

Poly[diaqua(μ_2 -3-carboxypyrazine-2-carboxylato)(μ_2 -pyrazine-2,3-dicarboxylic acid)potassium(I)]

 Mustafa Tombul,^{a*} Kutalmis Güven^b and Ingrid Svoboda^c

^aDepartment of Chemistry, Faculty of Arts and Science, University of Kirikkale, Campus Yahsihan, 71450 Kirikkale, Turkey, ^bDepartment of Physics, Faculty of Arts and Science, University of Kirikkale, Campus Yahsihan, 71450 Kirikkale, Turkey, and ^cStructural Research, Materials Science, Darmstadt University of Technology, Petersen Strasse 23, D-64287 Darmstadt, Germany
Correspondence e-mail: mustafatombul38@gmail.com

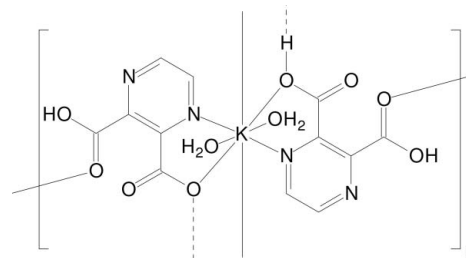
Received 17 October 2007; accepted 8 December 2007

Key indicators: single-crystal X-ray study; $T = 303$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.029; wR factor = 0.089; data-to-parameter ratio = 11.6.

The structural unit of the title compound, $[\text{K}(\text{C}_6\text{H}_3\text{N}_2\text{O}_4)(\text{C}_6\text{H}_4\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2]_n$, consists of one potassium cation, one hydrogen pyrazine-2,3-dicarboxylate anion, one pyrazine-2,3-dicarboxylic acid molecule and two water molecules; this is twice the asymmetric unit, since the potassium cation lies on an inversion centre. Each anion or acid molecule is linked to two potassium cations, while the potassium cation has contacts to four symmetry-equivalent organic ligands, with two different coordination modes towards this cation. In addition, each potassium cation is coordinated by two water O atoms, raising the coordination number to eight. One of the carboxyl groups of the acid retains its H atom, which forms a hydrogen bond to a coordinated water molecule. The other carboxyl group is deprotonated in half of the ligands and protonated in the other half, taking part in a strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond disordered over an inversion centre. The stabilization of the crystal structure is further assisted by $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds in which water acts as the donor.

Related literature

For related literature, see: Clegg & Liddle (2004); Cuesta *et al.* (2003); Ptasiwicz-Bak & Leciejewicz (1997*a,b*); Starosta & Leciejewicz (2005); Takusagawa & Shimada (1973); Tombul *et al.* (2006, 2007). Richard *et al.* (1973). Nepveu *et al.* (1993).



Experimental

Crystal data

$[\text{K}(\text{C}_6\text{H}_3\text{N}_2\text{O}_4)(\text{C}_6\text{H}_4\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2]$
 $M_r = 410.35$
 Triclinic, $P\bar{1}$
 $a = 7.4171$ (11) Å
 $b = 8.0252$ (12) Å
 $c = 8.1153$ (13) Å
 $\alpha = 68.39$ (2)°
 $\beta = 81.18$ (1)°
 $\gamma = 64.24$ (2)°
 $V = 404.43$ (13) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.40$ mm⁻¹
 $T = 303$ (2) K
 $0.40 \times 0.36 \times 0.14$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector
 Absorption correction: numerical [using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)]
 $T_{\min} = 0.858$, $T_{\max} = 0.947$
 4541 measured reflections
 1639 independent reflections
 1357 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.089$
 $S = 0.82$
 1639 reflections
 141 parameters
 3 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.30$ e Å⁻³
 $\Delta\rho_{\min} = -0.24$ e Å⁻³

Table 1

Selected bond lengths (Å).

