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Potassium L-2-nitrimino-1,3-diazepane-4-carboxylate monohydrate

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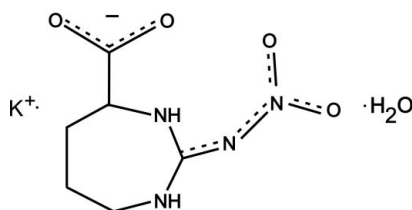
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.065; wR factor = 0.193; data-to-parameter ratio = 20.4.

The title compound, $\text{K}^+ \cdot \text{C}_6\text{H}_9\text{N}_4\text{O}_4^- \cdot \text{H}_2\text{O}$, crystallizes with the K atoms located on special positions related by pseudocentres of symmetry. Each K atom is coordinated by six O-atom donors. The N and water H atoms are involved in inter- and intramolecular $\text{N}-\text{H} \cdots \text{O}$, $\text{N}-\text{H} \cdots \text{N}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonding. The data indicate inversion twinning.

Related literature

For related literature, see: Apreyan & Petrosyan (2008); Apreyan *et al.* (2008*a,b*); Karapetyan (2008*a,b*); Karapetyan *et al.* (2007); Kurtz & Perry (1968); Paul *et al.* (1961); Petrosyan *et al.* (2005).



Experimental

Crystal data

$\text{K}^+ \cdot \text{C}_6\text{H}_9\text{N}_4\text{O}_4^- \cdot \text{H}_2\text{O}$
 $M_r = 258.29$
 Orthorhombic, $I222$
 $a = 7.3883$ (15) Å
 $b = 10.087$ (2) Å
 $c = 29.031$ (6) Å

$V = 2163.5$ (8) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.51$ mm⁻¹
 $T = 293$ (2) K
 $0.21 \times 0.14 \times 0.11$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Absorption correction: none
 5030 measured reflections
 3141 independent reflections

1736 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 3 standard reflections every 400 reflections
 intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.193$
 $S = 1.04$
 3141 reflections
 154 parameters
 3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.42$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.39$ e Å⁻³
 Absolute structure: Flack (1983), 1350 Friedel pairs
 Flack parameter: 0.48 (20)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O5}-\text{H11} \cdots \text{O1}^i$	0.87 (2)	2.09 (5)	2.885 (5)	153 (10)
$\text{O5}-\text{H10} \cdots \text{O3}^{ii}$	0.856 (19)	2.03 (4)	2.793 (4)	148 (6)
$\text{N2}-\text{H9} \cdots \text{N3}^{iii}$	0.86	2.39	3.080 (4)	138
$\text{N1}-\text{H2} \cdots \text{O3}$	0.86	2.09	2.561 (5)	114

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

Data collection: *DATCOL* in *CAD-4 Software* (Enraf–Nonius, 1988); cell refinement: *LS* in *CAD-4 Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The author expresses his thanks to Dr R. A. Apreyan and Dr A. M. Petrosyan for providing the crystals and to Dr R. A. Tamazyan for valuable discussion of the results.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2410).

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supplementary materials

Acta Cryst. (2008). E64, m1369 [doi:10.1107/S1600536808023817]

Potassium L-2-nitrimino-1,3-diazepane-4-carboxylate monohydrate

H. A. Karapetyan

Comment

Cyclic L-2-nitrimino-1,3-diazepane-4-carboxylic acid (L-NIDCA), produced by elimination of amine from L-nitroarginine (Paul *et al.*, 1961), may generate new non-linear optical materials like L-nitroarginine itself [Apreyan *et al.* (2008a, 2008b); Karapetyan *et al.* (2007); Petrosyan *et al.* (2005)]; the crystal structures of L-NIDCA and its monohydrate have been recently reported [Karapetyan (2008a, 2008b)].

This paper presents a structural study of the potassium salt of L-NIDCA monohydrate. The structure was solved and refined in the orthorhombic unit cell with I222 space group. The choice of the non-centric space group was based on the generation of second harmonic observed on a powder sample (YAG:Nd laser, Kurtz-Perry method [Kurtz & Perry, 1968]). In this structure, two independent potassium cations occupy special positions. These potassium atoms are located about pseudo-inversion centers, which is most likely the reason for the presence of high level pseudosymmetry in the structure. Both potassium cations are coordinated by six oxygen atoms with K \cdots O bond lengths in the ranges 2.712 (5)-2.815 (7) Å for K1 and 2.642 (5)-2.783 (6) Å for K2.

