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# Poly[aquadi-$\mu$-hippurato-potassium(I)]

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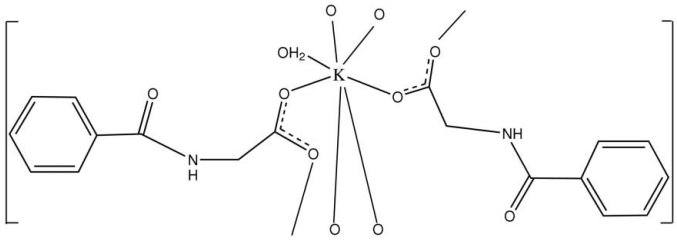
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.007 Å; disorder in main residue; $R$ factor = 0.074; $wR$ factor = 0.248; data-to-parameter ratio = 10.0.

The title compound, $[K(C_9H_8N_2O_3)_2(H_2O)]$, has one potassium cation, two hippurate anions and one coordinated water molecule in the asymmetric unit. The coordination number of the $K^+$ cation is seven, leading to a pentagonal–bipyramidal structure in which the polyhedron is constituted by a central K atom coordinated by six carboxylate O atoms and one water O atom. The benzene rings exhibit orientational disorder (0.55:0.45), leading to two different orientations in both hippurates. Even though the metal coordination dominates the crystal packing, it is further stabilized by hydrogen-bonding interactions. The hydrogen-bonding interactions form an intramolecular $S(7)$ motif and an intermolecularly connected $C_2^2(7)$ chain motif.

## Related literature

For related literature on hydrogen-bond motifs, see Etter (1990), and on values of bond lengths, see Allen *et al.* (1987). For related structures, see Natarajan *et al.* (2007), and for information about the importance of hippuric acid, see Ramachandran & Natarajan (2005).




## Experimental

### Crystal data

$[K(C_9H_8N_2O_3)_2(H_2O)]$
$M_r$ = 413.44
Triclinic, $P\overline{1}$
$a$ = 4.867 (3) Å
$b$ = 9.921 (7) Å
$c$ = 20.076 (9) Å
$\alpha$ = 92.59 (4)°
$\beta$ = 91.45 (3)°
$\gamma$ = 101.33 (5)°
$V$ = 948.9 (10) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.32 mm$^{-1}$
$T$ = 293 (2) K
0.21 × 0.18 × 0.16 mm

### Data collection

Nonius MACH-3 diffractometer
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.926, $T_{max}$ = 0.955
4593 measured reflections
3327 independent reflections
2044 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.040
3 standard reflections
frequency: 60 min
intensity decay: none

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.074
$wR(F^2)$ = 0.248
$S$ = 1.08
3327 reflections
333 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.76 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.64 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N11—H11···O23$^{i}$ | 0.86 | 2.09 | 2.905 (7) | 158 |
| N21—H21···O1$W^{ii}$ | 0.86 | 2.15 | 2.929 (6) | 151 |
| O1$W$—H1$W$···O22$^{iii}$ | 0.84 (6) | 1.97 (7) | 2.758 (7) | 156 (6) |
| O1$W$—H2$W$···O13$^{iv}$ | 0.79 (7) | 1.92 (7) | 2.680 (6) | 160 (7) |

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL/PC* (Bruker, 2000); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2185).

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# supplementary materials

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# Poly[aquadi-μ-hippurato-potassium(I)]

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## Comment

Hippuric acid (HA) is an organic acid found in the urine of horses and other animals. High concentrations of HA can also indicate a toluene intoxication. When many aromatic compounds such as benzoic acid and toluene are taken internally, they are converted to HA by reaction with the amino acid glycine. Exposure to toluene may result in central nervous system depression and decreased memory. The crystal growth and morphological studies on HA, which is also one of the minor constituents of urinary stones were carried out in the author's laboratory, recently (Ramachandran & Natarajan, 2005). Presently the structure eluzidation of a series of metal hippurates are undertaken and the title compound (I) is one such case. From the Cambridge Structural Database (Version 5.28; Allen, 2002), it is observed that, among the 24 related structures of hippuric acid, 17 complexes are metal coordinated complexes which clearly indicates the interest of coordination complexes in HA. Recently, we have reported the structure of HA with Ba (Natarajan *et al.*, 2007).

In the present structure (I), potassium has a sevenfold coordination and the polyhedra is a pentagonal bipyramid (Fig. 1). The corners of the pentagon are occupied by four carboxylate O atoms from different hippurates and one water O atom, *viz*., O12, $O11^{i}$, $O21^{ii}$, $O22^{iii}$ and O1w. Further two carboxylate O atoms (O22 & $O11^{i}$) are situated on top and bottom of the sheet of the pentagon forming two five-faced pyramids taking this pentagon as base [Symmetry codes are as given in Table 1]. The K—O coordination distances vary from 2.761 (5) to 3.049 (4) Å. The asymmetric unit of the title compound contains one potassium, two hippurate anions and one coordinated water molecule. The benzene rings of the hippurates are in 'orientational disorder' adopting two different orientations. The angles between the two different orientations are 45.8 (6)° and 46.0 (7)° for residue A (C11–17/N11/O11—O13) and B (C21–27/N21/O21—O23), respectively.