N1—K1	2.8655 (15)	K1—O3 ⁱ	2.8771 (15)
O1—K1	2.8995 (12)	K1—O1 ⁱ	2.8995 (12)
O3—K1	2.8771 (15)	K1—O2 ⁱⁱ	3.0897 (13)
K1—N1 ⁱ	2.8655 (15)	K1—O2 ⁱⁱⁱ	3.0897 (13)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O3—H3A \cdots O4 ^{iv}	0.85 (2)	1.899 (10)	2.7334 (17)	167 (2)
O3—H3B \cdots N2 ⁱⁱ	0.848 (9)	2.035 (10)	2.8701 (19)	168 (2)
O5—H5 \cdots O3 ^v	0.86 (3)	1.76 (3)	2.5994 (17)	168 (2)
O1—H1 \cdots O1 ^{iv}	0.80 (4)	1.68 (4)	2.480 (2)	171 (5)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Mercury* (Macrae *et al.*, 2006);

software used to prepare material for publication: *publCIF* (Westrip, 2008).

The authors gratefully acknowledge Kırıkkale University for the financial support of this research and Professor Dr Hartmut Fuess, Darmstadt University of Technology, for use of the diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2158).

References

- Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* **A51**, 887–897.
- Clegg, W. & Liddle, S. T. (2004). *Acta Cryst.* **E60**, m1495–m1497.
- Cuesta, R., Glidewell, C., López, R. & Low, J. N. (2003). *Acta Cryst.* **C59**, m315–m318.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Nepveu, F., Berkaoui, M. 'H. & Walz, L. (1993). *Acta Cryst.* **C49**, 1465–1466.
- Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis CCD*. Versions 1.171.31.4 Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Ptasiewicz-Bak, H. & Leciejewicz, J. (1997a). *Pol. J. Chem.* **71**, 493–500.
- Ptasiewicz-Bak, H. & Leciejewicz, J. (1997b). *Pol. J. Chem.* **71**, 1603–1610.
- Richard, P., Tran Qui, D. & Bertaut, E. F. (1973). *Acta Cryst.* **B29**, 1111–1115.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Starosta, W. & Leciejewicz, J. (2005). *J. Coord. Chem.* **58**, 963–968.
- Takusagawa, T. & Shimada, A. (1973). *Chem. Lett.* pp. 1121–1126.
- Tombul, M., Güven, K. & Alkış, N. (2006). *Acta Cryst.* **E62**, m945–m947.
- Tombul, M., Güven, K. & Büyükgüngör, O. (2007). *Acta Cryst.* **E63**, m1783–m1784.
- Westrip, S. P. (2008). *publCIF*. In preparation.

supplementary materials

Acta Cryst. (2008). E64, m246-m247 [doi:10.1107/S1600536807066202]

Poly[diaqua(μ_2 -3-carboxypyrazine-2-carboxylato)(μ_2 -pyrazine-2,3-dicarboxylic acid)potassium(I)]

M. Tombul, K. Güven and I. Svoboda

Comment

Pyrazine-2,3-dicarboxylic acid (Takusagawa & Shimada, 1973) and its dianion (Richard *et al.*, 1973; Nepveu *et al.*, 1993) have been reported to be well suited for the construction of multidimensional frameworks (nD, n = 1–3), owing to the presence of two adjacent carboxylate groups (O donor atoms) as substituents on the N-heterocyclic pyrazine ring (N donor atoms). In recent years, a variety of metal-organic compound of pyrazine-2,3-dicarboxylic acid have been characterized crystallographically due to growing interest in supramolecular chemistry. These include the calcium (Ptasiewicz-Bak- & Leciejewicz, 1997a; Starosta & Leciejewicz, 2005), magnesium (Ptasiewicz-Bak- H. & Leciejewicz, 1997b), sodium (Tombul *et al.*, 2006) and caesium (Tombul *et al.*, 2007) complexes. We present here the synthesis and crystal structure of the hydrated potassium complex, (I), formed with pyrazine-2,3-dicarboxylic acid.