A view of the asymmetric unit is shown in Fig. 1. The high value of U_{eq} of atom C3 of the 1,3-diazepane ring compared to those of its neighbors indicates potential disorder of this atom. In the crystal structure, the nitrogen-bound H atoms and the water H atoms are involved in N—H \cdots O, N—H \cdots N and O—H \cdots O hydrogen bonding (Table 1), one of them being intra- and the other three intermolecular, linking anions and water molecules in infinite layers parallel to the *bc* plane (Fig. 2).

Experimental

The title compound was synthesized from a mixture of aqueous solutions containing L-nitroarginine (2 g, Sigma-Aldrich) and KOH (0.512 g) at room temperature. Single crystals of the title compound were obtained by slow evaporation of the solution. At 97° C decomposition of the crystals was observed.

Refinement

The data set was collected in a full sphere of reciprocal space. Space group I222 was chosen on the basis of the powder second harmonic of YAG:Nb laser generation property of the crystals of the title compound. In spite of the fact that all H atoms appear in difference Fourier maps in reasonable positions, they became unacceptable after refinement. Because of this, all the H atoms except those belonging to the water molecule were placed in geometrically calculated positions and included in the refinement in a riding model approximation, with $U_{iso}(H) = 1.2U_{eq}(\text{carrier atom})$. The positions of the H atoms of the water molecule were located in difference Fourier maps and included in the refinement with fixed O—H (0.85 Å), H \cdots H (1.35 Å) distances and isotropic temperature parameters $U_{iso}(H) = 1.4U_{eq}(O)$. The absolute configuration has been determined using L-nitroarginine of known absolute configuration.

Figures

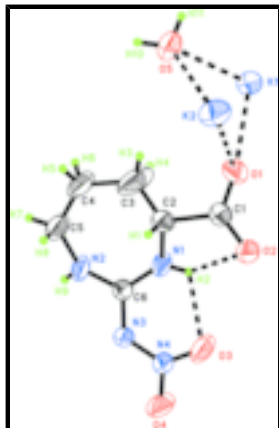


Fig. 1. A perspective view of the asymmetric unit, showing the atomic numbering and displacement ellipsoids drawn at the 50% probability level.

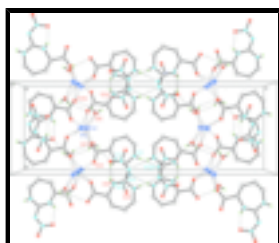
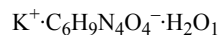


Fig. 2. Packing of the molecules. For clarity, only the donors in the original molecule and their corresponding acceptors are labelled. Symmetry codes are: (i) $x, y - 1, z$; (ii) $-x + 1/2, y - 1/2, -z + 1/2$; (iii) $x, 2 - y, 1 - z$. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

