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Potassium Tartronate and Ammonium Tartronate

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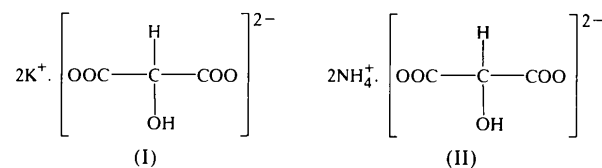
Abstract

Potassium tartronate (dipotassium hydroxypropanedioate, $2K^+ \cdot C_3H_2O_5^{2-}$), (I), crystallizes in the monoclinic space group $P2_1/n$, with $Z = 4$, and ammonium tartronate (diammonium hydroxypropanedioate, $2NH_4^+ \cdot C_3H_2O_5^{2-}$), (II), crystallizes in orthorhombic space group $Pna2_1$, with $Z = 4$. There are two symmetry-independent cations in both (I) and (II). The coordination number of the K^+ ion in (I) is seven, and the number of hydrogen bonds around the NH_4^+ ion in (II) is four. This difference arises from the fact that the hydrogen bonding governs the number of O atoms around NH_4^+ in (II), in contrast to the electrostatic interactions in (I).

Comment

Potassium hydrogen tartronate, (III) (Kroon & Kanters, 1982; Kanters & Kroon, 1976; Roelofsen *et al.*, 1978), and ammonium hydrogen tartronate, (IV) (Taka *et al.*, 1998), crystallize in the same space group, $P2_1/c$, and the crystal structures of (III) and (IV) are similar to each other. The differences in these structures are

interpreted in terms of the nature of the interactions around the cations (Taka *et al.*, 1998), *i.e.* electrostatic for K^+ and hydrogen bonding for NH_4^+ . The K^+ ion in (III) is coordinated by eight O atoms, while the NH_4^+ ion in (IV) forms six $N-H \cdots O$ hydrogen bonds, including two bifurcated hydrogen bonds. The present study was undertaken in order to obtain information on the interactions between the cation and the O atoms of the anion for the title salts of tartronic acid, *i.e.* potassium tartronate, (I), and ammonium tartronate, (II).



The asymmetric unit is composed of two cations and one tartronate anion in the crystals of both (I) and (II) (Fig. 1). The hydroxy group in (I) forms an intramolecular hydrogen bond [O1—H1O 0.70(3), H1O \cdots O4 2.07(3), O1 \cdots O4 2.586(3) Å and O1—H1O \cdots O4 131(4)°], while that in (II) forms an intermolecular hydrogen bond [O1—H1O 0.80(3), H1O \cdots O5^{iv} 2.17(3), O1 \cdots O5^{iv} 2.921(2) Å and O1—H1O \cdots O5^{iv}