As described in Natarajan *et al.*, 2007, the configuration of the hippurates can be described from the angles between three planes, *viz*., benzene ring, peptide and carboxylate planes. The angles between the benzene and peptide planes are observed to be 29.4 (6) [23.0 (5)] and 38.7 (5) [9.2 (9)]° for residues A and B respectively (values within the square brackets are attributed to minor components of the disordered benzene rings). The angles between the peptide and carboxylate planes are observed to be 78.7 (4) and 86.3 (3)° for residues A and B respectively. Fig. 2 shows the crystal packing of (I), the coordination polehedra is extended along *c*=0 plane and phenyl rings are sandwiched between these polyhedra near *c*=1/2 plane. Eventhough the interesting feature of this structure is the coordination geometry, the crystal packing is further stabilized through the hydrogen bonding interaction (Table 2). Four hydrogen bonding interactions are observed in (I), one as intramolecular and three as intermolecular interactions. The intramolecular H-bond leads to S(7) motif (Etter, 1990). Residue B and water molecule are linked through N21—H21···O1W and O1W—H1W···O22 ($x-1, y, z$) hydrogen bonds leading to $C_2^2(7)$ chain motif running along the *a* axis of the unit cell. This forms a layered structure in two directions and bordered by the aromatic rings which block further three dimensional extension.

### Experimental

The title compound was crystallized by the slow evaporation technique, using an aqueous solution containing potassium hydroxide and hippuric acid in a 1:1 stoichiometric ratio.

### Refinement

All the H atoms except the water H atoms were positioned in geometrically calculated positions, with C—H = 0.93(aromatic) and 0.97 (–$CH_2$) and N—H = 0.86 Å with $U_{iso}$(H) = 1.2 $U_{eq}$(parent atom). Water H atoms were located from the differnce fourier map and refined isotropically. Four atoms of the benzene rings in both hippurates are in positional disorder with the major and minor occupancies as 0.55 and 0.45, respectively. This lead to 'orientational disorder' with two different orientations for both the benzene rings.

### Figures

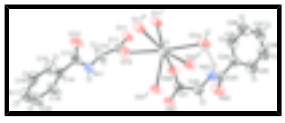

Fig. 1. The molecular structure of title compound with atom numbering scheme. Ellipsoids are drawn at the 50% probability level. Intramolecular H-bond is shown as dashed line. Only the major components of the disordered atoms are shown for claritly. The complete coordination sphere of the K atom is shown.

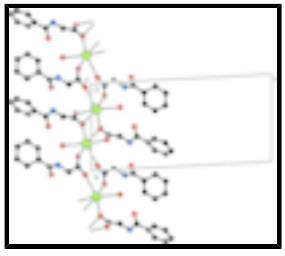

Fig. 2. Partial packing view down the *a* axis. The minor components of the disordered atoms and the H atoms have been omitted for clariry.

### Poly[aquadi-μ-hippurato-potassium(I)]

*Crystal data*

| | |
|---|---|
| $[K(C_9H_8N_2O_3)_2(H_2O)]$ | $Z = 2$ |
| $M_r = 413.44$ | $F_{000} = 430$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.447$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| $a = 4.867$ (3) Å | Cell parameters from 25 reflections |
| $b = 9.921$ (7) Å | $\theta = 9.8$–$13.9$º |
| $c = 20.076$ (9) Å | $\mu = 0.32$ mm$^{-1}$ |
| $\alpha = 92.59$ (4)º | $T = 293$ (2) K |
| $\beta = 91.45$ (3)º | Block, colourless |
| $\gamma = 101.33$ (5)º | 0.21 × 0.18 × 0.16 mm |
| $V = 948.9$ (10) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Nonius MACH-3 diffractometer | $R_{int}$ = 0.040 |
| Radiation source: fine-focus sealed tube | $\theta_{max}$ = 25.0º |
| Monochromator: graphite | $\theta_{min}$ = 2.0º |
| $T$ = 293(2) K | $h$ = −1→5 |
| ω–2θ scans | $k$ = −11→11 |
| Absorption correction: ψ scan (North *et al.*, 1968) | $l$ = −23→23 |
| $T_{min}$ = 0.926, $T_{max}$ = 0.955 | 3 standard reflections |
| 4593 measured reflections | every 60 min |
| 3327 independent reflections | intensity decay: none |
| 2044 reflections with $I > 2\sigma(I)$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.074 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.248 | $w = 1/[\sigma^2(F_o^2) + (0.1591P)^2 + 0.3972P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 1.08 | $(\Delta/\sigma)_{max}$ = 0.001 |
| 3327 reflections | $\Delta\rho_{max}$ = 0.76 e Å$^{-3}$ |
| 333 parameters | $\Delta\rho_{min}$ = −0.64 e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > 2\text{sigma}(F^2)$ 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* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| O11 | 0.3738 (7) | 0.5273 (4) | 0.04916 (17) | 0.0452 (9) | |
| K | −0.0752 (2) | 0.30691 (11) | 0.02817 (6) | 0.0440 (4) | |