Potassium L-2-nitrimino-1,3-diazepane-4-carboxylate monohydrate

Crystal data



$$M_r = 258.29$$

Orthorhombic, $I222$

Hall symbol: $I\ 2\ 2$

$$a = 7.3883\ (15)\ \text{\AA}$$

$$b = 10.087\ (2)\ \text{\AA}$$

$$c = 29.031\ (6)\ \text{\AA}$$

$$V = 2163.5\ (8)\ \text{\AA}^3$$

$$Z = 8$$

$$F_{000} = 1072$$

$$D_x = 1.586\ \text{Mg m}^{-3}$$

Mo $K\alpha$ radiation

$$\lambda = 0.71073\ \text{\AA}$$

Cell parameters from 24 reflections

$$\theta = 14\text{--}16^\circ$$

$$\mu = 0.51\ \text{mm}^{-1}$$

$$T = 293\ (2)\ \text{K}$$

Prism, yellow

$$0.21 \times 0.14 \times 0.11\ \text{mm}$$

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$$T = 293\ (2)\ \text{K}$$

$\omega/2\theta$ scans

Absorption correction: none

5030 measured reflections

$$R_{\text{int}} = 0.030$$

$$\theta_{\text{max}} = 30.0^\circ$$

$$\theta_{\text{min}} = 2.1^\circ$$

$$h = -10 \rightarrow 10$$

$$k = -13 \rightarrow 13$$

$$l = -38 \rightarrow 38$$

3 standard reflections

3141 independent reflections
 1726 reflections with $I > 2\sigma(I)$

every 400 reflections
 intensity decay: none

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.193$
 $S = 1.04$
 3141 reflections
 154 parameters
 3 restraints
 Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 6.1136P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983), 1350 Friedel pairs
 Flack parameter: 0.48 (20)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.5000	0.5000	0.26313 (7)	0.0481 (5)
K2	0.0000	0.5000	0.26268 (8)	0.0536 (5)
O1	0.2429 (10)	0.6833 (3)	0.28276 (9)	0.0510 (8)
O2	0.2513 (10)	0.8993 (3)	0.29658 (9)	0.0618 (10)
O3	0.2476 (15)	1.1286 (3)	0.37039 (10)	0.0905 (16)
O4	0.2389 (10)	1.2557 (3)	0.42935 (11)	0.0723 (12)
O5	0.2461 (12)	0.3267 (3)	0.30317 (11)	0.0644 (10)
N1	0.2755 (14)	0.8784 (3)	0.38382 (11)	0.0630 (19)
H2	0.3373	0.9320	0.3670	0.076*
N2	0.2659 (10)	0.8275 (3)	0.46137 (11)	0.0583 (14)
H9	0.3224	0.8526	0.4858	0.070*
N3	0.2516 (11)	1.0441 (3)	0.44244 (10)	0.0490 (10)
