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Tripotassium carboxylatomethylenebis(diazeniumdiolate) 2.5-hydrate

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The title compound, $3K^+\cdot C_2HN_4O_6^{3-}\cdot 2.5H_2O$, contains two diazeniumdiolate substituents which are nearly planar, with observed N—O and N—N double-bond distances in the range 1.276 (3)–1.309 (3) Å, revealing extensive double-bond delocalization over the four-atom groups. One water molecule lies on a twofold rotation axis.

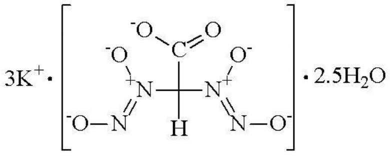
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.004 Å
R factor = 0.037
wR factor = 0.098
Data-to-parameter ratio = 11.4

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

Comment

Reactions of nitric oxide with some alcohols and ketones yield products containing one or more diazeniumdiolate groups (Arulsamy *et al.*, 2003; Arulsamy & Bohle, 2001). Such products are of interest due to their potential application as nitric oxide donors and as high energy density materials (HEDM). Recently, we reported the reaction of nitric oxide with dimethyl malonate, which yields a sydnone carboxylate together with the title compound, (I), as a minor product (Arulsamy & Bohle, 2002).



(I)

In the anion of (I), the central tertiary C atom is substituted with a carboxylate and two diazeniumdiolate groups. The mean planes passing through the two diazeniumdiolate substituents are at 79.06 (17)° to each other. As can be seen from Fig. 1, the diazeniumdiolate and carboxylate groups are arranged as blades in a propeller-shaped anion. A similar propeller-type structure has previously been observed for the methanetris(diazeniumdiolate) anion (Arulsamy & Bohle, 2001). Both diazeniumdiolate substituents in (I) assume a Z configuration and are nearly planar, with small O—N—N—O torsion angles (Table 1). The N—O and N—N bond distances (Table 1) are neither close to the respective single bonds nor close to double bonds, similar to those in the latter anion (Arulsamy & Bohle, 2001) and in other carbon-bound diazeniumdiolates, indicating extensive double-bond delocalization (Arulsamy & Bohle, 2005; Klebe *et al.*, 1996; Bryden, 1959).

The K^+ ions are surrounded by the anionic diazeniumdiolate and carboxylate groups and by the solvent water molecules, as shown in Fig. 2. The coordination polyhedron around each of the K^+ cations is different. The diazeniumdiolates coordinate to the cations through their O atoms as chelating and as monodentate ligands, but the N atoms are also situated close to the cations, with the associated K—O

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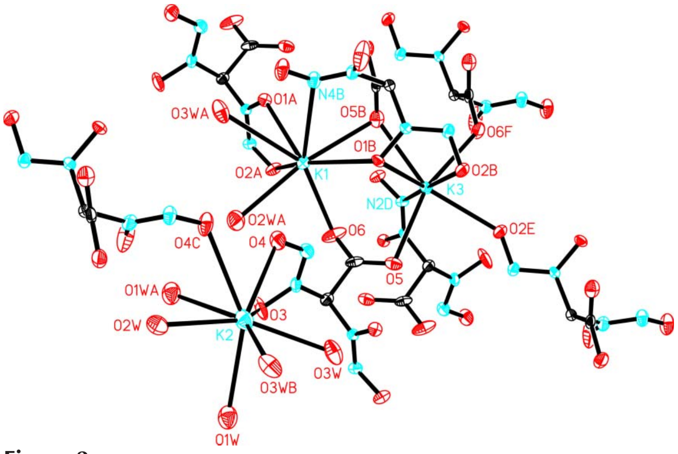

Figure 2
The coordination environment of the K^+ cations in (I). H atoms have been omitted and some atoms are unlabeled for clarity.

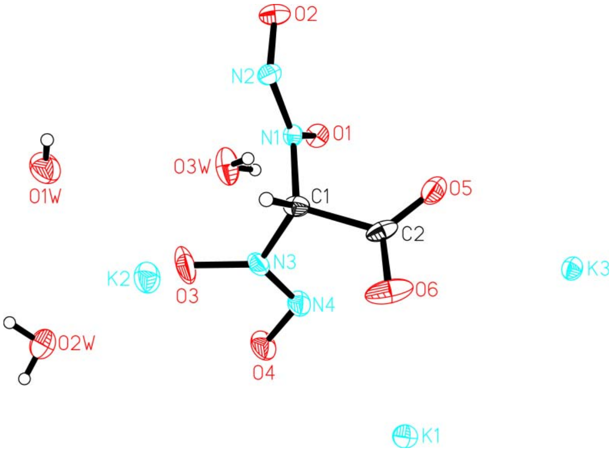

Figure 1
A view of the asymmetric unit of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

and K—N distances being in the range 2.628 (2)–3.232 (3) Å.