The structural unit of the title compound, (I), contains one potassium cation, one hydrogen pyrazine-2,3-dicarboxylate anion, one pyrazine-2,3-dicarboxylic acid molecule and two water molecules; this is twice the asymmetric unit, as the potassium ion lies on an inversion centre. Pyrazine-2,3-dicarboxylic acid is, on average, only half deprotonated at one of the carboxylate groups (O1) and together with the symmetry-related oxygen atom (O1^V) which is also half deprotonated, completes the charge balance of the cation. In the crystal structure, the anion or acid molecule is linked to two potassium cations, while the K⁺ cation is surrounded by four organic ligands, two of which are coordinated by utilizing both N and O atoms and the other two are coordinated solely by O atoms. In addition, each potassium cation is coordinated by two water molecules, achieving a coordination number of eight. The primary coordination comprises six oxygen atoms, together with two nitrogen atoms. The planes of the carboxylic/carboxylate groups (O4/C5/O1) and (O2/C6/O5) form dihedral angles with the ring plane of 54.33 (14) and 53.75 (14)°, respectively. The K—O distances are in the range 2.877 (2) Å to 3.089 (2) Å, in accordance with the corresponding values reported for other potassium complexes (Clegg & Liddle, 2004; Cuesta *et al.*, 2003).

In the crystal structure, an asymmetric strong hydrogen bond occurs, linking carboxylate O atoms (Table 2). Atom H1 is involved in this bond and maintains the charge balance within the structure. The ordered carboxyl group forms a hydrogen bond in which water serves as acceptor. The water molecules are involved in normal, slightly bent, hydrogen bonds with hydrogen pyrazine-2,3-dicarboxylate (Table 2); the acceptors are carboxylate O atoms and N atoms of the aromatic ring.

Experimental

K₂CO₃ (346 mg, 2.5 mmol) was carefully added to an aqueous solution (20 ml) of pyrazine-2,3-dicarboxylic acid (1680 mg, 10 mmol), until no further bubbles formed. The reaction mixture gave a colourless and clear solution which was stirred at 333 K for 2.5 h, until it solidified. The solid product was redissolved in water (10 ml) and allowed to stand for a week at room temperature, after which transparent fine crystals were harvested.

Refinement

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically and treated as riding, with C—H in the range 0.93–0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. O-bound H atoms were refined freely.

Figures

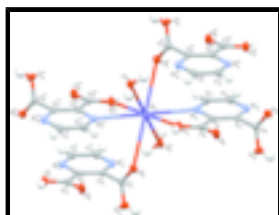


Fig. 1. A segment of the structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry Codes: (ii) $-x + 1, -y, -z + 1$; (iv) $-x, -y + 1, -z + 1$; (v) $x - 1, y + 1, z$.]

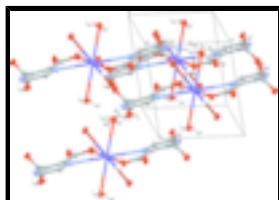


Fig. 2. A packing diagram for (I). Dashed lines indicate hydrogen bonds. (H1A and H2 are omitted for clarity). [Symmetry Codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z + 1$; (iii) $x + 1, y - 1, z + 1$.]

Poly[*diaqua*(μ_2 -3-carboxypyrazine-2-carboxylato)(μ_2 -pyrazine-2,3-dicarboxylic acid)potassium(I)]

Crystal data

[K(C₆H₃N₂O₄)(C₆H₄N₂O₄)(H₂O)₂]

$M_r = 410.35$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 7.4171$ (11) Å

$b = 8.0252$ (12) Å

$c = 8.1153$ (13) Å

$\alpha = 68.39$ (2)°

$\beta = 81.18$ (1)°

$\gamma = 64.24$ (2)°

$V = 404.43$ (13) Å³

$Z = 1$

$F_{000} = 210$

$D_x = 1.685$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2574 reflections

$\theta = 2.7$ – 27.5 °

$\mu = 0.40$ mm⁻¹

$T = 303$ (2) K

Prism, colorless

$0.40 \times 0.36 \times 0.14$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector

Radiation source: Enhance (Mo) X-ray Source

Monochromator: graphite

Detector resolution: 8.4012 pixels mm⁻¹

$T = 303$ (2) K

1639 independent reflections

1357 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\text{max}} = 26.4$ °

$\theta_{\text{min}} = 2.7$ °

ω and φ scans $h = -9 \rightarrow 9$
 Absorption correction: numerical
 [using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)] $k = -9 \rightarrow 9$
 $T_{\min} = 0.858$, $T_{\max} = 0.947$ $l = -10 \rightarrow 10$
 4541 measured reflections