N4	0.2478 (12)	1.1416 (3)	0.41290 (11)	0.0526 (10)
C1	0.2419 (12)	0.7820 (4)	0.30906 (13)	0.0433 (11)

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C2	0.2101 (7)	0.7544 (4)	0.36059 (14)	0.0397 (12)
H1	0.0794	0.7470	0.3657	0.048*
C3	0.294 (2)	0.6381 (6)	0.37834 (19)	0.118 (5)
H4	0.4240	0.6514	0.3793	0.142*
H3	0.2697	0.5645	0.3578	0.142*
C4	0.2262 (15)	0.6022 (4)	0.42740 (17)	0.069 (2)
H5	0.1150	0.5526	0.4232	0.082*
H6	0.3139	0.5404	0.4399	0.082*
C5	0.1931 (9)	0.6894 (5)	0.46054 (17)	0.0601 (19)
H7	0.2319	0.6481	0.4891	0.072*
H8	0.0624	0.6974	0.4624	0.072*
C6	0.2498 (15)	0.9152 (4)	0.42687 (13)	0.0475 (10)
H10	0.288 (8)	0.279 (5)	0.3251 (13)	0.07 (2)*
H11	0.288 (14)	0.287 (8)	0.2790 (13)	0.16 (5)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0547 (12)	0.0388 (11)	0.0507 (11)	0.0026 (10)	0.000	0.000
K2	0.0566 (12)	0.0404 (12)	0.0637 (13)	-0.0021 (11)	0.000	0.000
O1	0.070 (2)	0.0423 (15)	0.0409 (14)	0.000 (3)	0.008 (3)	-0.0129 (13)
O2	0.115 (3)	0.0374 (15)	0.0326 (13)	0.013 (4)	-0.002 (4)	0.0002 (11)
O3	0.202 (5)	0.0350 (16)	0.0343 (15)	-0.001 (5)	-0.009 (5)	0.0075 (12)
O4	0.136 (4)	0.0279 (13)	0.0534 (18)	0.006 (4)	-0.007 (4)	-0.0024 (13)
O5	0.103 (3)	0.0470 (17)	0.0436 (17)	-0.009 (4)	-0.003 (4)	0.0143 (15)
N1	0.134 (6)	0.0286 (16)	0.0266 (16)	-0.021 (4)	0.012 (3)	-0.0014 (12)
N2	0.115 (4)	0.0309 (16)	0.0291 (15)	-0.017 (3)	0.012 (4)	-0.0006 (13)
N3	0.087 (3)	0.0286 (14)	0.0312 (15)	0.007 (4)	0.006 (4)	0.0001 (12)
N4	0.088 (3)	0.0310 (16)	0.0393 (17)	0.005 (4)	0.014 (4)	0.0017 (13)
C1	0.057 (3)	0.039 (2)	0.0339 (18)	0.007 (4)	-0.010 (3)	-0.0022 (15)
C2	0.049 (3)	0.0352 (19)	0.0344 (19)	0.004 (2)	-0.002 (2)	-0.0046 (16)
C3	0.267 (17)	0.043 (3)	0.043 (3)	0.046 (7)	-0.002 (6)	0.008 (2)
C4	0.125 (6)	0.029 (2)	0.052 (2)	-0.013 (4)	-0.008 (5)	0.0091 (18)
C5	0.098 (6)	0.037 (2)	0.045 (3)	0.001 (3)	0.004 (3)	0.011 (2)
C6	0.079 (3)	0.0335 (17)	0.0298 (17)	-0.002 (5)	0.001 (5)	-0.0016 (14)

