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Disodium 3-oxobutane-2,2-diylbis(diazeniumdiolate) dihydrate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.117
Data-to-parameter ratio = 10.9

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

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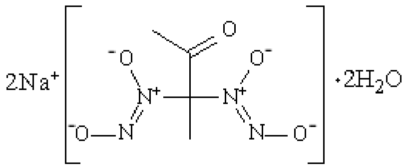
The two diazeniumdiolate substitutents in the anion of the title compound, $2Na^+\cdot C_4H_6N_4O_5^{2-}\cdot 2H_2O$, adopt a Z configuration and are chelated to the Na^+ cations. The water molecules are also coordinated to the cations.

Comment

Diazeniumdiolate-substituted products are obtained from the reaction of nitric oxide gas with ketones (Arulsamy & Bohle, 2001, 2005*a*; Arulsamy *et al.*, 2003). The title compound, (I), was synthesized from 2-butanone (Arulsamy & Bohle, 2005*a*), and is currently the only structurally characterized diazeniumdiolate with an α-keto group.



(I)

The structure of (I) demonstrates the selective disubstitution of the α-methylene C atom and non-substitution of the α-methyl group. In the anion, atom C3 (Fig. 1), with three large substituents, adopts a distorted tetrahedral geometry, with the associated bond angles in the range 105.18 (16)–

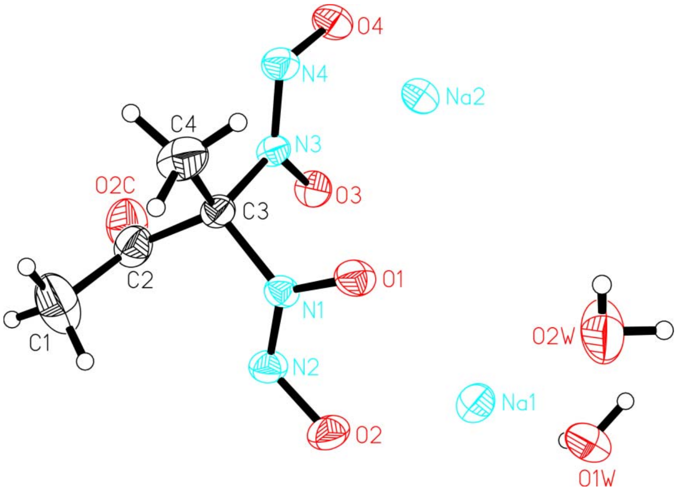


Figure 1
A view of the asymmetric unit of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

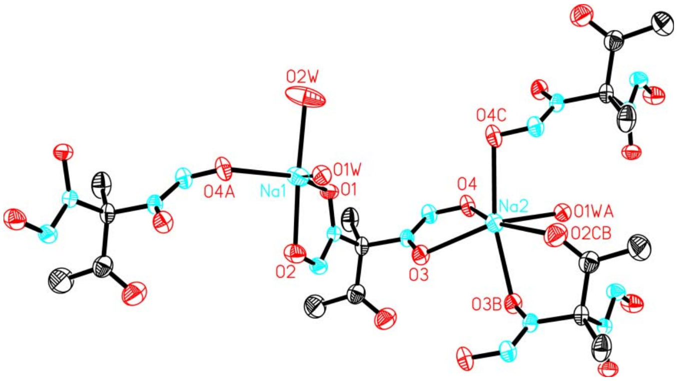


Figure 2
The coordination environment of the Na^+ cations of (I). H atoms have been omitted and some atoms have been left unlabeled for clarity.

112.41 (18)°. The carbonyl C═O bond distance of 1.206 (3) Å is typical. The dihedral angle between the mean planes passing through the two diazeniumdiolate substituents is 86.13 (10)°. The substituents adopt a *Z* configuration, and exhibit similar structural characteristics (Table 1) to those observed in other C-bound diazeniumdiolates (Arulsamy & Bohle, 2001, 2005*a*,*b*; Klebe *et al.*, 1996). The N—N and N—O bond distances are in the range 1.280 (3)–1.312 (2) Å and the diazeniumdiolate groups are nearly planar, with small dihedral angles.