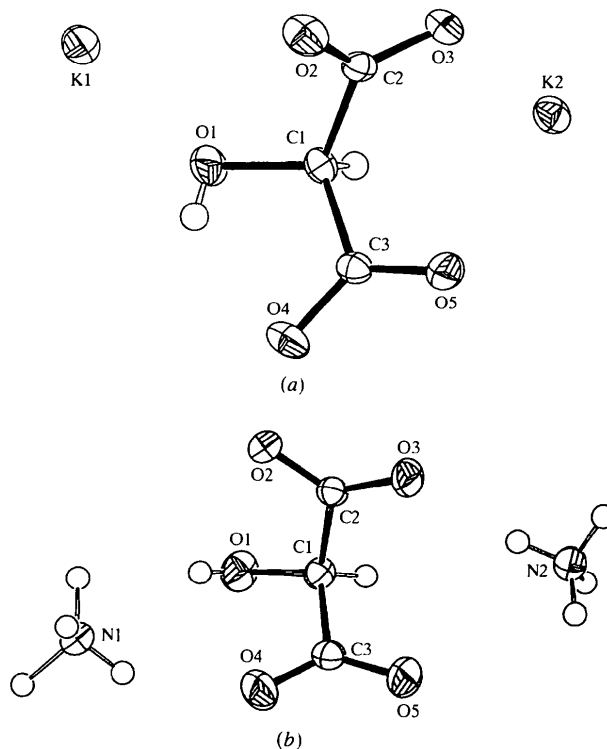


Fig. 1. ORTEP (Johnson, 1976) representations of (a) potassium tartronate, (I), and (b) ammonium tartronate, (II), with the atomic numbering of the asymmetric units. Displacement ellipsoids are shown at the 50% probability level for non-H atoms and H atoms are drawn as spheres with $B_{iso} = 1.0 \text{ \AA}^2$.

156(3)°; symmetry code: (iv) $-x, 2-y, z-\frac{1}{2}$, as in Table 2]. Significant differences in the molecular geometries of the tartronate anions in (I) and (II) are observed only with respect to the conformations; O1—C1—C2—O2 and O1—C1—C3—O4 are 41.9(3) and 15.2(3)° in (I), while these torsion angles are 17.3(2) and -26.1(2)°, respectively, in (II).

As shown in Fig. 2, each K⁺ ion in (I) is coordinated by seven O atoms, while each NH₄⁺ ion in (II) participates in four N—H···O hydrogen bonds. Geometric parameters of the coordination in (I) and the hydrogen bonding in (II) are listed in Tables 1 and 2, respectively. The number of O atoms around each NH₄⁺ ion in (II) is restricted by the hydrogen bonding, as found in (IV). The number in (II) is smaller than that around each K⁺ ion in (I) because of the restriction due to the hydrogen bonding.

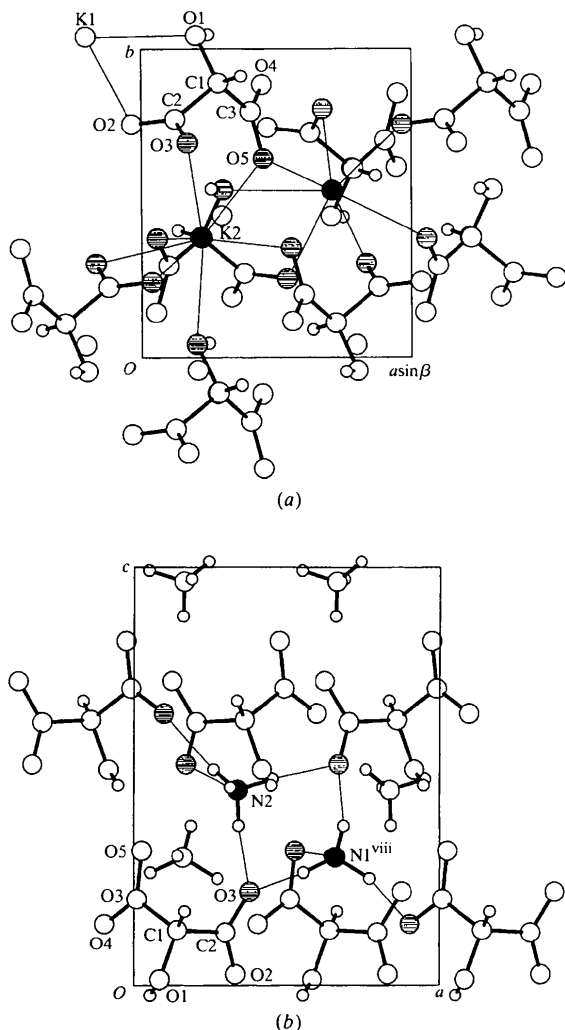


Fig. 2. (a) The coordination around the K⁺ ions in (I) viewed down the *c* axis. (b) The hydrogen bonds with the NH₄⁺ ions in (II) viewed down the *b* axis. [Symmetry code: (viii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$.]