Geometric parameters (\AA , $^\circ$)

K1—O1	2.712 (5)	O4—N4	1.247 (4)
K1—O1 ⁱ	2.712 (5)	O5—H10	0.856 (19)
K1—O2 ⁱⁱ	2.736 (6)	O5—H11	0.87 (2)
K1—O2 ⁱⁱⁱ	2.736 (6)	N1—C6	1.318 (5)
K1—O5 ⁱ	2.815 (7)	N1—C2	1.502 (6)
K1—O5	2.815 (7)	N1—H2	0.8600
K1—C1 ⁱⁱ	3.524 (5)	N2—C6	1.342 (5)
K1—C1 ⁱⁱⁱ	3.524 (5)	N2—C5	1.494 (7)
K1—K2	3.6942 (8)	N2—H9	0.8600

K1—K2 ^{iv}	3.6942 (8)	N3—N4	1.305 (4)
K1—H11	2.70 (11)	N3—C6	1.377 (5)
K2—O1	2.642 (5)	C1—C2	1.540 (6)
K2—O1 ^v	2.642 (5)	C1—K1 ^{viii}	3.524 (5)
K2—O2 ^{vi}	2.714 (6)	C2—C3	1.423 (9)
K2—O2 ⁱⁱ	2.714 (6)	C2—H1	0.9800
K2—O5	2.783 (6)	C3—C4	1.552 (9)
K2—O5 ^v	2.783 (6)	C3—H4	0.9700
K2—K1 ^{vii}	3.6942 (8)	C3—H3	0.9700
K2—H11	3.06 (6)	C4—C5	1.326 (7)
O1—C1	1.255 (4)	C4—H5	0.9700
O2—C1	1.239 (5)	C4—H6	0.9700
O2—K2 ^{viii}	2.714 (6)	C5—H7	0.9700
O2—K1 ^{viii}	2.736 (6)	C5—H8	0.9700
O3—N4	1.241 (4)		
O1—K1—O1 ⁱ	155.74 (15)	O2 ⁱⁱ —K2—K1 ^{vii}	132.78 (15)
O1—K1—O2 ⁱⁱ	84.89 (16)	O5—K2—K1 ^{vii}	130.69 (16)
O1 ⁱ —K1—O2 ⁱⁱ	110.81 (14)	O5 ^v —K2—K1 ^{vii}	49.08 (15)
O1—K1—O2 ⁱⁱⁱ	110.81 (14)	O1—K2—K1	47.16 (12)
O1 ⁱ —K1—O2 ⁱⁱⁱ	84.89 (16)	O1 ^v —K2—K1	132.72 (12)
O2 ⁱⁱ —K1—O2 ⁱⁱⁱ	101.4 (2)	O2 ^{vi} —K2—K1	132.78 (15)
O1—K1—O5 ⁱ	87.51 (15)	O2 ⁱⁱ —K2—K1	47.57 (13)
O1 ⁱ —K1—O5 ⁱ	82.52 (14)	O5—K2—K1	49.08 (15)
O2 ⁱⁱ —K1—O5 ⁱ	160.81 (11)	O5 ^v —K2—K1	130.69 (16)
O2 ⁱⁱⁱ —K1—O5 ⁱ	65.09 (14)	K1 ^{vii} —K2—K1	179.60 (13)
O1—K1—O5	82.52 (14)	O1—K2—H11	89 (2)
O1 ⁱ —K1—O5	87.51 (15)	O1 ^v —K2—H11	87 (2)
O2 ⁱⁱ —K1—O5	65.09 (14)	O2 ^{vi} —K2—H11	146.2 (10)
O2 ⁱⁱⁱ —K1—O5	160.81 (11)	O2 ⁱⁱ —K2—H11	50.6 (8)
O5 ⁱ —K1—O5	131.23 (19)	O5—K2—H11	16.1 (6)
O1—K1—C1 ⁱⁱ	101.25 (17)	O5 ^v —K2—H11	146.1 (6)
O1 ⁱ —K1—C1 ⁱⁱ	93.15 (14)	K1 ^{vii} —K2—H11	134 (2)
O2 ⁱⁱ —K1—C1 ⁱⁱ	17.69 (15)	K1—K2—H11	46 (2)
O2 ⁱⁱⁱ —K1—C1 ⁱⁱ	101.48 (14)	C1—O1—K2	133.3 (6)
O5 ⁱ —K1—C1 ⁱⁱ	166.12 (17)	C1—O1—K1	132.3 (5)
O5—K1—C1 ⁱⁱ	61.33 (12)	K2—O1—K1	87.26 (8)
O1—K1—C1 ⁱⁱⁱ	93.15 (14)	C1—O2—K2 ^{viii}	125.5 (5)
O1 ⁱ —K1—C1 ⁱⁱⁱ	101.25 (17)	C1—O2—K1 ^{viii}	120.1 (6)
O2 ⁱⁱ —K1—C1 ⁱⁱⁱ	101.48 (14)	K2 ^{viii} —O2—K1 ^{viii}	85.34 (8)
O2 ⁱⁱⁱ —K1—C1 ⁱⁱⁱ	17.69 (15)	K2—O5—K1	82.59 (8)
O5 ⁱ —K1—C1 ⁱⁱⁱ	61.33 (12)	K2—O5—H10	155 (4)
O5—K1—C1 ⁱⁱⁱ	166.12 (17)	K1—O5—H10	114 (5)

