metal-organic papers

Dipotassium ethane-1,1-diylbis(diazeniumdiolate) monohydrate

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The ethane-1,1-bis(diazeniumdiolate) anion in the title compound, $2K^+ \cdot C_2H_4N_4O_4{}^{2-} \cdot H_2O$, acts as a complex bridging ligand. Both the N and the O atoms of the diazeniumdiolate substituents are coordinated to the K^+ cations, revealing the delocalization of a negative charge over the four-atom groups.

Comment

Thermally explosive diazeniumdiolate-substituted products are synthesized by the reaction of nitric oxide gas with ketones and with alcohols in the presence of alkali alcoholates. Our interest in these compounds stems from their exothermic decomposition and NO-donor properties (Arulsamy & Bohle, 2001, 2005b; Arulsamy et al., 2003). The title compound, (I), can be synthesized either from 2-butanone or from 1-propanol (Arulsamy & Bohle, 2005b).

(I)
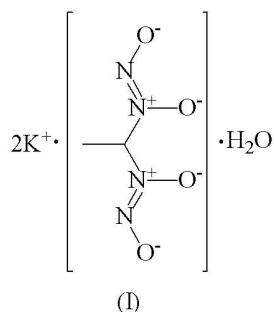
The ethane-1,1-bis(diazeniumdiolate) anion contains two planar diazeniumdiolate groups. The dihedral angle between these two groups is 81.88 (10)° (Fig. 1). Geometric parameters (Table 1) associated with the substituents are consistent with those in other diazeniumdiolate compounds (Arulsamy & Bohle, 2001, 2005a; Klebe et al., 1996). The anion interacts with the two K^+ cations in a complex manner, as shown in Fig. 2. Firstly, each of the two pairs of the diazeniumdiolate O atoms is coordinated to each of the two cations with the anion acting as a bridging dinucleating ligand. Secondly, the diazeniumdiolate O atoms interact with two different cations and act as single atom bridges. Thirdly, the terminal N and O atoms together bind a single cation, forming three-membered chelate rings. These interactions suggest that the negative charge of the anionic substituent is delocalized over the four-atom groups.

The water molecule is coordinated to both cations (Table 1), and is also involved in a moderately strong hydrogen-bonding interaction with the anion (Table 2). Significantly, the tertiary C—H group is not associated with any of the electronegative groups or with the water molecule through hydrogen bonding.
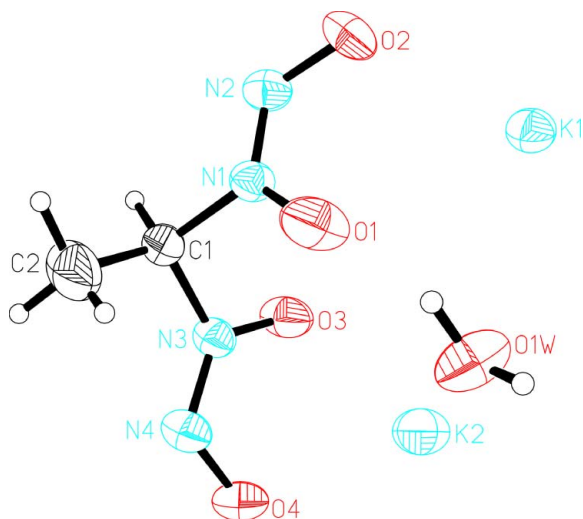
Figure 1
Drawing of the asymmetric unit, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
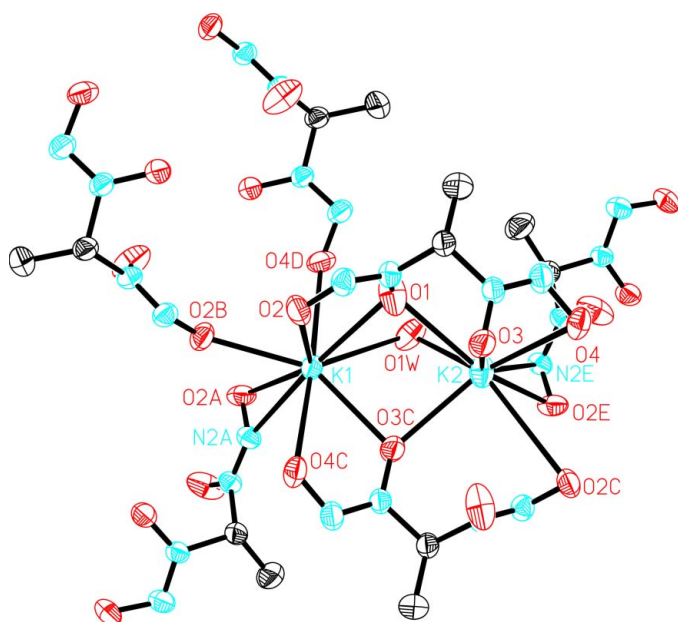

Figure 2
Coordination environment of the K+ cations. H atoms have been omitted and some atoms are unlabeled for clarity.

