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Disodium 4-hydroxybutane-1,1-diylbis(diazeniumdiolate) sesquihydrate

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Key indicators

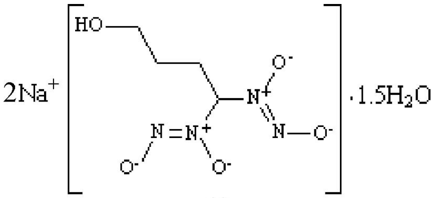
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.002 Å
H-atom completeness 73%
Disorder in main residue
R factor = 0.029
wR factor = 0.074
Data-to-parameter ratio = 8.7

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

The title compound, $2Na^+\cdot C_4H_8N_4O_5^{2-}\cdot 1.5H_2O$, contains a 4-hydroxybutane-1,1-diylbis(diazeniumdiolate) anion with two planar diazeniumdiolate substituents. The dihedral angle between the mean planes passing through the substituents is 57.52 (7)°.

Comment

Nitric oxide is known to react with sodium ethoxide in ethanol to form sodium methanebis(diazeniumdiolate) (MacDonald & Masson, 1894). We have extended this reaction to higher homologues in our continuing effort toward the synthesis of polydiazeniumdiolate compounds. Our previous studies have shown that diazeniumdiolate compounds possess exothermic decomposition properties and therefore are potential high energy density materials (Arulsamy & Bohle, 2001). In general, the above reactions proceed with the formation of a bis(diazeniumdiolate) together with sodium formate. Assuming that a tetrakis(diazeniumdiolate) salt could be synthesized from an aliphatic α,ω-diol, we studied the reaction of 1,5-pentanediol with nitric oxide in the presence of sodium methoxide. Surprisingly, the reaction forms the title compound, (I) (Fig. 1), a bis(diazeniumdiolate) (Arulsamy & Bohle, 2005*d*).



(I)

The anion contains a tertiary C atom (C1), with a hydroxypropyl and two diazeniumdiolate ($-N_2O_2^-$) substituents. The diazeniumdiolate substituents exhibit a Z configuration with respect to the two N—O bonds, and are nearly planar, their geometric parameters being comparable to those in other diazeniumdiolate-substituted compounds (Arulsamy & Bohle, 2001, 2005*a*,*b*,*c*; Arulsamy *et al.*, 2003; Bryden, 1959; Cherepinskii-Malov *et al.*, 1983; Jalal *et al.*, 1986; Keefer *et al.*, 2001; Klebe *et al.*, 1996). The anion interacts with the cations through the diazeniumdiolate N and O atoms and the hydroxypropyl O atom, the associated Na—N and Na—O bond distances being in the range 2.3822 (12)–2.706 (5) Å.

Specifically, atom Na1 is in a seven-coordinate NaO_7 geometry, with the seven O atoms belonging to five anions (Fig. 2). One of the anions is coordinated through both of the O atoms of one of its two diazeniumdiolate groups, while

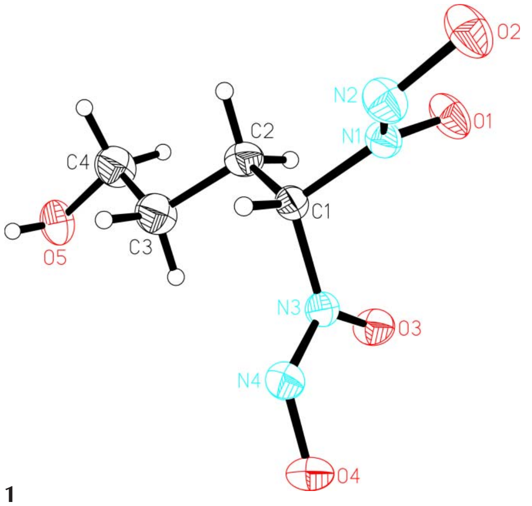


Figure 1
A view of the anion in (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms).

another anion binds Na1 through the two inner diazeniumdiolate O atoms. Two anions bind Na1 through a terminal diazeniumdiolate O atom, and the fifth anion is coordinated through its hydroxypropyl O atom.

Atom Na2 is situated on a twofold rotation axis in an eight-coordinate NaO_6N_2 geometry, the coordinated atoms belonging to two *O*,*O*-chelating and two *O*,*N*-chelating anions (Fig. 3). Two of the anions bind to Na2 through the two O atoms belonging to one of their diazeniumdiolate groups, whereas the remaining two anions bind the cation through the terminal N and O atoms of one of their diazeniumdiolate groups, forming two three-membered (—Na2—O2—N2—) chelate rings.