| | | | | | |
|---|---|---|---|---|---|
| O12 | 0.7805 (8) | 0.6516 (4) | 0.08733 (19) | 0.0550 (10) | |
| C11 | 0.5384 (10) | 0.6037 (5) | 0.0949 (2) | 0.0374 (11) | |
| C12 | 0.3837 (12) | 0.6258 (7) | 0.1571 (3) | 0.0573 (16) | |
| H11A | 0.2376 | 0.6755 | 0.1458 | 0.069* | |
| H11B | 0.2925 | 0.5365 | 0.1715 | 0.069* | |
| C13 | 0.6991 (12) | 0.6366 (5) | 0.2522 (3) | 0.0443 (12) | |
| C14 | 0.8172 (11) | 0.7091 (5) | 0.3171 (2) | 0.0408 (12) | |
| C17 | 1.0128 (16) | 0.8194 (8) | 0.4422 (3) | 0.0713 (19) | |
| H17 | 1.0911 | 0.8632 | 0.4821 | 0.086* | |
| C15 | 1.039 (3) | 0.6699 (14) | 0.3482 (7) | 0.058 (3) | 0.55 |
| H15 | 1.1311 | 0.6080 | 0.3264 | 0.069* | 0.55 |
| C16 | 1.127 (4) | 0.7209 (18) | 0.4112 (8) | 0.071 (4) | 0.55 |
| H16 | 1.2677 | 0.6872 | 0.4332 | 0.086* | 0.55 |
| C18 | 0.783 (3) | 0.8527 (17) | 0.4138 (7) | 0.082 (4) | 0.55 |
| H18 | 0.6846 | 0.9093 | 0.4375 | 0.098* | 0.55 |
| C19 | 0.691 (3) | 0.8039 (13) | 0.3502 (6) | 0.059 (3) | 0.55 |
| H19 | 0.5443 | 0.8352 | 0.3295 | 0.071* | 0.55 |
| C15' | 0.888 (3) | 0.6268 (13) | 0.3685 (7) | 0.046 (3) | 0.45 |
| H15' | 0.8617 | 0.5318 | 0.3611 | 0.055* | 0.45 |
| C16' | 0.998 (4) | 0.687 (2) | 0.4299 (9) | 0.060 (5) | 0.45 |
| H16' | 1.0595 | 0.6345 | 0.4620 | 0.072* | 0.45 |
| C18' | 0.965 (3) | 0.9073 (14) | 0.3899 (6) | 0.047 (3) | 0.45 |
| H18' | 1.0088 | 1.0026 | 0.3967 | 0.057* | 0.45 |
| C19' | 0.853 (3) | 0.8465 (12) | 0.3287 (6) | 0.037 (3) | 0.45 |
| H19' | 0.8016 | 0.9009 | 0.2958 | 0.045* | 0.45 |
| N11 | 0.5499 (10) | 0.6994 (5) | 0.2126 (2) | 0.0489 (11) | |
| H11 | 0.5518 | 0.7856 | 0.2200 | 0.059* | |
| O13 | 0.7350 (11) | 0.5198 (4) | 0.2387 (2) | 0.0720 (13) | |
| O21 | −0.3007 (8) | 0.0504 (4) | −0.03381 (19) | 0.0494 (10) | |
| C21 | −0.2419 (11) | −0.0434 (5) | −0.0744 (2) | 0.0387 (11) | |
| O22 | −0.3492 (8) | −0.1653 (4) | −0.07225 (18) | 0.0471 (9) | |
| C22 | −0.0232 (11) | 0.0059 (5) | −0.1245 (3) | 0.0459 (13) | |
| H22A | −0.0269 | 0.1008 | −0.1336 | 0.055* | |
| H22B | 0.1609 | 0.0031 | −0.1056 | 0.055* | |
| C23 | −0.2591 (11) | −0.0581 (6) | −0.2308 (3) | 0.0443 (12) | |
| C24 | −0.3003 (11) | −0.1504 (6) | −0.2926 (3) | 0.0464 (13) | |
| C27 | −0.3959 (17) | −0.3087 (9) | −0.4102 (4) | 0.079 (2) | |
| H27 | −0.4215 | −0.3643 | −0.4493 | 0.095* | |
| C25 | −0.357 (3) | −0.0844 (16) | −0.3550 (6) | 0.075 (4) | 0.55 |
| H25 | −0.3585 | 0.0091 | −0.3553 | 0.090* | 0.55 |
| C26 | −0.407 (4) | −0.1681 (19) | −0.4129 (7) | 0.086 (4) | 0.55 |
| H26 | −0.4479 | −0.1319 | −0.4531 | 0.103* | 0.55 |
| C28 | −0.350 (3) | −0.3623 (17) | −0.3534 (8) | 0.078 (4) | 0.55 |
| H28 | −0.3536 | −0.4563 | −0.3523 | 0.093* | 0.55 |
| C29 | −0.296 (3) | −0.2807 (13) | −0.2954 (6) | 0.060 (3) | 0.55 |
| H29 | −0.2556 | −0.3211 | −0.2564 | 0.072* | 0.55 |
| C25' | −0.544 (3) | −0.1608 (13) | −0.3305 (6) | 0.047 (3) | 0.45 |
| H25' | −0.6790 | −0.1126 | −0.3161 | 0.056* | 0.45 |
| C26' | −0.593 (3) | −0.2394 (16) | −0.3883 (7) | 0.059 (4) | 0.45 |