supplementary materials

C1 ⁱⁱ —K1—C1 ⁱⁱⁱ	107.02 (17)	K2—O5—H11	101 (5)
O1—K1—K2	45.59 (12)	K1—O5—H11	74 (7)
O1 ⁱ —K1—K2	134.53 (12)	H10—O5—H11	102 (3)
O2 ⁱⁱ —K1—K2	47.09 (13)	C6—N1—C2	127.9 (6)
O2 ⁱⁱⁱ —K1—K2	132.56 (15)	C6—N1—H2	116.0
O5 ⁱ —K1—K2	131.90 (15)	C2—N1—H2	116.0
O5—K1—K2	48.33 (15)	C6—N2—C5	124.8 (5)
C1 ⁱⁱ —K1—K2	59.38 (14)	C6—N2—H9	117.6
C1 ⁱⁱⁱ —K1—K2	120.34 (15)	C5—N2—H9	117.6
O1—K1—K2 ^{iv}	134.53 (12)	N4—N3—C6	119.7 (3)
O1 ⁱ —K1—K2 ^{iv}	45.59 (12)	O3—N4—O4	118.6 (3)
O2 ⁱⁱ —K1—K2 ^{iv}	132.56 (15)	O3—N4—N3	125.0 (3)
O2 ⁱⁱⁱ —K1—K2 ^{iv}	47.09 (13)	O4—N4—N3	116.4 (3)
O5 ⁱ —K1—K2 ^{iv}	48.33 (15)	O2—C1—O1	125.4 (4)
O5—K1—K2 ^{iv}	131.90 (15)	O2—C1—C2	117.8 (3)
C1 ⁱⁱ —K1—K2 ^{iv}	120.34 (15)	O1—C1—C2	116.6 (4)
C1 ⁱⁱⁱ —K1—K2 ^{iv}	59.38 (14)	O2—C1—K1 ^{viii}	42.2 (4)
K2—K1—K2 ^{iv}	179.60 (13)	O1—C1—K1 ^{viii}	97.8 (3)
O1—K1—H11	95.8 (12)	C2—C1—K1 ^{viii}	127.8 (4)
O1 ⁱ —K1—H11	80.1 (15)	C3—C2—N1	112.6 (5)
O2 ⁱⁱ —K1—H11	54.4 (13)	C3—C2—C1	115.8 (5)
O2 ⁱⁱⁱ —K1—H11	142.9 (4)	N1—C2—C1	103.6 (4)
O5 ⁱ —K1—H11	144.2 (12)	C3—C2—H1	108.2
O5—K1—H11	17.9 (4)	N1—C2—H1	108.2
C1 ⁱⁱ —K1—H11	46.4 (10)	C1—C2—H1	108.2
C1 ⁱⁱⁱ —K1—H11	153.2 (8)	C2—C3—C4	112.6 (8)
K2—K1—H11	54.5 (15)	C2—C3—H4	109.1
K2 ^{iv} —K1—H11	125.5 (15)	C4—C3—H4	109.1
O1—K2—O1 ^v	154.51 (16)	C2—C3—H3	109.1
O1—K2—O2 ^{vi}	109.73 (14)	C4—C3—H3	109.1
O1 ^v —K2—O2 ^{vi}	86.68 (16)	H4—C3—H3	107.8
O1—K2—O2 ⁱⁱ	86.68 (16)	C5—C4—C3	124.8 (4)
O1 ^v —K2—O2 ⁱⁱ	109.73 (14)	C5—C4—H5	106.1
O2 ^{vi} —K2—O2 ⁱⁱ	101.3 (2)	C3—C4—H5	106.1
O1—K2—O5	84.41 (15)	C5—C4—H6	106.1
O1 ^v —K2—O5	84.89 (16)	C3—C4—H6	106.1
O2 ^{vi} —K2—O5	160.93 (12)	H5—C4—H6	106.3
O2 ⁱⁱ —K2—O5	65.81 (15)	C4—C5—N2	124.3 (5)
O1—K2—O5 ^v	84.89 (16)	C4—C5—H7	106.3
O1 ^v —K2—O5 ^v	84.41 (15)	N2—C5—H7	106.3
O2 ^{vi} —K2—O5 ^v	65.81 (15)	C4—C5—H8	106.3