Atom Na3, with 50% site occupancy, adopts a distorted octahedral NaO_6 geometry (neglecting the adjacent O1*W* atom), the ligands being four anions and two disordered water molecules (Fig. 2). Three of the anions are coordinated through one of the diazeniumdiolate O atoms and the other is coordinated through the hydroxypropyl O atom. The water molecule occupies two sites with 50% site occupancy, and these two sites complete the coordination octahedron around atom Na3.

Except for one of the water O atoms (O1*W*), all the O atoms are coordinated to more than one cation, and the interaction between the anions and cations results in a three-dimensional network. The hydroxypropyl O atom is involved in a hydrogen-bonding interaction with a terminal diazeniumdiolate N atom of a neighboring anion (Table 2).

Experimental

To a freshly prepared solution of Na metal (3.45 g, 0.15 atom) in methanol (100 ml) was added 1,5-pentanediol (5.2 g, 0.05 mol). The cloudy solution was allowed to react with nitric oxide by a previously described procedure (Arulsamy & Bohle, 2001). The white precipitate was filtered and dried under reduced pressure at room temperature. The crude product was recrystallized from water to yield crystals of (I) (Arulsamy & Bohle, 2005*b*). IR (cm^{-1}): 3520–3340 (*b*, ν_{OH}), 1318 (*m*, ν_{ONNO}), 1260 (*s*, ν_{NO}).

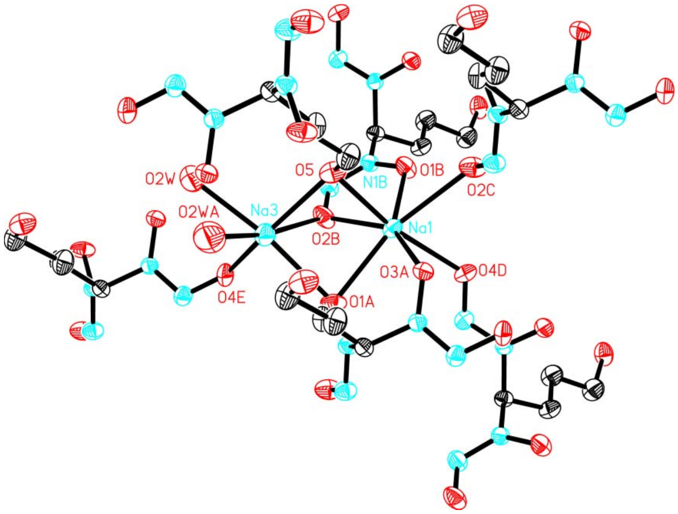


Figure 2
Coordination environments of Na1 and Na3. H atoms have been omitted and some atoms are unlabeled for clarity. The anions containing atoms O1*A*, O1*B*, O2*C*, O4*D* and O4*E* were generated by the symmetry operations $(-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1)$, $(x, -y + 1, z + \frac{1}{2})$, $(-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1)$, $(x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2})$ and $(-x + 1, -y + 2, -z + 1)$, respectively.

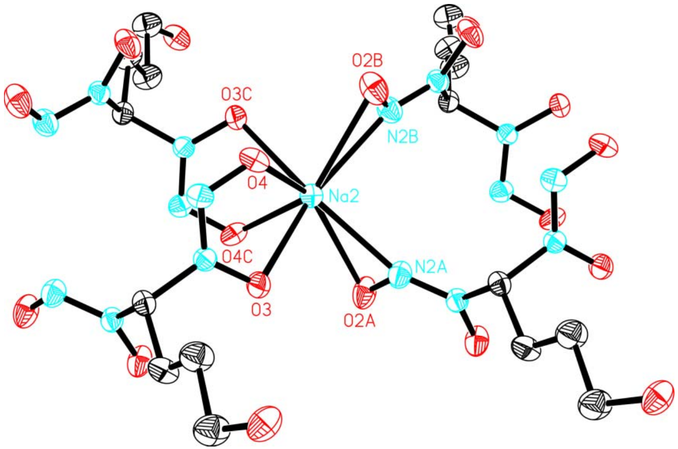


Figure 3
Coordination environment of Na2. H atoms have been omitted and some atoms are unlabeled for clarity. The anions containing atoms O2*A*, O2*B* and O2*C* were generated by the symmetry operations $(x, y + 1, z)$, $(-x + 1, y + 1, -z + \frac{1}{2})$ and $(-x + 1, y, -z + \frac{1}{2})$, respectively.