| | | | | | |
|---|---|---|---|---|---|
| H26' | −0.7599 | −0.2457 | −0.4127 | 0.070* | 0.45 |
| C28' | −0.160 (4) | −0.3163 (16) | −0.3699 (7) | 0.061 (4) | 0.45 |
| H28' | −0.0377 | −0.3735 | −0.3824 | 0.073* | 0.45 |
| C29' | −0.115 (3) | −0.2356 (13) | −0.3106 (6) | 0.046 (3) | 0.45 |
| H29' | 0.0401 | −0.2383 | −0.2829 | 0.055* | 0.45 |
| N21 | −0.0693 (9) | −0.0768 (5) | −0.1859 (2) | 0.0454 (11) | |
| H21 | 0.0280 | −0.1391 | −0.1935 | 0.055* | |
| O23 | −0.3999 (10) | 0.0312 (5) | −0.2215 (2) | 0.0738 (14) | |
| O1W | −0.2285 (11) | 0.2994 (5) | 0.1596 (2) | 0.0539 (11) | |
| H1W | −0.386 (14) | 0.260 (6) | 0.143 (3) | 0.050 (18)* | |
| H2W | −0.203 (15) | 0.372 (7) | 0.180 (3) | 0.06 (2)* | |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O11 | 0.039 (2) | 0.050 (2) | 0.045 (2) | 0.0106 (16) | −0.0056 (16) | −0.0148 (16) |
| K | 0.0432 (7) | 0.0403 (6) | 0.0494 (7) | 0.0102 (5) | −0.0011 (5) | 0.0050 (5) |
| O12 | 0.037 (2) | 0.079 (3) | 0.045 (2) | 0.0051 (19) | −0.0012 (17) | −0.0068 (19) |
| C11 | 0.034 (3) | 0.038 (3) | 0.041 (3) | 0.011 (2) | −0.001 (2) | 0.002 (2) |
| C12 | 0.044 (3) | 0.082 (4) | 0.044 (3) | 0.017 (3) | −0.003 (3) | −0.021 (3) |
| C13 | 0.048 (3) | 0.043 (3) | 0.043 (3) | 0.013 (2) | 0.006 (2) | −0.007 (2) |
| C14 | 0.042 (3) | 0.042 (3) | 0.040 (3) | 0.012 (2) | 0.003 (2) | 0.001 (2) |
| C17 | 0.076 (5) | 0.091 (5) | 0.047 (4) | 0.021 (4) | −0.014 (3) | −0.016 (3) |
| C15 | 0.041 (7) | 0.076 (9) | 0.059 (8) | 0.023 (6) | −0.003 (6) | −0.003 (6) |
| C16 | 0.080 (12) | 0.087 (12) | 0.055 (10) | 0.034 (10) | −0.012 (8) | 0.025 (8) |
| C18 | 0.081 (10) | 0.102 (11) | 0.066 (9) | 0.040 (9) | −0.023 (8) | −0.038 (8) |
| C19 | 0.070 (9) | 0.065 (7) | 0.048 (7) | 0.029 (7) | −0.012 (6) | −0.014 (6) |
| C15' | 0.052 (9) | 0.039 (7) | 0.054 (8) | 0.023 (6) | 0.014 (7) | 0.012 (6) |
| C16' | 0.068 (12) | 0.072 (12) | 0.037 (9) | 0.005 (9) | −0.011 (8) | 0.019 (8) |
| C18' | 0.055 (8) | 0.045 (7) | 0.043 (7) | 0.011 (6) | 0.002 (6) | −0.004 (5) |
| C19' | 0.027 (6) | 0.047 (7) | 0.036 (6) | 0.001 (5) | 0.010 (5) | 0.009 (5) |
| N11 | 0.051 (3) | 0.058 (3) | 0.039 (2) | 0.018 (2) | −0.006 (2) | −0.013 (2) |
| O13 | 0.101 (4) | 0.050 (2) | 0.070 (3) | 0.032 (2) | −0.006 (3) | −0.020 (2) |
| O21 | 0.047 (2) | 0.0400 (19) | 0.060 (2) | 0.0088 (16) | 0.0071 (18) | −0.0132 (17) |
| C21 | 0.038 (3) | 0.034 (3) | 0.044 (3) | 0.013 (2) | −0.009 (2) | −0.006 (2) |
| O22 | 0.046 (2) | 0.040 (2) | 0.057 (2) | 0.0112 (16) | 0.0036 (17) | −0.0016 (16) |
| C22 | 0.042 (3) | 0.044 (3) | 0.052 (3) | 0.011 (2) | −0.003 (2) | −0.003 (2) |
| C23 | 0.031 (3) | 0.054 (3) | 0.050 (3) | 0.014 (2) | 0.003 (2) | 0.003 (2) |
| C24 | 0.038 (3) | 0.059 (3) | 0.046 (3) | 0.019 (2) | 0.001 (2) | 0.000 (2) |
| C27 | 0.083 (6) | 0.100 (6) | 0.048 (4) | 0.007 (4) | 0.002 (4) | −0.017 (4) |