Experimental

Crystals of (I) were grown by slow evaporation from an aqueous solution containing equimolar amounts of tartronic acid (SIGMA T-0657) and potassium carbonate. Crystals of (II) were grown by slow evaporation from an aqueous solution containing tartronic acid and ammonia in a molar ratio of 0.5:1.

Compound (I)

Crystal data



$M_r = 196.24$

Monoclinic

$P2_1/n$

$a = 6.933(4) \text{ \AA}$

$b = 7.826(4) \text{ \AA}$

$c = 11.969(7) \text{ \AA}$

$\beta = 104.05(5)^\circ$

$V = 630.0(6) \text{ \AA}^3$

$Z = 4$

$D_x = 2.069 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 20 reflections

$\theta = 9.5-11.0^\circ$

$\mu = 1.459 \text{ mm}^{-1}$

$T = 295 \text{ K}$

Prismatic

$0.45 \times 0.40 \times 0.35 \text{ mm}$

Colourless

Data collection

Rigaku AFC-5R diffractometer

$\omega/2\theta$ scans

Absorption correction: none

1563 measured reflections

1447 independent reflections

1307 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\text{max}} = 27.5^\circ$

$h = 0 \rightarrow 8$

$k = 0 \rightarrow 10$

$l = -15 \rightarrow 15$

3 standard reflections

every 97 reflections

intensity decay: none

Refinement

Refinement on F

$R = 0.031$

$wR = 0.034$

$S = 1.96$

1307 reflections

99 parameters

All H atoms refined

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\text{max}} = 0.01$

$\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for X-ray

Crystallography (Vol. IV)

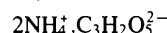
Table 1. Selected geometric parameters (\AA) for (I)

K1···O1	2.853(3)	K2···O1 ^{vi}	2.786(2)
K1···O2	2.822(2)	K2···O2 ^{vi}	2.875(2)
K1···O2 ⁱⁱ	2.749(2)	K2···O3	2.856(2)
K1···O3 ⁱⁱ	2.959(2)	K2···O3 ^{vi}	2.782(2)
K1···O3 ⁱⁱⁱ	2.989(2)	K2···O4 ^{vi}	2.675(3)
K1···O4 ⁱⁱ	2.816(2)	K2···O5	2.739(2)
K1···O5 ⁱ	2.860(2)	K2···O5 ^{ix}	2.695(3)

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

Compound (II)

Crystal data



$M_r = 154.12$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Orthorhombic

 $Pna2_1$ $a = 8.012 (3) \text{ \AA}$ $b = 7.638 (3) \text{ \AA}$ $c = 10.842 (5) \text{ \AA}$ $V = 663.6 (8) \text{ \AA}^3$ $Z = 4$ $D_x = 1.543 \text{ Mg m}^{-3}$ D_m not measured

Cell parameters from 25 reflections

 $\theta = 10.5\text{--}12.5^\circ$ $\mu = 0.146 \text{ mm}^{-1}$ $T = 295 \text{ K}$

Prismatic

 $0.40 \times 0.37 \times 0.14 \text{ mm}$

Colourless

Kanters, J. A. & Kroon, J. (1976). *Nature (London)*, **260**, 600–601.Kroon, J. & Kanters, J. A. (1982). *Croat. Chem. Acta*, **55**, 99–104.Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, Research Forest Drive, The Woodlands, TX 77381, USA.Rigaku Corporation (1990). *RASAI. X-ray Data Collection Package*. Rigaku Corporation, Tokyo, Japan.Roelofsen, G., Kanters, J. A., Kroon, J., Doesburg, H. M. & Koops, T. (1978). *Acta Cryst.* **B34**, 2565–2570.Taka, J., Ogino, S. & Kashino, S. (1998). *Acta Cryst.* **C54**, 384–386.