Crystal data

$2Na^+\cdot C_4H_8N_4O_5^{2-}\cdot 1.5H2O$
$M_r = 265.15$
Monoclinic, *C*2/*c*
$a = 15.2039$ (13) Å
$b = 7.0727$ (6) Å
$c = 19.4242$ (19) Å
$\beta = 104.018$ (12)°
$V = 2026.5$ (3) Å^3
$Z = 8$

$D_x = 1.738$ Mg m$^{-3$}
Mo *K*α radiation
Cell parameters from 34 reflections
$\theta = 5.0$–12.5°
$\mu = 0.23$ mm^{-1}
$T = 298$ (2) K
Prism, colorless
0.54 × 0.40 × 0.30 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*SHELXS97*; Sheldrick, 1997)
$T_{min} = 0.882$, $T_{max} = 0.930$
4119 measured reflections
1761 independent reflections
1664 reflections with $I > 2\sigma(I)$

$R_{int} = 0.015$
$\theta_{max} = 25.0°$
$h = -17 \rightarrow 17$
$k = -8 \rightarrow 1$
$l = -23 \rightarrow 23$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.074$
$S = 1.08$
1761 reflections
203 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 1.8675P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0121 (8)

Table 1
Selected geometric parameters (Å, °).

Na1—O4^{i}	2.3822 (12)	Na3—O5	2.4678 (18)
Na1—O1^{ii}	2.4176 (12)	Na3—O1^{iii}	2.510 (2)
Na1—O5	2.4216 (13)	Na3—O2^{ii}	2.619 (3)
Na1—O2^{ii}	2.4330 (13)	Na3—O2*WA*	2.706 (5)
Na1—O1^{iii}	2.4742 (13)	O1—N1	1.2997 (15)
Na1—O3^{iii}	2.5264 (12)	N1—N2	1.2876 (18)
Na1—O2^{iv}	2.6496 (13)	N1—C1	1.4712 (18)
Na2—O4	2.4259 (12)	N2—O2	1.2826 (17)
Na2—N2^{v}	2.4503 (14)	O3—N3	1.2948 (16)
Na2—O3	2.4553 (11)	N3—N4	1.2920 (17)
Na2—O2^{v}	2.6072 (12)	N3—C1	1.4691 (18)
Na3—O2*W*^{vi}	2.395 (3)	N4—O4	1.2840 (17)
Na3—O4^{vi}	2.4278 (18)		
N2—N1—O1	124.91 (12)	N4—N3—O3	124.65 (12)
N2—N1—C1	114.25 (11)	N4—N3—C1	114.75 (11)
O1—N1—C1	120.55 (11)	O3—N3—C1	120.49 (11)
O2—N2—N1	114.73 (12)	O4—N4—N3	114.14 (12)
O1—N1—N2—O2	−0.8 (2)	O3—N3—N4—O4	1.34 (18)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···N4^{vii}	0.81 (3)	2.09 (3)	2.8956 (18)	173 (2)

Symmetry code: (vii) $-x+1, -y+1, -z+1$.

All H atoms, except those of the water molecules, were located in difference maps and freely refined. The disordered Na3 and O1*W* species are located *ca* 0.9 Å apart. Their site occupancies were refined such that the sum of occupancies was equal to unity. The refinements resulted in 0.5 occupancy for both Na3 and O1*W* giving exact charge balance. The site occupancies of the adjacent, distorted, atoms O2*W* and O2*WA* were refined, yielding final occupancies of 0.532 (5) and 0.468 (5), respectively, for these two atoms.

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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References

Arulsamy, N. & Bohle, D. S. (2001). *J. Am. Chem. Soc.* **123**, 10860–10869.
Arulsamy, N. & Bohle, D. S. (2005*a*). *Acta Cryst.* E**61**, m764–m766.
Arulsamy, N. & Bohle, D. S. (2005*b*). *Acta Cryst.* E**61**, m838–m840.
Arulsamy, N. & Bohle, D. S. (2005*c*). *Acta Cryst.* E**61**, m930–m932.
Arulsamy, N. & Bohle, D. S. (2005*d*). *J. Am. Chem. Soc.* In preparation.
Arulsamy, N., Bohle, D. S., Korich, A. L. & Mondanaro, K. R. (2003). *Tetrahedron Lett.* **44**, 4267–4269.
Bruker (1996). *XSCANS* (Version 2.31) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Bryden, J. H. (1959). *Acta Cryst.* **12**, 581–585.
Cherepinskii-Malov, V. D., Mukhametzyanov, A. S., Andrianov, V. G. & Marchenko, G. A. (1983). *Z. Strukt. Khim. (Engl. Translation)*, **24**, 157–158.
Jalal, M. A. F., Hossain, M. B. & Van der Helm, D. (1986). *Acta Cryst.* C**42**, 733–738.
Keefer, L. K., Flippen-Anderson, J. L., George, G., Shanklin, A. P., Dunams, T. M., Christodoulou, D., Saavedra, J. E., Sagan, E. S. & Bohle, D. S. (2001). *Nitric Oxide*, **5**, 377–394.
Klebe, G., Hadicke, E., Boehn, K. H., Reuther, W. & Hickman, E. (1996). *Z. Kristallogr.* **211**, 798–803.
MacDonald, G. W. & Masson, O. (1894). *J. Chem. Soc.* pp. 944–949.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.