Disodium rhodizonate: a powder diffraction study

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The crystal structure of the title compound, disodium 1,2,3,4-tetraoxo-5-cyclohexene-5,6-diolate, $2Na^+ \cdot C_6O_6^{2-}$, is built up of alternating layers of hexagonally packed Na^+ cations and rhodizonate dianions. The rhodizonate dianion has a slightly twisted conformation.

Key indicators

Powder synchrotron study

T = 298 K

Mean σ(C–C) = 0.001 Å

R factor = 0.086

wR factor = 0.078

Data-to-parameter ratio = 0.11

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

Comment

Rhodizonic acid and its salts, especially the sodium and potassium salts, have been used, among others, in combination with tartaric acid as a test reagent for gunpowder, the so called 'rhodizonate staining technique' in forensic medicine (Marty *et al.*, 2002; Bartsch *et al.*, 1996). Academic interest has raised the question of whether oxocarbon dianions, $C_nO_n^{2-}$, with their prototype $C_6O_6^{2-}$ (rhodizonate), are aromatic or not (West, 1980; Braga *et al.*, 2001). Recent studies of the solid-state structure of the rhodizonate dianion have shown that planar ($2Rb^+ \cdot C_6O_6^{2-}$; Braga *et al.*, 2001) as well as twisted boat-like ($2K^+ \cdot C_6O_6^{2-}$; Cowan & Howard, 2004) conformations are possible. Here, we report the crystal structure determination of the homologue $2Na^+ \cdot C_6O_6^{2-}$, (I), from synchrotron powder diffraction data.

(I)
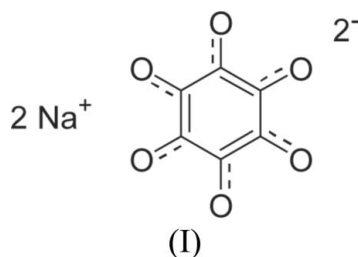
Disodium rhodizonate (Fig. 1) is isostructural with dipotassium rhodizonate (Cowan & Howard, 2004). Layers of hexagonally packed cations alternate with layers of similarly packed anions, as shown in Fig. 2, where the cations lie $a/4$ above the anions. The C—O bond lengths [1.250 (2) and 1.253 (1) Å] are similar to those of the higher homologues [K: 1.254 (5) and 1.255 (3) Å; Rb: 1.252 (9) and 1.255 (3) Å], whereas the C—C bond lengths [1.451 (2) and 1.466 (1) Å] are closer to those observed in the rubidium salt [1.468 (6) and 1.469 (6) Å] rather than those in the potassium salt [1.480 (5) and 1.479 (3) Å].