The anion acts as a bridge between the two Na^+ cations, with both of the diazeniumdiolate moieties chelating to the cations, as shown in Fig. 2. One of the cations, Na1, is pentacoordinate, the rest of the ligands being the two solvent water molecules and a terminal diazeniumdiolate O atom of another anion. The other cation, Na2, is in a hexacoordinate geometry and interacts with two other anions, one of which chelates through the keto O atom and an inner diazeniumdiolate O atom, while the other coordinates through a terminal diazeniumdiolate O atom. These ionic interactions lead to a three-dimensional network of the ions. The network is further strengthened by hydrogen-bonding interactions between the anions of one asymmetric unit and the water molecules of a neighboring unit (Table 2). One of the water molecules is hydrogen bonded to an inner diazeniumdiolate O atom of an anion, and the other water molecule is hydrogen bonded to the inner and outer diazeniumdiolate O atoms of two anions.

Experimental

Compound (I) was synthesized and recrystallized as described elsewhere by Arulsamy & Bohle (2005*a*).

Crystal data

$2Na^+\cdot C_4H_6N_4O_5^{2-}\cdot 2H_2O$
$M_r = 272.14$
Triclinic, $P\overline{1}$
$a = 6.625$ (1) Å
$b = 8.525$ (1) Å
$c = 9.821$ (2) Å
$\alpha = 92.62$ (1)°
$\beta = 103.42$ (1)°
$\gamma = 96.89$ (1)°
$V = 534.07$ (15) Å^3

$Z = 2$
$D_x = 1.692$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 27 reflections
$\theta = 4.8$–12.5°
$\mu = 0.22$ mm^{-1}
$T = 298$ (2) K
Chunk, colorless
0.76 × 0.52 × 0.44 mm

Data collection

Bruker P4 diffractometer
ω scans
Absorption correction: none
2371 measured reflections
1854 independent reflections
1751 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.011$

$\theta_{\max} = 25.0°$
$h = -7 \rightarrow 1$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 11$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.117$
$S = 1.05$
1854 reflections
170 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.5532P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.66$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Na1—O2*W*	2.318 (2)	Na2—O2$C^{\rm iii}$	2.536 (2)
Na1—O2	2.3317 (19)	Na2—O4$^{\rm v}$	2.561 (2)
Na1—O4$^{\rm i}$	2.3336 (19)	Na2—Na2$^{\rm v}$	3.7457 (19)
Na1—O1	2.3682 (18)	Na2—Na2$^{\rm iii}$	3.7528 (19)
Na1—O1*W*	2.377 (2)	C3—N1	1.475 (3)
Na1—Na2$^{\rm i}$	3.6781 (14)	C3—N3	1.476 (3)
Na1—Na2$^{\rm ii}$	3.6889 (14)	N1—N2	1.290 (3)
Na1—Na1$^{\rm ii}$	3.926 (2)	N1—O1	1.303 (2)
Na2—O4	2.414 (2)	N2—O2	1.280 (2)
Na2—O3$^{\rm iii}$	2.4311 (19)	N3—N4	1.287 (3)
Na2—O1$W^{\rm iv}$	2.448 (2)	N3—O3	1.312 (2)
Na2—O3	2.4968 (18)	N4—O4	1.290 (2)
N2—N1—O1	124.89 (17)	N4—N3—O3	124.93 (17)
N2—N1—C3	116.45 (17)	N4—N3—C3	117.00 (17)
O1—N1—C3	118.40 (17)	O3—N3—C3	117.97 (16)
O2—N2—N1	114.19 (17)	N3—N4—O4	113.62 (18)
O1—N1—N2—O2	1.9 (3)	O3—N3—N4—O4	−0.7 (3)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, -y, -z+2$; (iii) $-x+1, -y+1, -z+2$; (iv) $x, y+1, z$; (v) $-x, -y+1, -z+2$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1···O1$^{\rm ii}$	0.81 (4)	1.96 (4)	2.761 (3)	173 (3)
O2*W*—H3···O3$^{\rm ii}$	0.87 (4)	1.94 (4)	2.699 (3)	144 (3)
O2*W*—H4···O2$^{\rm vi}$	0.74 (6)	2.05 (6)	2.774 (3)	166 (6)

Symmetry codes: (ii) $-x, -y, -z+2$; (vi) $x-1, y, z$.

The methyl H atoms were placed in calculated positions and treated as riding atoms, with C—H distances of 0.96 Å and $U_{\rm iso}(H) = 1.5U_{\rm eq}(C)$. All other H atoms were located and refined isotropically.

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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