Experimental

The title compound was synthesized and recrystallized as described elsewhere (Arulsamy & Bohle, 2005b).

Crystal data

$2K^+\cdot C_2H_4N_4O_4^-\cdot H_2O$	Mo $K\alpha$ radiation
$M_r = 244.31$	Cell parameters from 73
Rhombohedral, $R\bar{3}$	reflections
$a = 14.2510\,(12)$ Å	$\theta = 4.6–12.5°$
$\alpha = 116.402\,(7)°$	$\mu = 1.02$ mm^{-1}
$V = 1390.9\,(8)$ Å^3	$T = 298\,(2)$ K
$Z = 6$	Block, colorless
$D_x = 1.750$ Mg m^{-3}	$0.42 \times 0.36 \times 0.32$ mm

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.026$
ω scans	$\theta_{max} = 30.0°$
Absorption correction: ψ scan	$h = -10 \rightarrow 20$
($SHELXS97$; Sheldrick, 1997)	$k = -19 \rightarrow 4$
$T_{min} = 0.667$, $T_{max} = 0.721$	$l = -10 \rightarrow 20$
3377 measured reflections	3 standard reflections
2631 independent reflections	every 97 reflections
2106 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$+ 0.3737P]$
$wR(F^2) = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.002$
2631 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
130 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

K1—O2^i	2.6436 (13)	K2—O1	2.8507 (18)
K1—O3^{ii}	2.6748 (13)	K2—O4	3.006 (2)
K1—O1	2.7933 (18)	K2—N4	3.117 (2)
K1—O4^{ii}	2.8420 (16)	K2—N2^{vi}	3.168 (2)
K1—N2^{iii}	2.889 (2)	K2—N3	3.188 (3)
K1—O4^{iv}	2.9374 (15)	K2—O3	3.236 (3)
K1—O1W	2.9506 (18)	O1—N1	1.292 (2)
K1—O2	2.969 (3)	N1—N2	1.2841 (19)
K1—O2^{iii}	3.173 (3)	N1—C1	1.465 (2)
K1—K2^{iv}	3.7814 (7)	N2—O2	1.290 (2)
K1—K1^v	3.8632 (19)	O3—N3	1.3038 (19)
K2—O1W	2.722 (3)	N3—N4	1.283 (2)
K2—O3^{ii}	2.7248 (14)	N3—C1	1.475 (2)
K2—O2^{vi}	2.7944 (16)	N4—O4	1.291 (2)
N2—N1—O1	125.46 (14)	N4—N3—O3	124.88 (14)
N2—N1—C1	115.81 (15)	N4—N3—C1	119.06 (14)
O1—N1—C1	118.67 (14)	O3—N3—C1	115.93 (13)
N1—N2—O2	113.61 (15)	N3—N4—O4	113.20 (14)
O1—N1—N2—O2	−1.5 (2)	O1—N1—C1—C2	62.7 (2)
O2—N2—N1—C1	−178.69 (14)	O1—N1—C1—N3	−61.3 (2)
N2—N1—C1—C2	−119.95 (19)	O3—N3—C1—N1	−54.37 (19)
N2—N1—C1—N3	116.04 (16)	O3—N3—C1—C2	−176.51 (18)
N1—C1—N3—O3	−54.37 (19)	O3—N3—N4—O4	−0.6 (2)
C1—N3—N4—O4	−176.22 (14)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1A⋯O4^{iv}	0.85 (3)	1.95 (3)	2.773 (2)	163 (3)
O1W—H1B⋯O3^{vii}	0.81 (4)	2.10 (4)	2.908 (4)	175 (3)

Symmetry codes: (iv) $-y + 1, -z + 1, -x + 1$; (vii) $x + 1, y + 1, z + 1$.

The methyl H atoms were positioned geometrically at distances of 0.96 Å from the parent C atom, and a riding model was used during the refinement process [$U_{iso}(H) = 1.5U_{eq}(C)$]. The remaining H atoms were located in a difference synthesis and were refined isotropically [C—H = 1.02 (2) Å and O—H = 0.81 (4) and 0.85 (3) Å].

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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