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Dipotassium L-Tartrate Semihydrate

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(*Received* 24 *February* 1995; *accepted* 24 *April* 1995)

Abstract

The single crystal and powder X-ray diffraction analyses of the title compound, $2K^+.C_4H_4O_6^{2-}.0.5H_2O$, are presented. The discussion contains comparisons with the structures of potassium hydrogen tartrate and calcium tartrate tetrahydrate. The title compound belongs to the class of tartrates that are generally ideal for X-ray structure investigations on single crystals within the framework of teaching seminars. The relevance of the powder X-ray diffraction method in the field of wine analysis, with a view to detecting unallowed blending of wines, is emphasized.

Comment

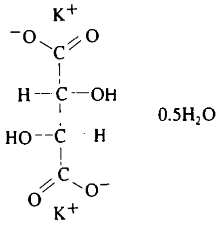
Structure determinations of various salts of tartaric acid occasionally appear in crystallographic journals (Buschmann & Luger, 1985; Boese & Heinemann, 1993). Prominent representatives of these compounds are potassium and calcium tartrates, which play an important role in the process of vinification (Gould, 1976; Amerine & Ough, 1980). In this context these salts are often described as winestone or tartar (Neumüller, 1983; Falbe & Regitz, 1992), which can be obtained as beautifully formed crystals by searching through the sediments in wine barrels or in bottled wines. Hence, tartrates can be an attractive starting point for practical courses in single-crystal X-ray diffraction analysis for students and sometimes surprising results are achieved by detecting new crystal structures of natural products (Boese & Heinemann, 1993).

Much experience in X-ray seminars has shown that natural tartrates are an ideal class of compounds for didactical purposes (see also Luger, 1980): the crystals are usually perfect in shape having grown over a long time, translucent, mechanically stable for mounting, chemically inert and well suited for optical investigations under polarized light. Also, the formula units are small enough for a 12 h data collection, the crystals are characterized by a distinct space group (*e.g.* $P2_12_12_1$), both direct methods and Patterson analysis can be applied for structure solution, and it is also possible to determine the absolute structure because of the presence of heavy atoms. We were able to achieve good R values of *ca* 2–4% in our seminars.

In recent years the field of wine analysis (Gould, 1976; Amerine & Ough, 1980; Campbell, Orr & Noble, 1977; Campbell *et al.*, 1975) has gained importance because of the improvement of wine-making methods and especially because of unlawful vinification manipulations (Kalinowski, 1988). As mentioned above, several solid-state compounds play an important role in the production of wine. Consequently, introducing powder X-ray diffraction analysis for investigating solid-state wine components such as winestone is an additional possibility for detecting unallowed blending of wines. The powder X-ray data, *e.g.* of a compound of a wine sediment, can be compared with JCPDS (Jenkins & Smith, 1987) and Cambridge Structural Database (Allen, Kennard & Taylor, 1983) data, allowing distinct substance identification.

In the literature dealing with wine analysis, the crystal structures of tartrates and the number and position of possible associated water molecules are usually ignored, although this information could be helpful. For example, the single-crystal X-ray structure determination of a natural calcium tartrate obtained from a bottle of wine has shown that the tartrate molecule was associated with four water molecules (Boese & Heinemann, 1993). Also, the single-crystal X-ray analysis of different natural potassium tartrate samples in our seminars revealed that $C_4H_5O_6K$ crystallizes without associated water. In the sediments from a bottled wine, we also found calcium D-galactarate tetrahydrate ($C_6H_8O_8Ca.4H_2O$), which presumably can also be classified as a natural product.

We have therefore investigated the title compound, $C_4H_4O_6K_2.0.5H_2O$, (I), which to the best of our knowledge does not belong to the class of natural products. Some crystallographic data were reported in 1948 (McCrone & Bond, 1948).



(I)

The anion possesses slightly distorted local C_2 symmetry; the structure is displayed in Fig. 1. The distortion results from differences in torsion angles in the two halves of the anion (Δ_{max} ~5°, see Table 2) and can be attributed to the different ionic contact distances (see below). In the comparable potassium hydrogen tartrate and calcium tartrate tetrahydrate (Boese & Heinemann, 1993), the C_2 symmetry is distorted to a greater extent (Δ_{max} = 11 and 20°, respectively). The central C—C bond length is equal within the level of significance to those of the above-mentioned tartrates; the same holds for the C—O(H) distances. However, the remaining C—C bond distances [mean value 1.541 (2) Å] are significantly longer than in the calcium derivative [mean value 1.531 (2) Å] and in the hydrogen tartrate, which has two different C—C terminal distances [1.532 (2) and 1.524 (2) Å] (Buschmann & Luger, 1985), the shorter being connected to the COOH fragment. This effect can be attributed to the higher charge density at the carboxylate groups of the dipotassium salt. Three of the C—O distances in the carboxylate groups are equal [mean value 1.251 (2) Å] whereas one is longer [C4—O6 1.263 (2) Å], which can be explained by the fact that O1, O2 and O5 are each coordinated by two and three K atoms, respectively, whereas O6 has only one cation in its vicinity (see Table 2).

