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

## Harutyun A. Karapetyan

Molecule Structure Research Center, National Academy of Sciences RA, Azatutyan Avenue 26, 375014 Yerevan, Republic of Armenia
Correspondence e-mail: harkar@nfsat.am

The title compound, $K^+ \cdot C_6H_9N_4O_4^- \cdot H_2O$, 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 N—H$\cdots$O, N—H$\cdots$N and O—H$\cdots$O hydrogen bonding. The data indicate inversion twinning.

## Related literature

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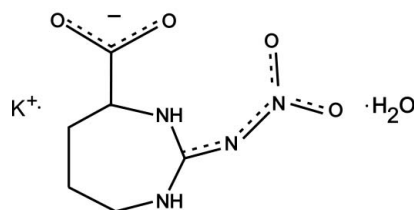


## Experimental

### Crystal data

| | |
|---|---|
| $K^+ \cdot C_6H_9N_4O_4^- \cdot H_2O$ | $V$ = 2163.5 (8) Å$^3$ |
| $M_r$ = 258.29 | $Z$ = 8 |
| Orthorhombic, $I222$ | Mo $K\alpha$ radiation |
| $a$ = 7.3883 (15) Å | $\mu$ = 0.51 mm$^{-1}$ |
| $b$ = 10.087 (2) Å | $T$ = 293 (2) K |
| $c$ = 29.031 (6) Å | $0.21 \times 0.14 \times 0.11$ mm |

### Data collection

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | 1736 reflections with $I > 2\sigma(I)$ |
| Absorption correction: none | $R_{int}$ = 0.030 |
| 5030 measured reflections | 3 standard reflections |
| 3141 independent reflections | every 400 reflections |
| | intensity decay: none |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.065 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.193 | |
| $S$ = 1.04 | |
| 3141 reflections | $\Delta\rho_{max}$ = 0.42 e Å$^{-3}$ |
| 154 parameters | $\Delta\rho_{min}$ = $-0.39$ e Å$^{-3}$ |
| 3 restraints | Absolute structure: Flack (1983), 1350 Friedel pairs |
| | Flack parameter: 0.48 (20) |

**Table 1**
Hydrogen-bond geometry (Å, °).

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

## References

Apreyan, R. A., Karapetyan, H. A. & Petrosyan, A. M. (2008a). *J. Mol. Struct.* **874**, 187–193.
Apreyan, R. A., Karapetyan, H. A. & Petrosyan, A. M. (2008b). *J. Mol. Struct.* **875**, 272–281.
Apreyan, R. A. & Petrosyan, A. M. (2008). In preparation.
Enraf–Nonius (1988). *CAD-4 Manual.* Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Karapetyan, H. A. (2008a). *Acta Cryst.* E**64**, o943.
Karapetyan, H. A. (2008b). *Acta Cryst.* E**64**, o1222.
Karapetyan, H. A., Antipin, M. Yu., Sukiasyan, R. P. & Petrosyan, A. M. (2007). *J. Mol. Struct.* **831**, 90–96.
Kurtz, S. K. & Perry, T. T. (1968). *J. Appl. Phys.* **39**, 3798–3812.
Paul, R., Anderson, G. W. & Callahan, F. M. (1961). *J. Org. Chem.* **26**, 3347–3350.
Petrosyan, A. M., Sukiasyan, R. P., Karapetyan, H. A., Antipin, M. Yu. & Apreyan, R. A. (2005). *J. Cryst. Growth*, **275**, e1927–e1933.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (1997). *HELENA.* University of Utrecht, The Netherlands.

**supplementary materials**

## 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···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···O, N—H···N and O—H···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 $U_{iso}(H) = 1.2U_{eq}$(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···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.
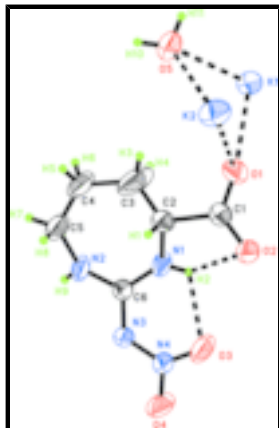
# supplementary materials

**Figures**



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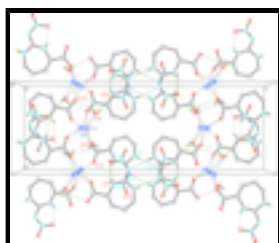


Fig. 2. Packing of the molecules. For clarity, only the donors in the original molecule and their corresponding acceptors are labelled. Symmetry codes are: (i) $x$, $y$ - 1, $z$; (ii)-$x$ + 1/2, $y$ - 1/2, -$z$ + 1/2; (iii) $x$, 2 - $y$, 1 - $z$. Dashed lines indicate hydrogen bonds. H atoms not involved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

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

*Crystal data*
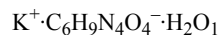
| | |
|---|---|
| $K^+ \cdot C_6H_9N_4O_4{}^- \cdot H_2O_1$ | $F_{000} = 1072$ |
| $M_r = 258.29$ | $D_x = 1.586$ Mg m$^{-3}$ |
| Orthorhombic, $I222$ | Mo $K\alpha$ radiation <br> $\lambda = 0.71073$ Å |
| Hall symbol: I 2 2 | Cell parameters from 24 reflections |
| $a = 7.3883$ (15) Å | $\theta = 14–16º$ |
| $b = 10.087$ (2) Å | $\mu = 0.51$ mm$^{-1}$ |
| $c = 29.031$ (6) Å | $T = 293$ (2) K |
| $V = 2163.5$ (8) Å$^3$ | Prism, yellow |
| $Z = 8$ | $0.21 \times 0.14 \times 0.11$ mm |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | $R_{int} = 0.030$ |
| Radiation source: fine-focus sealed tube | $\theta_{max} = 30.0º$ |
| Monochromator: graphite | $\theta_{min} = 2.1º$ |
| $T = 293(2)$ K | $h = -10 \rightarrow 10$ |
| $\omega/2\theta$ scans | $k = -13 \rightarrow 13$ |
| Absorption correction: none | $l = -38 \rightarrow 38$ |
| 5030 measured reflections | 3 standard reflections |

| 3141 independent reflections | every 400 reflections |
| 1726 reflections with $I > 2\sigma(I)$ | intensity decay: none |

*Refinement*

| | |
| --- | --- |
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.065$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.193$ | $w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 6.1136P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.04$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 3141 reflections | $\Delta\rho_{max} = 0.43$ e Å$^{-3}$ |
| 154 parameters | $\Delta\rho_{min} = -0.39$ e Å$^{-3}$ |
| 3 restraints | Absolute structure: Flack (1983), 1350 Friedel pairs |
| Primary atom site location: structure-invariant direct methods | 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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
| --- | --- | --- | --- | --- |
| 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) |

| | | | | |
|---|---|---|---|---|
| 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 (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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 (Å, °)*

| | | | |
|---|---|---|---|
| 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) |

| | | | |
|---|---|---|---|
| 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) |

| | | | |
|---|---|---|---|
| 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 (Å, °)*

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