O2 ⁱⁱ —K2—O5 ^v	160.93 (12)	N2—C5—H8	106.3
O5—K2—O5 ^v	130.0 (2)	H7—C5—H8	106.4
O1—K2—K1 ^{vii}	132.72 (12)	N1—C6—N2	120.6 (4)
O1 ^v —K2—K1 ^{vii}	47.16 (12)	N1—C6—N3	125.2 (4)
O2 ^{vi} —K2—K1 ^{vii}	47.57 (13)	N2—C6—N3	112.1 (3)
O1 ^v —K2—O1—C1	-49.9 (4)	O2 ⁱⁱ —K1—O5—K2	-53.73 (14)
O2 ^{vi} —K2—O1—C1	77.6 (4)	O2 ⁱⁱⁱ —K1—O5—K2	-101.4 (5)
O2 ⁱⁱ —K2—O1—C1	178.5 (4)	O5 ⁱ —K1—O5—K2	114.12 (11)
O5—K2—O1—C1	-115.5 (4)	C1 ⁱⁱ —K1—O5—K2	-73.12 (16)
O5 ^v —K2—O1—C1	15.6 (4)	C1 ⁱⁱⁱ —K1—O5—K2	-38.4 (6)
K1 ^{vii} —K2—O1—C1	27.7 (5)	K2 ^{iv} —K1—O5—K2	-179.55 (14)
K1—K2—O1—C1	-151.7 (4)	C6—N3—N4—O3	-2.1 (16)
O1 ^v —K2—O1—K1	101.82 (8)	C6—N3—N4—O4	175.9 (10)
O2 ^{vi} —K2—O1—K1	-130.65 (16)	K2 ^{viii} —O2—C1—O1	-49.8 (12)
O2 ⁱⁱ —K2—O1—K1	-29.78 (10)	K1 ^{viii} —O2—C1—O1	57.6 (12)
O5—K2—O1—K1	36.21 (12)	K2 ^{viii} —O2—C1—C2	135.8 (5)
O5 ^v —K2—O1—K1	167.33 (12)	K1 ^{viii} —O2—C1—C2	-116.8 (5)
K1 ^{vii} —K2—O1—K1	179.47 (16)	K2 ^{viii} —O2—C1—K1 ^{viii}	-107.4 (3)
O1 ⁱ —K1—O1—C1	49.8 (4)	K2—O1—C1—O2	-114.3 (9)
O2 ⁱⁱ —K1—O1—C1	-178.2 (4)	K1—O1—C1—O2	105.4 (9)
O2 ⁱⁱⁱ —K1—O1—C1	-77.9 (4)	K2—O1—C1—C2	60.2 (8)
O5 ⁱ —K1—O1—C1	-15.8 (4)	K1—O1—C1—C2	-80.1 (8)
O5—K1—O1—C1	116.3 (4)	K2—O1—C1—K1 ^{viii}	-79.4 (3)
C1 ⁱⁱ —K1—O1—C1	175.0 (4)	K1—O1—C1—K1 ^{viii}	140.3 (2)
C1 ⁱⁱⁱ —K1—O1—C1	-76.9 (5)	C6—N1—C2—C3	-67.0 (11)
K2—K1—O1—C1	152.2 (4)	C6—N1—C2—C1	167.2 (9)
K2 ^{iv} —K1—O1—C1	-28.3 (5)	O2—C1—C2—C3	-146.7 (9)
O1 ⁱ —K1—O1—K2	-102.45 (8)	O1—C1—C2—C3	38.4 (11)
O2 ⁱⁱ —K1—O1—K2	29.60 (10)	K1 ^{viii} —C1—C2—C3	164.0 (6)
O2 ⁱⁱⁱ —K1—O1—K2	129.84 (15)	O2—C1—C2—N1	-22.9 (10)
O5 ⁱ —K1—O1—K2	-168.04 (12)	O1—C1—C2—N1	162.2 (8)
O5—K1—O1—K2	-35.89 (12)	K1 ^{viii} —C1—C2—N1	-72.2 (6)
C1 ⁱⁱ —K1—O1—K2	22.82 (11)	N1—C2—C3—C4	72.2 (10)
C1 ⁱⁱⁱ —K1—O1—K2	130.87 (14)	C1—C2—C3—C4	-168.9 (7)
K2 ^{iv} —K1—O1—K2	179.46 (17)	C2—C3—C4—C5	-39.8 (16)
O1—K2—O5—K1	-34.97 (11)	C3—C4—C5—N2	-19.3 (15)
O1 ^v —K2—O5—K1	168.20 (12)	C6—N2—C5—C4	52.9 (12)
O2 ^{vi} —K2—O5—K1	104.1 (5)	C2—N1—C6—N2	42.7 (16)
O2 ⁱⁱ —K2—O5—K1	53.89 (13)	C2—N1—C6—N3	-154.9 (9)
O5 ^v —K2—O5—K1	-113.49 (10)	C5—N2—C6—N1	-43.0 (15)
K1 ^{vii} —K2—O5—K1	-179.56 (14)	C5—N2—C6—N3	152.5 (8)

supplementary materials

O1—K1—O5—K2	34.09 (11)	N4—N3—C6—N1	12.3 (17)
O1 ⁱ —K1—O5—K2	-168.08 (12)	N4—N3—C6—N2	176.0 (9)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H11 ⁱⁱ —O1 ⁱⁱ	0.87 (2)	2.09 (5)	2.885 (5)	153 (10)
O5—H10 ^{ix} —O3 ^{ix}	0.856 (19)	2.03 (4)	2.793 (4)	148 (6)
N2—H9 ^x —N3 ^x	0.86	2.39	3.080 (4)	138
N1—H2 ^o —O3	0.86	2.09	2.561 (5)	114

