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Dipotassium rhodizonate

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Dipotassium rhodizonate, $2K^+ \cdot C_6O_6^{2-}$, crystallizes in space group *Fddd*. The rhodizonate anions lie in hexagonal layers connected by the potassium ions, which lie between the planes and connect adjacent layers. The conformation of the rhodizonate ion is distinct from previous observations. The site symmetry of the potassium ions is 2 and the site symmetry of the centroid of the rhodizonate ions is 222.

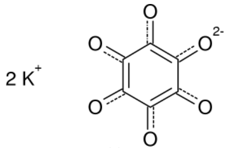
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.093
Data-to-parameter ratio = 13.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The crystal structures of potassium and rubidium rhodizonates were determined by Neumann (1965); however, the coordinates were unavailable in the Cambridge Structural Database (Version 5.25, update of January 2004; Allen, 2002). Rubidium rhodizonate has recently been re-reported by Braga *et al.* (2001). We wished to compare the cocrystallization behaviour of rhodizonic acid ($C_6O_6H_2$) with 2,6-dihydroxybenzoquinone ($C_6O_4H_4$) and tetrahydroxybenzoquinone ($C_6O_6H_4$). While we have produced crystals containing these molecules (Cowan *et al.*, 2001*a*,*b*), so far we have been unable to produce a cocrystal containing rhodizonic acid. We have obtained the potassium salt, (I), as a by-product of this project and redetermined its structure.



(I)

Rhodizonic acid is an intriguing molecule used by crime fighters to detect traces of lead produced by gunfire (Bartsch *et al.*, 1996). It is a weak organic acid, which should participate in a variety of different hydrogen bonds, and upon deprotonation to rhodizonate its shape and properties change significantly.

Potassium rhodizonate (Fig. 1) crystallizes in space group *Fddd*. The metal ion lies between four rhodizonate anions, bonding with eight O atoms (Fig. 2). The rhodizonate anions lie in hexagonal layers connected by the potassium ions, which lie between the planes and connect adjacent layers (Fig. 3). The site symmetry of the potassium ions is 2 and the site symmetry of the centroid of the rhodizonate ions is 222. This structure is incompatable with the cell dimensions and space group, which are availiable in the CSD, of the original structure (Neumann, 1965) and may be a polymorph or a low-temperature phase.

There are four previously published structures containing the rhodizonate ion, in which there are two distinct conformations; the conformation in the present structure is distinct

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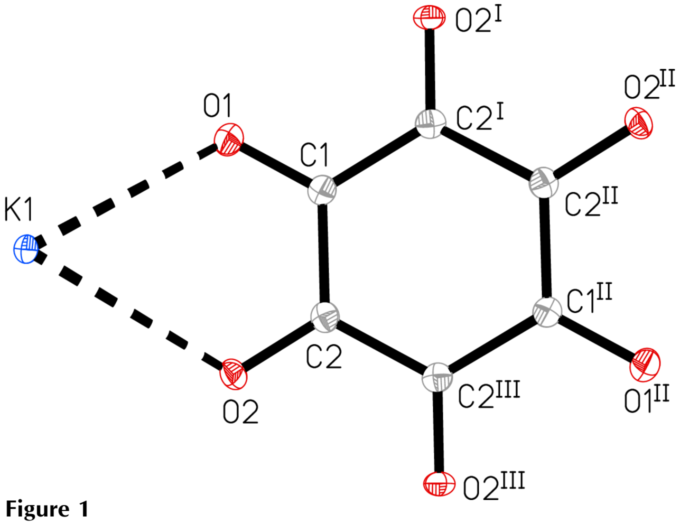

Figure 1
The ions of the title compound, shown with 50% probability displacement ellipsoids. [Symmetry codes: (I) $\frac{5}{4} - x, \frac{5}{4} - y, z$; (II) $\frac{5}{4} - x, y, \frac{1}{4} - z$; (III) $x, \frac{5}{4} - y, \frac{1}{4} - z$.]