Data collection

Rigaku AFC-5R diffractometer

 $\omega/2\theta$ scans

Absorption correction: none

1808 measured reflections

1418 independent reflections

1186 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.038$ $\theta_{\text{max}} = 34^\circ$ $h = 0 \rightarrow 12$ $k = 0 \rightarrow 12$ $l = -1 \rightarrow 16$

3 standard reflections

every 97 reflections

intensity decay: none

Refinement

Refinement on F $R = 0.039$ $wR = 0.038$ $S = 1.26$

1186 reflections

131 parameters

All H atoms refined

 $w = 1/\sigma^2(F)$ $(\Delta/\sigma)_{\text{max}} = 0.07$ $\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$

Extinction correction:

 $I_{\text{corr}} = I_o(1 + gI_c)$

Extinction coefficient:

 $g = 1.42 \times 10^{-5}$ Scattering factors from *International Tables for X-ray**Crystallography* (Vol. IV)*Acta Cryst.* (1998). **C54**, 1259–1261 μ -Acetato- μ -aqua- μ -hydroxo-bis[(1,4-dimethyl-1,4,7-triazacyclononane- κ^3N)-copper(II)] Diperchlorate

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Table 2. Hydrogen-bonding geometry (\AA , $^\circ$) for (II)

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$N1\text{---}H1N1\cdots O2'$	0.87 (3)	2.02 (3)	2.847 (2)	158 (3)
$N1\text{---}H2N1\cdots O3''$	0.97 (3)	1.86 (3)	2.786 (2)	160 (2)
$N1\text{---}H3N1\cdots O4'''$	1.14 (4)	1.72 (4)	2.796 (3)	154 (3)
$N1\text{---}H4N1\cdots O5''''$	0.80 (4)	2.30 (4)	3.082 (3)	167 (3)
$N2\text{---}H1N2\cdots O2'$	0.91 (3)	1.93 (3)	2.843 (2)	173 (3)
$N2\text{---}H2N2\cdots O3$	0.86 (3)	1.94 (3)	2.795 (3)	172 (2)
$N2\text{---}H3N2\cdots O4''$	0.93 (3)	1.99 (3)	2.869 (3)	158 (2)
$N2\text{---}H4N2\cdots O2''''$	0.98 (3)	1.97 (3)	2.888 (2)	155 (2)

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

Data collection and cell refinement were carried out with RASAI (Rigaku Corporation, 1990). The structures of (I) and (II) were solved by direct methods using MITHRIL (Gilmore, 1984) and refined by full-matrix least squares using TEXSAN (Molecular Structure Corporation, 1985). H atoms were located from difference Fourier maps and refined isotropically. The displacement ellipsoid plots were made with the aid of ORTEPII (Johnson, 1976). The calculations were performed on a VAX 3100 computer using TEXSAN at the X-ray Laboratory of Okayama University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1017). Services for accessing these data are described at the back of the journal.

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Abstract

The structural characterization of the title complex, $[\text{Cu}_2(\text{OH})(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_8\text{H}_{19}\text{N}_3)_2(\text{H}_2\text{O})](\text{ClO}_4)_2$, provides only the third example of a binuclear copper complex containing a bridging water molecule. The three bridging groups (aqua, acetato and hydroxo) are all different, a rare feature for spontaneous self-assembly reactions. The resulting geometry about the two Cu atoms is distorted octahedral, with the Cu—O(H) distance of 1.963 (2) \AA distinguished from the Cu—O(H₂) distance of 2.737 (5) \AA . The cation has crystallographically imposed mirror symmetry.

Comment

A triangular trinuclear arrangement of Cu atoms is necessary for the four-electron reduction of dioxygen to water for the blue copper oxidases (BCOs). This biologically unique arrangement has been structurally characterized for one member of the BCOs, ascorbate oxidase (Messerschmidt *et al.*, 1992). However, structural evidence in the form of intermediates supporting the proposed mechanism during enzymic activity remains elusive. The title complex, (I), addresses this deficit, providing a structural model complex for the Type 3 binuclear site [the Cu atoms are classified according to their spectroscopic properties as Type 1,