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

Fig. 1

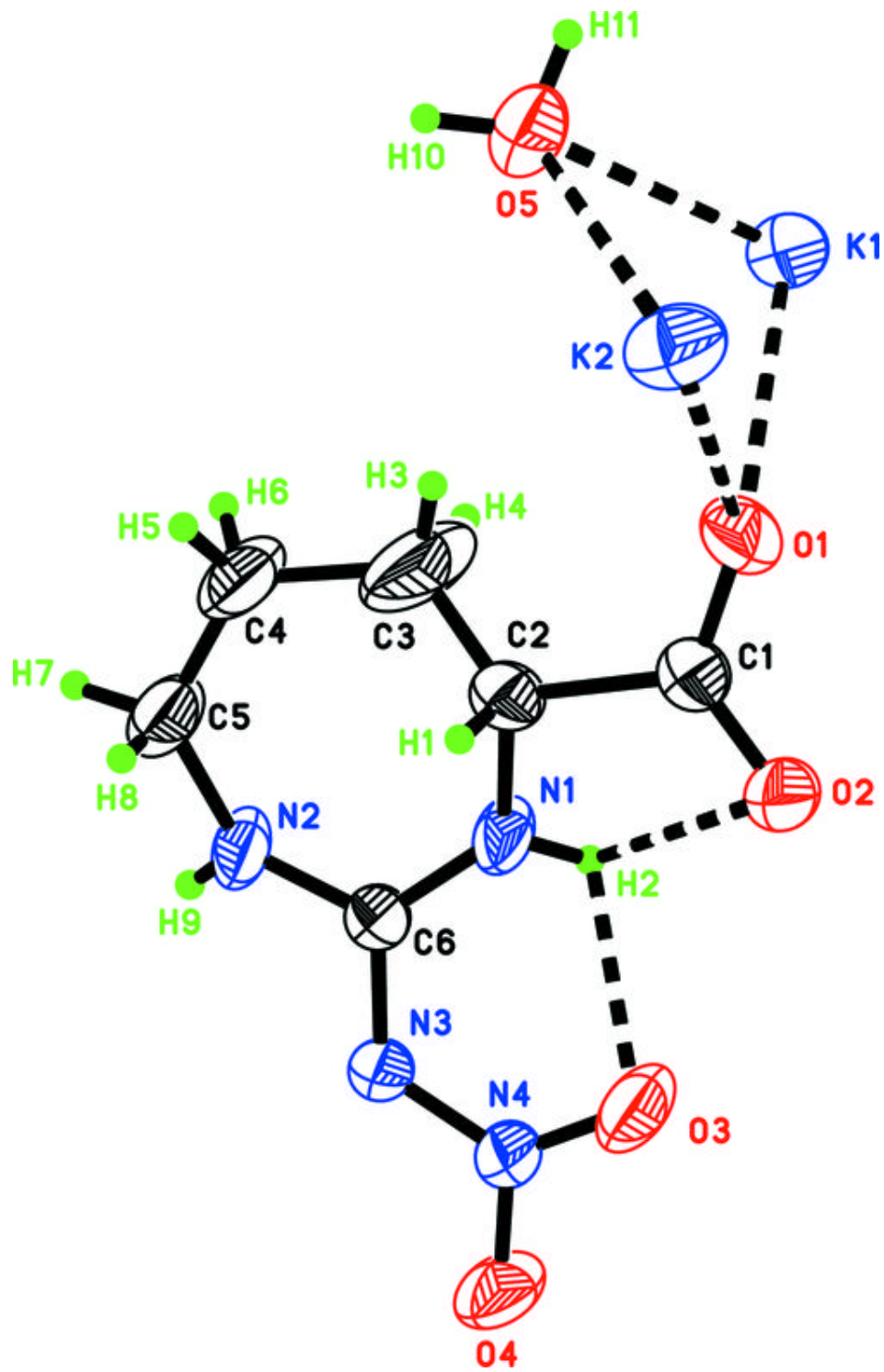


Fig. 2