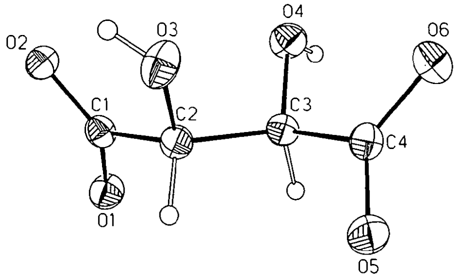


Fig. 1. Anion structure showing 50% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

The two independent K^+ cations have distorted octahedral environments: K1 is surrounded by $O1^{viii}$, $O2^{ix}$, $O4^{ix}$, O5, $O6^{iii}$ and $O7^{ix}$ at distances from 2.701 to 2.810 Å; K2 has $O1^{x}$, $O2^{viii}$, $O2^{vi}$, O3, O5 and $O5^{xi}$ as closest neighbours (2.725–2.962 Å) (for symmetry codes see Table 2).

The K2 atoms, stacked along the y axis (Fig. 2), are separated only by carboxylate O atoms at distances slightly shorter than the corresponding sum of the ionic radii (2.76 Å); the K1 stacks are also separated by water molecules, situated at special positions ($\frac{1}{2}$, y, 0) with C_2 symmetry.

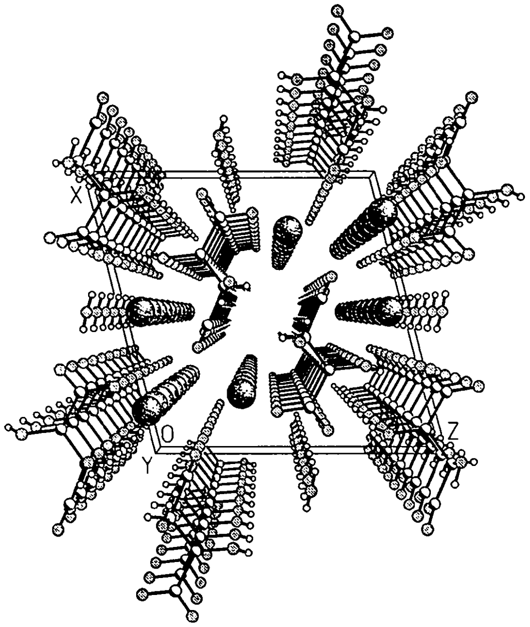


Fig. 2. Packing diagram viewed down the y axis.

Experimental

Transparent single crystals of the title compound were obtained by cooling a saturated aqueous solution ($C_4H_4O_6K_2$.-$0.5H_2O$, Riedel-De Haën AG, Seelze-Hannover).

Crystal data

$2K^+.C_4H_4O_6^{2-}.0.5H_2O$
M_r = 235.28
Monoclinic
$I2$
a = 12.551 (2) Å
b = 5.0137 (10) Å
c = 12.700 (2) Å
β = 104.62 (2)°
V = 773.2 (3) Å^3
Z = 4
D_x = 2.017 Mg m^{-3}
D_m = 1.987 Mg m^{-3}
(McCrone & Bond, 1948)

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 50 reflections
θ = 10–12.5°
μ = 1.22 mm^{-1}
T = 135 K
Transparent cuboid
0.83 × 0.69 × 0.47 mm
Colourless

Data collection

Siemens $P4$ diffractometer
Wyckoff scans
Absorption correction: none

θ_{max} = 30°
h = −15 → 17
k = −7 → 7
l = −17 → 17

3381 measured reflections
2251 independent reflections
2232 observed reflections
$[F_o \geq 4\sigma(F_o)]$
$R_{\rm int} = 0.0409$

2 standard reflections
monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.0339$
$wR = 0.0341$
$S = 1.0505$
2232 reflections
135 parameters
H-atom positional parameters and isotropic U refined
$w = 1/[\sigma^2(F_o) + 0.0015F_o^2]$
$(\Delta/\sigma)_{\rm max} = 0.0141$
$\Delta\rho_{\rm max} = 1.32$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.60$ e Å^{-3}

Extinction correction: $F^* = F_c/[(1 + 0.002xF_c^2)/\sin 2\theta]^{1/4}$
Extinction coefficient: $x = 0.0045$ (5)
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1991)
Absolute configuration: Rogers (1981); $\eta = 1.03$ (6)

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

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

	x	y	z	$U_{\rm eq}$
K1	0.99997 (3)	0.5	0.65842 (3)	0.0237 (1)
K2	0.72990 (3)	1.03407 (12)	0.62006 (2)	0.0227 (1)
C1	0.46097 (11)	0.5308 (4)	0.32945 (11)	0.0190 (4)
C2	0.57391 (12)	0.6065 (4)	0.40429 (12)	0.0191 (4)
C3	0.66911 (13)	0.5101 (4)	0.35925 (12)	0.0190 (4)
C4	0.77554 (12)	0.6014 (4)	0.44105 (12)	0.0204 (4)
O1	0.44014 (10)	0.2868 (3)	0.31639 (11)	0.0261 (4)
O2	0.39808 (9)	0.7165 (3)	0.28795 (10)	0.0220 (3)
O3	0.58556 (11)	0.8858 (3)	0.42287 (11)	0.0262 (4)
O4	0.65726 (11)	0.6137 (3)	0.25300 (9)	0.0257 (4)
O5	0.78938 (10)	0.5182 (3)	0.53652 (9)	0.0262 (3)
O6	0.83983 (11)	0.7569 (3)	0.40875 (10)	0.0272 (4)
O7	1/2	0.6231 (5)	0	0.0313 (6)