Fig. 3 shows the environment of the alkali metal. Like $K_2C_6O_6$, the alkali metal in (I) is coordinated by eight O atoms from four different rhodizonate dianions, leading to a distorted quadratic antiprismatic coordination. Fig. 4 displays the slightly twisted conformation of the $C_6O_6^{2-}$ anion (r.m.s. deviation from the mean plane is 0.113 Å).
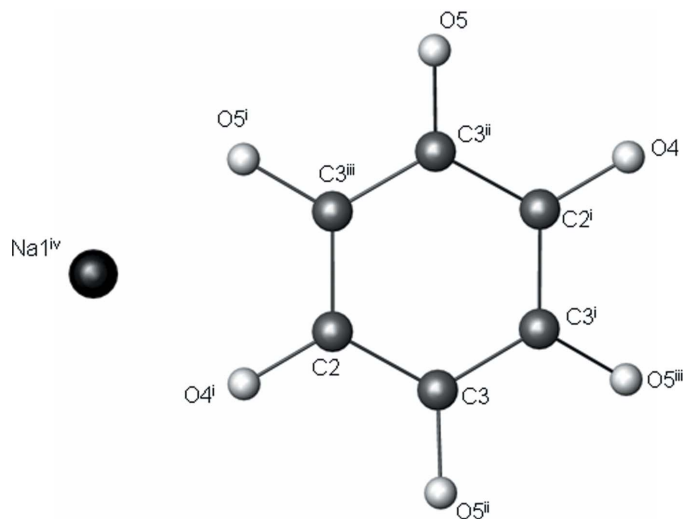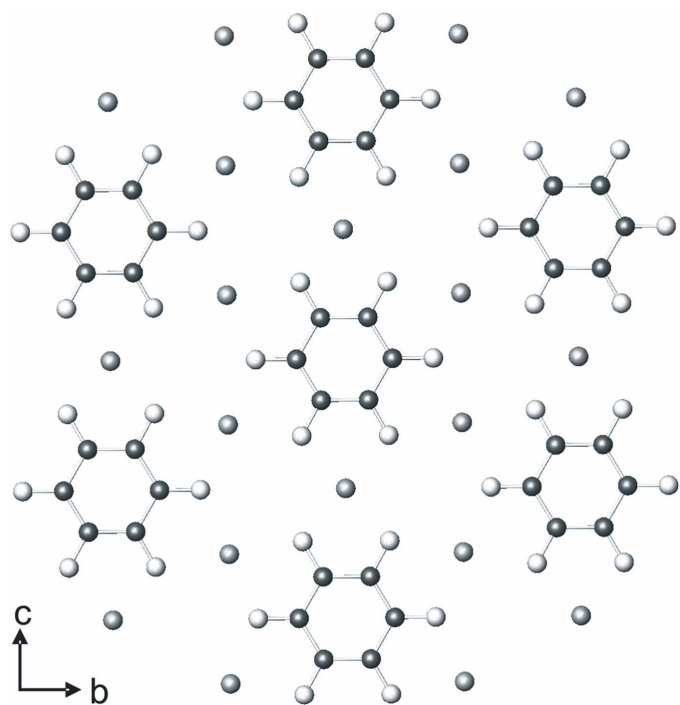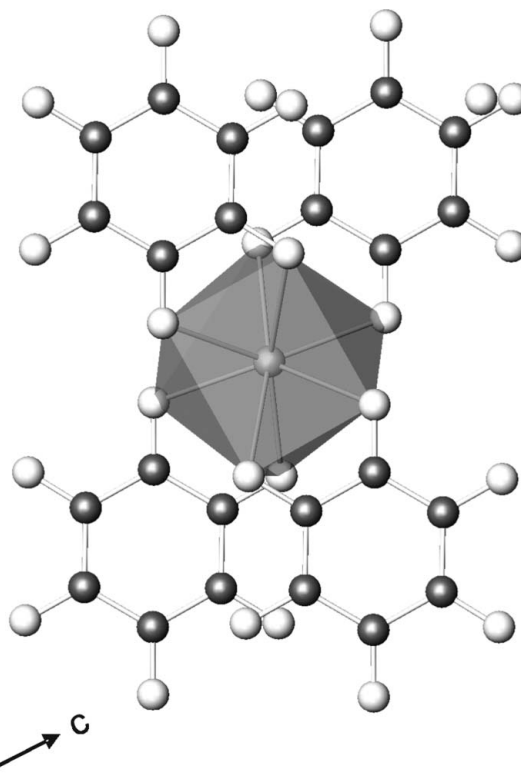
Figure 1
A view of (I), showing the atom-labelling scheme. [Symmetry codes: (i) $-x + \frac{1}{4}, -y + \frac{1}{4}, z$; (ii) $x, -y + \frac{1}{4}, -z + \frac{1}{4}$; (iii) $-x + \frac{1}{4}, y, -z + \frac{1}{4}$; (iv) $x + \frac{1}{4}, y + \frac{1}{4}, -z$].

Experimental

Disodium rhodizonate (97%, Aldrich) was dried *in vacuo* at 423 K over P_4O_{10} for 3 d.

Figure 3
The distorted quadratic antiprism of O (white) around Na (grey).

Figure 2
A view along [100]. Na^+ (grey) lies $a/4$ above $C_6O_6{}^{2-}$ C atoms are denoted by black and O atoms by white spheres.

Crystal data

$2Na^+ \cdot C_6O_6{}^{2-}$	Synchrotron radiation
$M_r = 214.04$	$\mu = 0.029$ mm^{-1}
Orthorhombic, *Fddd*	$T = 298$ K
$a = 11.48349$ (5) Å	Specimen shape: cylinder
$b = 14.32080$ (6) Å	$2 \times 0.3 \times 0.3$ mm
$c = 7.92477$ (3) Å	Specimen prepared at 101.3 kPa
$V = 1303.25$ (2) Å^3	Specimen prepared at 423 K
$Z = 8$	Particle morphology: block, colour-
$D_x = 2.182$ Mg m^{-3}	less

Data collection

ID31 at ESRF	Scan method: continuous
Specimen mounting: 0.7 mm lithium borate glass capillary	Absorption correction: none
	$2\theta_{min} = -11.0$, $2\theta_{max} = 32.9°$
Specimen mounted in transmission mode	Increment in $2\theta = 0.002°$

Refinement

Refinement on I_{net}	247 reflections
$R_p = 0.058$	28 parameters
$R_{wp} = 0.078$	Weighting scheme based on
$R_{exp} = 0.060$	measured s.u.'s; $w = 1/[\sigma(I)]^2$, with
$R_B = 0.086$	$\sigma = N^{1/2}$ (N is related to the total
$S = 1.30$	counts, peak and background for
Wavelength of incident radiation: 0.400094 Å	each reflection)
	$(\Delta/\sigma)_{max} = 2.25$
Excluded region(s): (-11.0)–2 and 26–32.92°	Preferred orientation correction: none
Profile function: pseudo-Voigt	