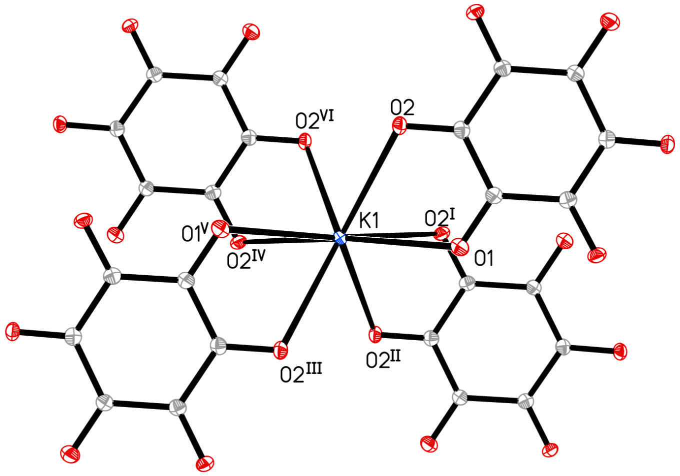

Figure 2
The coordination of the potassium ion in the title compound. [Symmetry codes: (I) $\frac{1}{4} - x, 1 - y, \frac{1}{2} - z$; (II) $\frac{1}{4} + x, 1 - y, \frac{1}{4} + z$; (III) $\frac{3}{4} - x, y, \frac{3}{4} - z$; (IV) $\frac{1}{2} - x, -\frac{1}{4} + y, \frac{1}{4} + z$; (V) $-\frac{1}{2} + x, \frac{5}{4} - y, \frac{3}{4} - z$; (VI) $\frac{1}{2} - x, 1 - y, \frac{1}{2} - z$.]

from either of those previously determined. The C—O bond lengths in the rhodizonate ion [1.254 (5) and 1.255 (3) Å] are essentially the same as those observed in the rubidium salt [1.252 (9) and 1.248 (6) Å] ; however, the C—C bond lengths [1.480 (5) and 1.479 (3) Å] are slightly longer than those in the rubidium salt [1.468 (6) and 1.469 (6) Å]. The rhodizonate ion, in contrast with the situation observed in the rubidium salt, is not planar but has a twisted-boat form (r.m.s. deviation from the plane = 0.108 Å); consequently, the molecular symmetry is not D_{6h} but D_2. It is worth noting that the rubidium salt is not isostructural with the potassium salt (Braga *et al.*, 2001). Lam & Mak (2001*a*,*b*) have produced organic cocrystals containing the rhodizonate ion acting as a multi-hydrogen-bond acceptor, in which the rhodizonate ion is smaller with a greater variation in its internal bond lengths; for example, a range of 1.421 (5)–1.458 (5) Å is found in the C—C bonds and 1.234 (4)–1.258 (4) Å in the C=O bonds in bis(tetra-*n*-butylammonium) rhodizonate tetrakis(phenylurea) clathrate (Lam & Mak, 2001*b*).

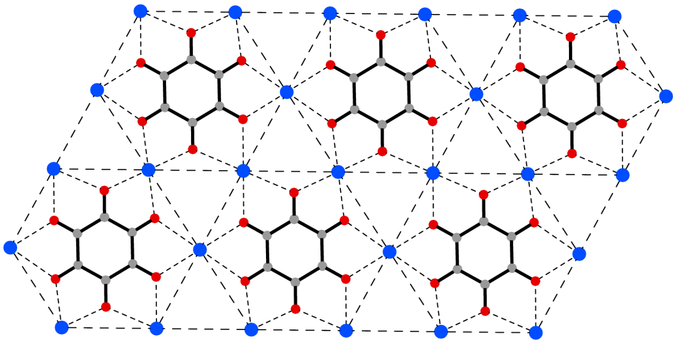

Figure 3
Packing diagram illustrating a layer of rhodizonate ions. The potassium ions connect the anions above and below the plane.

Experimental

Rhodizonic acid dihydrate (approximately 0.5 g), purchased from Aldrich Chemicals, was dissolved in 0.1 *M* potassium hydroxide, producing an intense deep-red solution. Crystals suitable for X-ray structure determination were prepared by slow evaporation of the solvent at room temperature.

Crystal data

$2K^+ \cdot C_6O_6^{2-}$
$M_r = 246.26$
Orthorhombic, *Fddd*
$a = 8.426$ (2) Å
$b = 12.011$ (3) Å
$c = 15.671$ (3) Å
$V = 1586.0$ (6) Å^3
$Z = 8$
$D_x = 2.063$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 982 reflections
$\theta = 12.4$–22.1°
$\mu = 1.19$ mm^{-1}
$T = 100$ (2) K
Block, dark red
0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
3525 measured reflections
462 independent reflections
392 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.049$
$\theta_{\rm max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.093$
$S = 1.06$
462 reflections
34 parameters

$w = 1/[\sigma^2(F_o^2) + (0.034P)^2 + 24.4908P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.47$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.47$ e Å^{-3}

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXL*97.