| C25 | 0.088 (10) | 0.096 (10) | 0.057 (7) | 0.052 (9) | 0.004 (7) | 0.019 (7) |
| C26 | 0.102 (12) | 0.112 (12) | 0.051 (8) | 0.039 (10) | −0.005 (8) | 0.004 (8) |
| C28 | 0.060 (9) | 0.085 (10) | 0.092 (11) | 0.027 (8) | 0.010 (8) | −0.018 (8) |
| C29 | 0.053 (8) | 0.066 (8) | 0.059 (7) | 0.009 (6) | −0.001 (6) | −0.006 (6) |
| C25' | 0.038 (7) | 0.056 (7) | 0.048 (7) | 0.008 (6) | 0.000 (6) | 0.012 (6) |
| C26' | 0.049 (8) | 0.081 (10) | 0.042 (7) | 0.006 (8) | −0.009 (6) | 0.001 (7) |
| C28' | 0.073 (11) | 0.065 (9) | 0.051 (8) | 0.028 (8) | 0.012 (8) | −0.006 (6) |
| C29' | 0.046 (8) | 0.046 (7) | 0.052 (7) | 0.023 (6) | 0.008 (6) | 0.001 (5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N21 | 0.047 (3) | 0.053 (3) | 0.043 (2) | 0.027 (2) | −0.001 (2) | −0.0044 (19) |
| O23 | 0.071 (3) | 0.084 (3) | 0.081 (3) | 0.057 (3) | −0.017 (2) | −0.016 (2) |
| O1W | 0.057 (3) | 0.049 (2) | 0.059 (3) | 0.023 (2) | −0.005 (2) | −0.014 (2) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O11—C11 | 1.312 (6) | C18'—C19' | 1.393 (17) |
| O11—K | 2.780 (4) | C18'—H18' | 0.9300 |
| O11—K$^{i}$ | 2.878 (4) | C19'—H19' | 0.9300 |
| K—O1W | 2.761 (5) | N11—H11 | 0.8600 |
| K—O12$^{ii}$ | 2.762 (4) | O21—C21 | 1.288 (6) |
| K—O21 | 2.789 (4) | C21—O22 | 1.223 (6) |
| K—O22$^{iii}$ | 2.861 (4) | C21—C22 | 1.509 (8) |
| K—O22$^{iv}$ | 3.049 (4) | C21—K$^{iii}$ | 3.437 (5) |
| K—C21$^{iii}$ | 3.437 (5) | O22—K$^{iii}$ | 2.861 (4) |
| K—K$^{i}$ | 3.978 (3) | C22—N21 | 1.438 (7) |
| K—K$^{v}$ | 4.867 (3) | C22—H22A | 0.9700 |
| K—K$^{vi}$ | 4.867 (3) | C22—H22B | 0.9700 |
| K—H1W | 2.80 (6) | C23—O23 | 1.233 (6) |
| O12—C11 | 1.197 (6) | C23—N21 | 1.319 (7) |
| C11—C12 | 1.504 (8) | C23—C24 | 1.494 (8) |
| C12—N11 | 1.442 (7) | C24—C29 | 1.295 (14) |
| C12—H11A | 0.9700 | C24—C25' | 1.377 (13) |
| C12—H11B | 0.9700 | C24—C29' | 1.396 (13) |
| C13—O13 | 1.225 (6) | C24—C25 | 1.485 (13) |
| C13—N11 | 1.319 (7) | C27—C28 | 1.313 (18) |
| C13—C14 | 1.503 (7) | C27—C26' | 1.354 (17) |
| C14—C19' | 1.350 (13) | C27—C28' | 1.406 (19) |
| C14—C15 | 1.362 (13) | C27—C26 | 1.410 (19) |
| C14—C19 | 1.376 (12) | C27—H27 | 0.9300 |
| C14—C15' | 1.421 (13) | C25—C26 | 1.38 (2) |
| C17—C16' | 1.31 (2) | C25—H25 | 0.9300 |
| C17—C18 | 1.347 (15) | C26—H26 | 0.9300 |
| C17—C16 | 1.351 (19) | C28—C29 | 1.377 (18) |
| C17—C18' | 1.437 (15) | C28—H28 | 0.9300 |
| C17—H17 | 0.9300 | C29—H29 | 0.9300 |
| C15—C16 | 1.37 (2) | C25'—C26' | 1.358 (18) |
| C15—H15 | 0.9300 | C25'—H25' | 0.9300 |
| C16—H16 | 0.9300 | C26'—H26' | 0.9300 |
| C18—C19 | 1.376 (16) | C28'—C29' | 1.392 (19) |
| C18—H18 | 0.9300 | C28'—H28' | 0.9300 |
| C19—H19 | 0.9300 | C29'—H29' | 0.9300 |
| C15'—C16' | 1.39 (2) | N21—H21 | 0.8600 |
| C15'—H15' | 0.9300 | O1W—H1W | 0.84 (6) |
| C16'—H16' | 0.9300 | O1W—H2W | 0.79 (7) |
| C11—O11—K | 144.3 (3) | C18—C17—H17 | 120.8 |
| C11—O11—K$^{i}$ | 110.7 (3) | C16—C17—H17 | 120.8 |

