373	−0·001	*	−0·005
H(1)	−0·708		−0·250	−0·125		0·219	−1·591		−1·732	−1·033		−0·788
H(2)	−0·160		−0·346	0·839		0·634	−0·925		−1·596	−0·397		−0·682
H(3)	0·029		−0·045	−1·550		−2·685	0·279		0·393	0·375		0·489
H(4)	3·102		1·453	0·089		−0·045	2·009		0·375	2·704		1·327
H(5)	0·221			−3·412			−0·432			0·011		

diate between a carboxylic acid and a carboxylate. In KH_2 *trans* A, the hydrogen bonds to each of the oxygen atoms of the carboxylate group are of equal strength and the C–O bond lengths are the same, just as would be expected for a carboxylate group.

Deviations of atoms from some least-squares planes through portions of the two anions are listed in Table 6. It may be seen that for the HA^{2-} anion, the group containing the double bond, C(6)–C(3)=C(4)–C(5), is almost exactly planar, and C(2) is out of the plane by 0·083 Å. The corresponding group of atoms in the H_2A^- anion is only somewhat less planar than in the HA^{2-} anion, but in this case C(2) is only 0·018 Å out of the plane. Also, from Table 6, it is seen that the carboxyl and carboxylate groups, CCOOH and CCOO, are planar. It should be noted, however, that none of the carboxyl or carboxylate groups are coplanar with the plane of the double bond system. In all four instances there is a twist about the single bond between the carboxyl group and the double bond. The non-ionized group on H_2A^-, C(6)O(5)O(6), is twisted 10·2° with respect to the plane of the double bond, while the corresponding carboxylate group on HA^{2-} is twisted by 15·8° with respect to the plane of the double bond in that anion. The carboxylate group, C(5)O(3)O(4), in H_2A^- displays a twist of 17·6° while the same group on HA^{2-} is twisted by 29·8°. The latter value is similar to the values found for the two carboxylate groups in KH_2 *trans* A, where the twist with respect to the plane of the double bond is 29·5° for C(5)O(3)O(4) and for C(6)O(5)O(6) the value for the twist is 28·9°.

It is unusual, indeed, to find two different ionization states of a multifunctional carboxylic acid in the same crystal. It is, however, not unique. The crystal structure of a potassium salt of fumaric acid containing the hydrogen fumarate ion and fumaric acid in a 2:1 ratio was reported by Gupta & Sahu (1970).

The author is grateful to Dr Jenny Glusker for carefully reading this manuscript and making helpful comments. This research was supported by U.S.P.H.S. grants CA-10925, CA-06927 and RR-05539 from the National Institutes of Health, U.S. Public Health Service and by an appropriation from the Commonwealth of Pennsylvania.

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