

## Dipotassium rhodizonate

John A. Cowan\* and Judith A. K. Howard

Department of Chemistry, University of Durham, Durham DH1 3LE, England

Correspondence e-mail: jacowan@anl.gov

## Key indicators

Single-crystal X-ray study

T = 100 K

Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$ 

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>.

Dipotassium rhodizonate,  $2\text{K}^+\cdot\text{C}_6\text{O}_6^{2-}$ , 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.

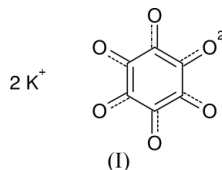
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## Comment

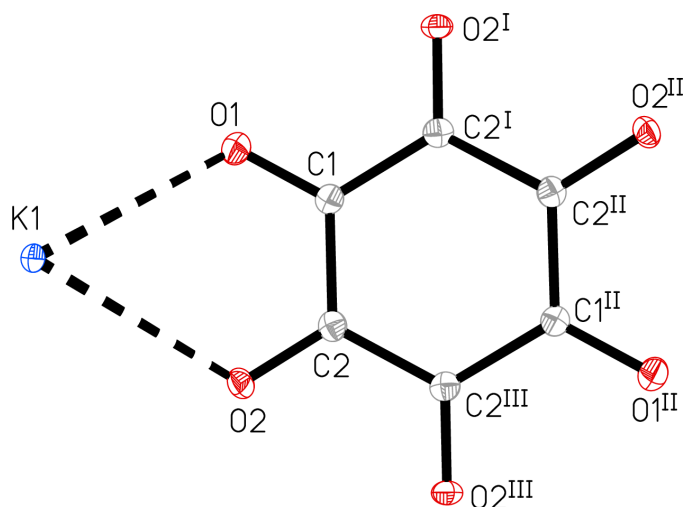
The crystal structures of potassium and rubidium rhodizonates were determined by Neumann (1965); however, the coordinates were unavailable in the Cambridge Structural Database (Version 5.25, update of January 2004; Allen, 2002). Rubidium rhodizonate has recently been re-reported by Braga *et al.* (2001). We wished to compare the cocrystallization behaviour of rhodizonic acid ( $\text{C}_6\text{O}_6\text{H}_2$ ) with 2,6-dihydroxybenzoquinone ( $\text{C}_6\text{O}_4\text{H}_4$ ) and tetrahydroxybenzoquinone ( $\text{C}_6\text{O}_6\text{H}_4$ ). 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.



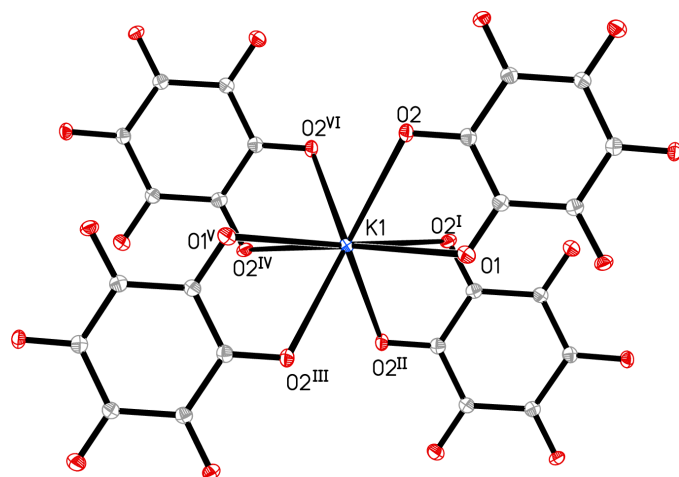
Rhodizonic acid is an intriguing molecule used by crime fighters to detect traces of lead produced by gunfire (Bartsch *et al.*, 1996). It is a weak organic acid, which should participate in a variety of different hydrogen bonds, and upon deprotonation to rhodizonate its shape and properties change significantly.

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 incompatible with the cell dimensions and space group, which are available 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

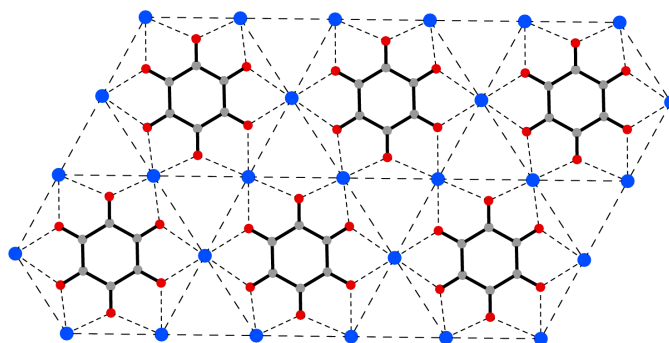


**Figure 1**  
The ions of the title compound, shown with 50% probability displacement ellipsoids. [Symmetry codes: (I)  $\frac{5}{4} - x, \frac{5}{4} - y, z$ ; (II)  $\frac{5}{4} - x, y, \frac{1}{4} - z$ ; (III)  $x, \frac{5}{4} - y, \frac{1}{4} - z$ .]



**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*-butyl-



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

ammonium) rhodizonate tetrakis(phenylurea) clathrate (Lam & Mak, 2001*b*).

## 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<sup>3</sup>  
 $Z = 8$   
 $D_x = 2.063$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
Cell parameters from 982 reflections  
 $\theta = 12.4$ – $22.1^\circ$   
 $\mu = 1.19$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
Block, dark red  
0.20 × 0.15 × 0.10 mm

### Data collection

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

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

### 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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.47$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.47$  e Å<sup>-3</sup>

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXL97*.

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