| | | | |
|---|---|---|---|
| K—O11—K$^{i}$ | 89.34 (12) | C18'—C17—H17 | 116.3 |
| O1W—K—O12$^{ii}$ | 164.17 (14) | C14—C15—C16 | 120.6 (12) |
| O1W—K—O11 | 95.43 (14) | C14—C15—H15 | 119.7 |
| O12$^{ii}$—K—O11 | 70.21 (12) | C16—C15—H15 | 119.7 |
| O1W—K—O21 | 107.51 (14) | C17—C16—C15 | 121.2 (13) |
| O12$^{ii}$—K—O21 | 83.98 (13) | C17—C16—H16 | 119.4 |
| O11—K—O21 | 149.38 (12) | C15—C16—H16 | 119.4 |
| O1W—K—O22$^{iii}$ | 84.39 (13) | C17—C18—C19 | 120.9 (12) |
| O12$^{ii}$—K—O22$^{iii}$ | 86.46 (13) | C17—C18—H18 | 119.5 |
| O11—K—O22$^{iii}$ | 79.86 (12) | C19—C18—H18 | 119.5 |
| O21—K—O22$^{iii}$ | 82.44 (12) | C14—C19—C18 | 120.1 (11) |
| O1W—K—O11$^{i}$ | 112.56 (12) | C14—C19—H19 | 119.9 |
| O12$^{ii}$—K—O11$^{i}$ | 75.28 (12) | C18—C19—H19 | 119.9 |
| O11—K—O11$^{i}$ | 90.66 (12) | C16'—C15'—C14 | 120.4 (12) |
| O21—K—O11$^{i}$ | 98.65 (12) | C16'—C15'—H15' | 119.8 |
| O22$^{iii}$—K—O11$^{i}$ | 161.45 (11) | C14—C15'—H15' | 119.8 |
| O1W—K—O22$^{iv}$ | 56.41 (14) | C17—C16'—C15' | 119.6 (14) |
| O12$^{ii}$—K—O22$^{iv}$ | 139.33 (11) | C17—C16'—H16' | 120.2 |
| O11—K—O22$^{iv}$ | 146.83 (11) | C15'—C16'—H16' | 120.2 |
| O21—K—O22$^{iv}$ | 63.43 (11) | C19'—C18'—C17 | 118.5 (11) |
| O22$^{iii}$—K—O22$^{iv}$ | 110.86 (13) | C19'—C18'—H18' | 120.8 |
| O11$^{i}$—K—O22$^{iv}$ | 85.76 (12) | C17—C18'—H18' | 120.8 |
| O1W—K—C21$^{iii}$ | 81.76 (13) | C14—C19'—C18' | 120.2 (10) |
| O12$^{ii}$—K—C21$^{iii}$ | 93.85 (14) | C14—C19'—H19' | 119.9 |
| O11—K—C21$^{iii}$ | 99.65 (13) | C18'—C19'—H19' | 119.9 |
| O21—K—C21$^{iii}$ | 65.03 (12) | C13—N11—C12 | 121.1 (5) |
| O22$^{iii}$—K—C21$^{iii}$ | 19.81 (11) | C13—N11—H11 | 119.5 |
| O11$^{i}$—K—C21$^{iii}$ | 161.63 (11) | C12—N11—H11 | 119.5 |
| O22$^{iv}$—K—C21$^{iii}$ | 93.55 (13) | C21—O21—K | 142.5 (3) |
| O1W—K—K$^{i}$ | 110.10 (11) | O22—C21—O21 | 123.1 (5) |
| O12$^{ii}$—K—K$^{i}$ | 65.14 (10) | O22—C21—C22 | 121.3 (4) |
| O11—K—K$^{i}$ | 46.34 (9) | O21—C21—C22 | 115.6 (4) |
| O21—K—K$^{i}$ | 135.24 (10) | O22—C21—K$^{iii}$ | 52.4 (3) |
| O22$^{iii}$—K—K$^{i}$ | 124.25 (10) | O21—C21—K$^{iii}$ | 124.6 (3) |
| O11$^{i}$—K—K$^{i}$ | 44.32 (8) | C22—C21—K$^{iii}$ | 93.3 (3) |
| O22$^{iv}$—K—K$^{i}$ | 122.10 (9) | C21—O22—K$^{iii}$ | 107.8 (3) |
| C21$^{iii}$—K—K$^{i}$ | 143.49 (10) | C21—O22—K$^{iv}$ | 131.2 (3) |
| O1W—K—K$^{v}$ | 106.80 (11) | K$^{iii}$—O22—K$^{iv}$ | 110.86 (13) |
| O12$^{ii}$—K—K$^{v}$ | 59.25 (9) | N21—C22—C21 | 111.9 (4) |
| O11—K—K$^{v}$ | 51.11 (9) | N21—C22—H22A | 109.2 |
| O21—K—K$^{v}$ | 101.71 (9) | C21—C22—H22A | 109.2 |