In addition to being coordinated to the cations, the solvent water molecules also form moderately strong hydrogen bonds with both of the diazeniumdiolate substituents (Table 2). The hydrogen-bonding interaction associated with the water molecule which is situated on a twofold axis and that associated with one of the water molecules in a general position serve to bridge two neighboring anions. The acidic C—H group in the anion is not associated with any hydrogen-bonding interaction.

Experimental

Compound (I) was synthesized and recrystallized as reported by Arulsamy & Bohle (2002). It crystallizes from water as the 2.5-hydrate. The crystals turn opaque on standing for several hours at room temperature, due to the loss of some of the solvent water. Therefore, the crystal used for the present X-ray data collection was enveloped with Paratone N oil and the data collection was carried out at 173 K.

Crystal data

$3K^+\cdot C_2HN_4O_6^{3-}\cdot 2.5H_2O$
$M_r = 339.41$
Monoclinic, $C2/c$
$a = 28.831$ (3) Å
$b = 9.3063$ (12) Å
$c = 8.6456$ (12) Å
$\beta = 100.642$ (10)°
$V = 2279.8$ (5) Å^3
$Z = 8$

$D_x = 1.978$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 27 reflections
$\theta = 5.0$–12.5°
$\mu = 1.24$ mm^{-1}
$T = 173$ (2) K
Rectangular prism, colorless
0.32 × 0.24 × 0.10 mm

Data collection

Bruker P4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.625$, $T_{max} = 0.883$
2403 measured reflections
1991 independent reflections
1737 reflections with $I > 2\sigma(I)$

$R_{int} = 0.025$
$\theta_{max} = 25.0°$
$h = -1 \rightarrow 34$
$k = -1 \rightarrow 11$
$l = -10 \rightarrow 10$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.098$
$S = 1.04$
1991 reflections
175 parameters
H atoms treated by independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 7.4865P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.023$
$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

K1—O6	2.628 (2)	K3—O6^{vi}	2.676 (2)
K1—O1^{i}	2.758 (2)	K3—O5	2.709 (2)
K1—O2W^{ii}	2.780 (3)	K3—O5^{iii}	2.709 (2)
K1—O2^{i}	2.845 (2)	K3—O2^{vii}	2.745 (2)
K1—O5^{iii}	2.861 (2)	K3—N2^{viii}	2.918 (3)
K1—O1^{iii}	2.880 (2)	K3—O2^{iii}	3.008 (2)
K1—N4^{iii}	3.051 (3)	K3—O1^{iii}	3.024 (2)
K1—O3W^{i}	3.146 (3)	O1—N1	1.309 (3)
K2—O2W	2.734 (3)	N1—N2	1.301 (3)
K2—O3W	2.736 (3)	N1—C1	1.458 (4)
K2—O3W^{iv}	2.828 (3)	N2—O2	1.276 (3)
K2—O4	2.922 (3)	O3—N3	1.307 (4)
K2—O1W	2.934 (3)	N3—N4	1.277 (4)
K2—O3	2.940 (4)	N3—C1	1.469 (4)
K2—O4^{ii}	3.012 (3)	N4—O4	1.291 (3)
K2—O1W^{v}	3.232 (3)		
N2—N1—O1	125.0 (2)	N4—N3—O3	124.1 (3)
N2—N1—C1	115.6 (2)	N4—N3—C1	117.5 (2)
O1—N1—C1	119.2 (2)	O3—N3—C1	118.2 (3)
O2—N2—N1	114.0 (2)	N3—N4—O4	114.0 (3)
O1—N1—N2—O2	−0.8 (4)	O3—N3—N4—O4	−2.9 (5)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W···O3^{ix}	0.83 (1)	2.02 (2)	2.805 (3)	158 (5)
O2W—H2W···O3^{v}	0.83 (1)	1.85 (1)	2.667 (4)	169 (5)
O3W—H4W···O4^{x}	0.82 (1)	1.90 (1)	2.723 (4)	174 (5)
O3W—H5W···O1	0.83 (1)	1.95 (2)	2.757 (3)	168 (5)

Symmetry codes: (v) $-x+1, -y, -z+1$; (ix) $x, -y, z-\frac{1}{2}$; (x) $x, -y+1, z-\frac{1}{2}$.

The asymmetric unit contains three K$^+$ cations, one ethanoate-2,2-diylbis(diazeniumdiolate) anion and two and a half solvent water molecules. All of these are well ordered. One of the solvent water molecules is located on a twofold symmetry axis. The H atom of the central C atom of the anion was placed in an idealized position, with C—H = 1.00 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Water H atoms were located in a difference Fourier map and then constrained to an idealized geometry, with O—H = 0.82 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(O).

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1996); 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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