Powder diffraction data were collected at the high-resolution powder diffractometer at beamline ID31 at the European Synchrotron Radiation Facility (ESRF). An Si 111 reflection was used to select an X-ray energy of 30.99 keV. The size of the beam was
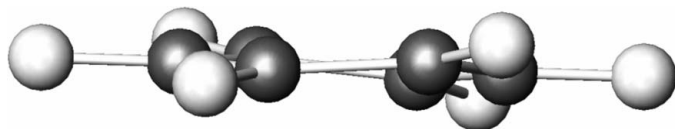
Figure 4
The twisted conformation of the rhodizonate dianion.

adjusted to 2×0.6 mm^2 using slits. The wavelength was determined as 0.40009 (5) Å from a silicon standard. The sample of (I) was contained in a 0.7 mm lithium borate glass (glass No. 50) capillary. The sample was rotated around θ in order to improve randomization of the crystallites. The diffracted beam was analyzed with a nine-crystal analyzer stage [nine Ge(111) crystals separated by 2° intervals] and detected with nine Na(Tl)I scintillation counters simultaneously. The incoming beam was monitored by an ion-chamber for normalization of the decay of the primary beam. 15 min scans were taken at $T = 298$ K in continuous mode for 1 h each, and later normalized and converted to step-scan data from -11.0 to $32.92°$ 2θ in steps of $0.002°$. To minimize the effect of decomposition due to radiation damage, only identical scans were summed. Data reduction of the powder diffraction pattern of (I) was performed using the *GUFI* program (Dinnebier & Finger, 1998). Indexing using *ITO* (Visser, 1969) led to an orthorhombic unit cell. The space group assignment of *Fddd* was made according to the extinction rules, which could later be confirmed by Rietveld refinement (Rietveld, 1969). The number of formula units per unit cell ($Z = 8$) followed directly from volume increments. The peak profiles and precise lattice parameters were determined by Le Bail fits (Le Bail *et al.*, 1988) using the program *GSAS* (Larson & Von Dreele, 1994). The background was modelled manually using *GUFI*. The peak profile was described by a pseudo-Voigt function (Thompson *et al.*, 1987) in combination with a special function that accounts for the asymmetry due to axial divergence (Finger *et al.*, 1994). The powder pattern of (I) exhibits some anisotropic peak broadening caused by lattice strain. The phenomenological strain model of Stephens (1999), as implemented in *GSAS*, was used to model the anisotropy of the full width at half maximum. Starting values for the unconstrained Rietveld refinement were taken from the isostructural compound $2K^+\cdot C_6O_6^{2-}$ (Cowan & Howard, 2004). The background and starting values for the peak profile were taken from the corresponding Le Bail fit. The Rietveld refinement converged satisfactorily (Fig. 5).

Data collection: ID31 software; cell refinement: *GSAS* (Larson & Von Dreele, 1994); data reduction: *GUFI* (Dinnebier & Finger, 1998);
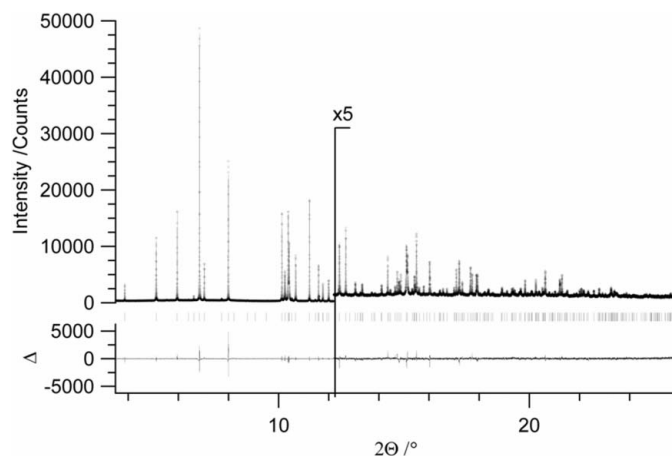

Figure 5
The Rietveld plot for (I). Shown are the observed pattern (diamonds), the best Rietveld-fit profile (line), and the difference curve between observed and calculated profile in an additional window below. The high-angle part of the plot is enlarged by a factor of five.

program(s) used to solve structure: *GSAS*; program(s) used to refine structure: *GSAS*; molecular graphics: *ATOMS* (Dowty, 2002); software used to prepare material for publication: *GSAS*.

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