| | | | |
|---|---|---|---|
| O22$^{iii}$—K—K$^{v}$ | 35.83 (8) | N21—C22—H22B | 109.2 |
| O11$^{i}$—K—K$^{v}$ | 127.12 (8) | C21—C22—H22B | 109.2 |
| O22$^{iv}$—K—K$^{v}$ | 146.69 (8) | H22A—C22—H22B | 107.9 |
| C21$^{iii}$—K—K$^{v}$ | 53.72 (10) | O23—C23—N21 | 121.0 (5) |
| K$^{i}$—K—K$^{v}$ | 89.88 (6) | O23—C23—C24 | 121.4 (5) |
| O1W—K—K$^{vi}$ | 73.20 (11) | N21—C23—C24 | 117.6 (5) |
| O12$^{ii}$—K—K$^{vi}$ | 120.75 (9) | C29—C24—C25' | 96.2 (9) |
| O11—K—K$^{vi}$ | 128.89 (9) | C29—C24—C29' | 42.2 (7) |
| O21—K—K$^{vi}$ | 78.29 (9) | C25'—C24—C29' | 118.4 (9) |
| O22$^{iii}$—K—K$^{vi}$ | 144.17 (8) | C29—C24—C25 | 118.7 (9) |
| O11$^{i}$—K—K$^{vi}$ | 52.88 (8) | C25'—C24—C25 | 49.3 (8) |
| O22$^{iv}$—K—K$^{vi}$ | 33.31 (8) | C29'—C24—C25 | 104.5 (8) |
| C21$^{iii}$—K—K$^{vi}$ | 126.28 (10) | C29—C24—C23 | 125.7 (7) |
| K$^{i}$—K—K$^{vi}$ | 90.12 (6) | C25'—C24—C23 | 118.4 (7) |
| K$^{v}$—K—K$^{vi}$ | 180.00 (5) | C29'—C24—C23 | 123.0 (7) |
| O1W—K—H1W | 17.4 (13) | C25—C24—C23 | 115.6 (7) |
| O12$^{ii}$—K—H1W | 178.4 (14) | C28—C27—C26' | 96.7 (10) |
| O11—K—H1W | 111.3 (13) | C28—C27—C28' | 43.8 (8) |
| O21—K—H1W | 94.7 (13) | C26'—C27—C28' | 121.0 (10) |
| O22$^{iii}$—K—H1W | 94.2 (13) | C28—C27—C26 | 121.1 (10) |
| O11$^{i}$—K—H1W | 104.1 (13) | C26'—C27—C26 | 49.9 (9) |
| O22$^{iv}$—K—H1W | 39.1 (14) | C28'—C27—C26 | 106.9 (11) |
| C21$^{iii}$—K—H1W | 86.3 (13) | C28—C27—H27 | 119.5 |
| K$^{i}$—K—H1W | 115.5 (12) | C26'—C27—H27 | 122.4 |
| K$^{v}$—K—H1W | 121.9 (14) | C28'—C27—H27 | 115.9 |
| K$^{vi}$—K—H1W | 58.1 (14) | C26—C27—H27 | 119.5 |
| C11—O12—K$^{ii}$ | 130.3 (3) | C26—C25—C24 | 117.2 (13) |
| O12—C11—O11 | 123.9 (5) | C26—C25—H25 | 121.4 |
| O12—C11—C12 | 124.5 (5) | C24—C25—H25 | 121.4 |
| O11—C11—C12 | 111.6 (4) | C25—C26—C27 | 119.2 (12) |
| N11—C12—C11 | 116.3 (5) | C25—C26—H26 | 120.4 |
| N11—C12—H11A | 108.2 | C27—C26—H26 | 120.4 |
| C11—C12—H11A | 108.2 | C27—C28—C29 | 120.5 (14) |
| N11—C12—H11B | 108.2 | C27—C28—H28 | 119.7 |
| C11—C12—H11B | 108.2 | C29—C28—H28 | 119.7 |
| H11A—C12—H11B | 107.4 | C24—C29—C28 | 123.2 (13) |
| O13—C13—N11 | 121.9 (5) | C24—C29—H29 | 118.4 |
| O13—C13—C14 | 119.4 (5) | C28—C29—H29 | 118.4 |
| N11—C13—C14 | 118.6 (5) | C26'—C25'—C24 | 121.8 (12) |
| C19'—C14—C15 | 106.3 (8) | C26'—C25'—H25' | 119.1 |
| C19'—C14—C19 | 40.3 (6) | C24—C25'—H25' | 119.1 |
| C15—C14—C19 | 118.0 (8) | C27—C26'—C25' | 119.7 (12) |
| C19'—C14—C15' | 119.3 (8) | C27—C26'—H26' | 120.2 |
| C15—C14—C15' | 37.3 (6) | C25'—C26'—H26' | 120.2 |