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supporting information

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Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 982 reflections
$\theta = 12.4–22.1°$
$\mu = 1.19$ mm^{-1}
$T = 100$ K
Block, dark red
0.2 × 0.15 × 0.1 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
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3525 measured reflections
462 independent reflections
392 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.049$
$\theta_{\max} = 27.5°$, $\theta_{\min} = 3.2°$
$h = -10\rightarrow10$
$k = -15\rightarrow15$
$l = -20\rightarrow20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.093$
$S = 1.06$
462 reflections
34 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.034P)^2 + 24.4908P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
K1	0.3750	0.52405 (7)	0.3750	0.0107 (3)
C1	0.6250	0.6250	0.2194 (2)	0.0115 (8)
O1	0.6250	0.6250	0.29940 (18)	0.0159 (6)
O2	0.3441 (2)	0.61034 (17)	0.21116 (12)	0.0129 (5)
C2	0.4733 (3)	0.6199 (2)	0.17206 (16)	0.0114 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0099 (4)	0.0144 (4)	0.0078 (4)	0.000	0.0011 (4)	0.000
C1	0.0129 (18)	0.0103 (17)	0.0113 (18)	−0.0009 (16)	0.000	0.000
O1	0.0160 (14)	0.0204 (15)	0.0113 (13)	−0.0020 (13)	0.000	0.000
O2	0.0100 (10)	0.0161 (10)	0.0126 (9)	0.0021 (8)	0.0026 (8)	0.0005 (8)
C2	0.0130 (13)	0.0090 (12)	0.0124 (13)	−0.0003 (11)	0.0008 (11)	0.0021 (11)

Geometric parameters (Å, º)

K1—O1	2.7038 (13)	C1—O1	1.254 (5)
K1—O2	2.781 (2)	C1—C2	1.479 (3)
K1—O2^{i}	2.799 (2)	O2—C2	1.255 (3)
K1—O2^{ii}	3.016 (2)	C2—C2^{iii}	1.480 (5)

O1—K1—O1^{iv}	126.72 (4)	O1^{iv}—K1—O2^{ii}	164.86 (5)
O1—K1—O2^{v}	99.46 (7)	O2^{v}—K1—O2^{ii}	126.79 (5)
O1^{iv}—K1—O2^{v}	60.09 (6)	O2—K1—O2^{ii}	83.51 (3)
O1—K1—O2	60.09 (6)	O2^{i}—K1—O2^{ii}	79.15 (7)
O1^{iv}—K1—O2	99.47 (7)	O2^{vi}—K1—O2^{ii}	55.69 (7)
O2^{v}—K1—O2	136.24 (9)	O2^{vii}—K1—O2^{ii}	98.63 (8)
O1—K1—O2^{i}	124.12 (6)	O1—C1—C2	120.11 (16)
O1^{iv}—K1—O2^{i}	87.49 (5)	O1—C1—C2^{viii}	120.11 (16)
O2^{v}—K1—O2^{i}	136.21 (7)	C2—C1—C2^{viii}	119.8 (3)
O2—K1—O2^{i}	73.01 (7)	C1—O1—K1^{viii}	115.99 (5)
O1—K1—O2^{vi}	87.49 (5)	C1—O1—K1	115.99 (5)
O1^{iv}—K1—O2^{vi}	124.12 (6)	K1^{viii}—O1—K1	128.03 (11)
O2^{v}—K1—O2^{vi}	73.01 (7)	C2—O2—K1	113.82 (16)
O2—K1—O2^{vi}	136.21 (7)	C2—O2—K1^{i}	112.93 (17)
O2^{i}—K1—O2^{vi}	109.58 (9)	K1—O2—K1^{i}	106.99 (7)
O1—K1—O2^{vii}	164.86 (5)	C2—O2—K1^{ix}	104.64 (16)
O1^{iv}—K1—O2^{vii}	67.63 (4)	K1—O2—K1^{ix}	135.52 (7)
O2^{v}—K1—O2^{vii}	83.51 (3)	K1^{i}—O2—K1^{ix}	75.90 (6)
O2—K1—O2^{vii}	126.79 (5)	O2—C2—C1	120.6 (2)
O2^{i}—K1—O2^{vii}	55.69 (7)	O2—C2—C2^{iii}	119.63 (15)

O2^{vi}—K1—O2^{vii}	79.15 (7)	C1—C2—C2^{iii}	119.77 (16)
O1—K1—O2^{ii}	67.63 (4)		

Symmetry codes: (i) −*x*+1/2, −*y*+1, −*z*+1/2; (ii) *x*+1/4, *y*−1/4, −*z*+1/2; (iii) *x*, −*y*+5/4, −*z*+1/4; (iv) *x*−1/2, −*y*+5/4, −*z*+3/4; (v) −*x*+3/4, *y*, −*z*+3/4; (vi) *x*+1/4, −*y*+1, *z*+1/4; (vii) −*x*+1/2, *y*−1/4, *z*+1/4; (viii) −*x*+5/4, −*y*+5/4, *z*; (ix) *x*−1/4, *y*+1/4, −*z*+1/2.