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

C1—O1	1.253 (2)	O7—K1$^{\rm vii}$	2.760 (2)
C1—O2	1.248 (2)	C4—O6	1.263 (2)
C1—C2	1.542 (2)	C4—O5	1.252 (2)
C2—O3	1.421 (2)	C3—C4	1.540 (2)
C2—C3	1.528 (2)	C3—O4	1.418 (2)
O5—K1	2.706 (1)	O5—K2$^{\rm iv}$	2.824 (2)
O3—K2	2.795 (1)	O5—K2	2.962 (2)
O1—K1$^{\rm i}$	2.723 (2)	O2—K2$^{\rm i}$	2.750 (1)
O1—K2$^{\rm ii}$	2.771 (2)	O2—K1$^{\rm v}$	2.724 (2)
O6—K1$^{\rm iii}$	2.701 (2)	O2—K2$^{\rm vi}$	2.725 (2)
O7—K1$^{\rm v}$	2.760 (2)	O4—K1$^{\rm v}$	2.810 (2)
O1—C1—O2	125.7 (1)	O5—C4—O6	125.2 (1)
O2—C1—C2	117.5 (2)	O6—C4—C3	118.8 (1)
O1—C1—C2	116.8 (1)	O5—C4—C3	116.0 (2)
C3—C2—O3	108.5 (1)	C2—C3—O4	109.6 (1)
C1—C2—O3	112.6 (1)	O4—C3—C4	113.4 (1)
C1—C2—C3	112.1 (1)	C2—C3—C4	106.3 (1)
K2—O3—C2	115.3 (1)	K1$^{\rm v}$—O4—C3	123.6 (1)
K1—O5—C4	116.2 (1)	C4—O6—K1$^{\rm iii}$	113.3 (1)
C4—O5—K2$^{\rm iv}$	131.7 (1)	C1—O1—K2$^{\rm ii}$	123.9 (1)
C1—O2—K2$^{\rm i}$	111.1 (1)	C1—O1—K1$^{\rm i}$	121.7 (1)
C1—O2—K1$^{\rm v}$	107.5 (1)	C1—O2—K2$^{\rm vi}$	129.3 (1)
K2—O5—C4	94.0 (1)		
O1—C1—C2—O3	−174.0 (1)	O4—C3—C4—O5	179.1 (2)
O2—C1—C2—O3	5.4 (2)	O4—C3—C4—O6	0.9 (2)
O2—C1—C2—C3	−117.2 (2)	C2—C3—C4—O6	−119.6 (2)
O1—C1—C2—C3	63.3 (2)	C2—C3—C4—O5	58.6 (2)
C1—C2—C3—C4	179.5 (1)	O3—C2—C3—O4	−68.5 (2)

Symmetry codes: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}$; (ii) $1 - x, y - 1, 1 - z$; (iii) $2 - x, y, 1 - z$; (iv) $x, y - 1, z$; (v) $x - \frac{1}{2}, \frac{1}{2} + y, z - \frac{1}{2}$; (vi) $1 - x, y, 1 - z$; (vii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (viii) $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z$; (ix) $\frac{1}{2} + x, y - \frac{1}{2}, \frac{1}{2} + z$; (x) $1 - x, 1 + y, 1 - z$; (xi) $x, 1 + y, z$.

The space group $I2$ was chosen because the monoclinic angle for $C2$ exceeded 120°. For $C2$, the cell dimensions are $a = 15.437$ (3), $b = 5.0137$ (10), $c = 12.551$ (2) Å, $\beta = 127.262$ (12)°. The powder diffraction pattern was recorded with a Siemens D5000 diffractometer (transmission technique) using graphite-monochromated Cu$K\alpha$ radiation (intensities and d values have been deposited as supplementary material) at room temperature; the powder was contained in a 0.7 mm Lindeman capillary and indexed based on the C-centered cell as given above. The cell dimensions, based on the powder data using the 2θ values of 67 automatically indexed reflections are: $a = 12.7523$ (18), $b = 5.0396$ (8), $c = 12.5629$ (20), $\beta = 104.778$ (12)°, $V = 780.7$ (2) Å^3. A simulated powder diffraction pattern from the single crystal X-ray data using the *SHELXTL-Plus* program package (*XPOW*) (Sheldrick, 1991) was in perfect agreement with the data recorded by the powder diffractometer.

Data collection: Siemens $P4$ X-ray four-circle diffractometer software. Cell refinement: Siemens $P4$ X-ray four-circle diffractometer software. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, along with a powder diffraction pattern and data, have been deposited with the IUCr (Reference: JZ1050). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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