| | | | |
|---|---|---|---|
| C19—C14—C15' | 103.8 (8) | C29'—C28'—C27 | 117.8 (13) |
| C19'—C14—C13 | 123.1 (6) | C29'—C28'—H28' | 121.1 |
| C15—C14—C13 | 119.3 (7) | C27—C28'—H28' | 121.1 |
| C19—C14—C13 | 122.3 (7) | C28'—C29'—C24 | 120.3 (12) |
| C15'—C14—C13 | 117.6 (7) | C28'—C29'—H29' | 119.8 |
| C16'—C17—C18 | 107.5 (12) | C24—C29'—H29' | 119.8 |
| C16'—C17—C16 | 33.5 (8) | C23—N21—C22 | 120.7 (4) |
| C18—C17—C16 | 118.4 (10) | C23—N21—H21 | 119.7 |
| C16'—C17—C18' | 121.0 (10) | C22—N21—H21 | 119.7 |
| C18—C17—C18' | 45.6 (9) | K—O1W—H1W | 84 (4) |
| C16—C17—C18' | 104.3 (10) | K—O1W—H2W | 115 (5) |
| C16'—C17—H17 | 121.4 | H1W—O1W—H2W | 123 (7) |

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

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N11—H11···O23$^{i}$ | 0.86 | 2.09 | 2.905 (7) | 158 |
| N21—H21···O1W$^{iii}$ | 0.86 | 2.15 | 2.929 (6) | 151 |
| O1W—H1W···O22$^{iv}$ | 0.84 (6) | 1.97 (7) | 2.758 (7) | 156 (6) |
| O1W—H2W···O13$^{vi}$ | 0.79 (7) | 1.92 (7) | 2.680 (6) | 160 (7) |

Symmetry codes: (i) −*x*, −*y*+1, −*z*; (iii) −*x*, −*y*, −*z*; (iv) −*x*−1, −*y*, −*z*; (vi) *x*−1, *y*, *z*.

**Fig. 1**

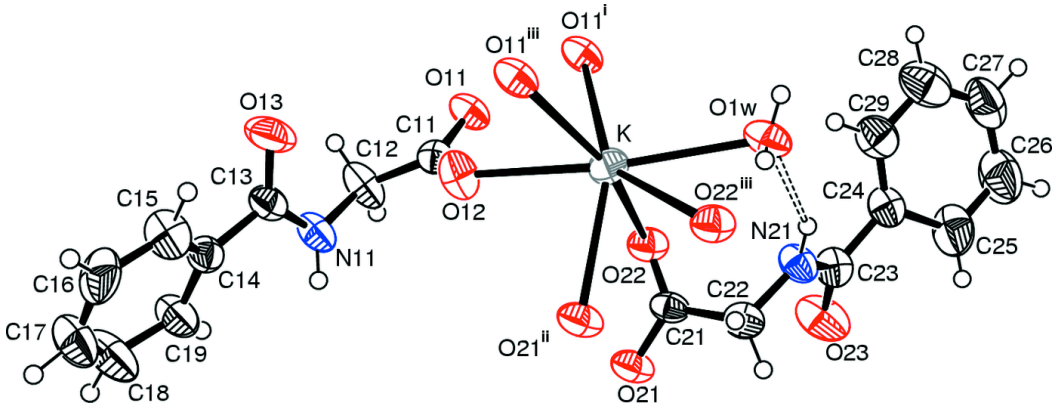
O11$^{i}$
O11$^{iii}$
O11
O13
C11
C12
K
O1w
C28
C27
C29
C26
C13
C15
O12
O22$^{iii}$
C24
N21
C25
N11
C14
O22
C22
C23
C16
C17
C19
C21
O23
O21$^{ii}$
C18
O21

**Fig. 2**