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
 Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites
 $R[F^2 > 2\sigma(F^2)] = 0.029$ H atoms treated by a mixture of independent and constrained refinement
 $wR(F^2) = 0.089$ $w = 1/[\sigma^2(F_o^2) + (0.0664P)^2 + 0.1925P]$
 $S = 0.82$ where $P = (F_o^2 + 2F_c^2)/3$
 1639 reflections $(\Delta/\sigma)_{\max} < 0.001$
 141 parameters $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$
 3 restraints $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$
 Primary atom site location: structure-invariant direct methods Extinction correction: SHELXL,
 $\text{Fc}^* = k\text{Fc}[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.043 (8)

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 $F^2 > \sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.2243 (2)	-0.0442 (2)	0.6857 (2)	0.0317 (4)	
H1A	0.0951	-0.0140	0.6552	0.038*	
C2	0.3500 (2)	-0.2386 (2)	0.7694 (2)	0.0335 (4)	
H2	0.3046	-0.3358	0.7905	0.040*	
C3	0.5925 (2)	-0.1443 (2)	0.78702 (18)	0.0249 (3)	
C4	0.4681 (2)	0.0507 (2)	0.69820 (18)	0.0236 (3)	
C5	0.5421 (2)	0.2104 (2)	0.6487 (2)	0.0289 (3)	
C6	0.8033 (2)	-0.2156 (2)	0.8493 (2)	0.0277 (3)	
N1	0.28268 (17)	0.10040 (18)	0.64756 (16)	0.0281 (3)	

supplementary materials

N2	0.53451 (18)	-0.28984 (18)	0.82048 (17)	0.0310 (3)	
O1	0.41860 (17)	0.38402 (16)	0.56448 (17)	0.0394 (3)	
H1	0.476 (7)	0.455 (6)	0.533 (5)	0.039 (11)*	0.50
O2	0.94651 (16)	-0.29530 (18)	0.77161 (16)	0.0392 (3)	
O3	0.14687 (17)	0.66521 (18)	0.15762 (17)	0.0407 (3)	
H3A	0.195 (3)	0.727 (3)	0.190 (3)	0.057 (6)*	
H3B	0.245 (2)	0.563 (2)	0.149 (3)	0.057 (6)*	
O4	0.71570 (17)	0.16296 (17)	0.68558 (19)	0.0476 (4)	
O5	0.80518 (19)	-0.1943 (2)	1.00104 (17)	0.0504 (4)	
H5	0.925 (4)	-0.241 (4)	1.038 (3)	0.065 (7)*	
K1	0.0000	0.5000	0.5000	0.0471 (2)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0200 (7)	0.0376 (8)	0.0396 (8)	-0.0125 (6)	-0.0024 (6)	-0.0137 (7)
C2	0.0279 (8)	0.0336 (8)	0.0424 (9)	-0.0165 (6)	0.0010 (6)	-0.0120 (7)
C3	0.0220 (7)	0.0276 (7)	0.0250 (7)	-0.0091 (6)	-0.0002 (5)	-0.0101 (5)
C4	0.0213 (7)	0.0259 (7)	0.0239 (7)	-0.0076 (6)	-0.0016 (5)	-0.0107 (5)
C5	0.0255 (7)	0.0271 (7)	0.0356 (8)	-0.0088 (6)	-0.0030 (6)	-0.0134 (6)
C6	0.0236 (7)	0.0241 (7)	0.0329 (8)	-0.0082 (6)	-0.0042 (6)	-0.0075 (6)
N1	0.0210 (6)	0.0293 (6)	0.0322 (7)	-0.0067 (5)	-0.0031 (5)	-0.0116 (5)
N2	0.0253 (6)	0.0274 (6)	0.0377 (7)	-0.0107 (5)	-0.0017 (5)	-0.0079 (5)
O1	0.0301 (6)	0.0261 (6)	0.0558 (8)	-0.0121 (5)	-0.0066 (5)	-0.0039 (5)
O2	0.0221 (5)	0.0465 (7)	0.0535 (7)	-0.0108 (5)	0.0004 (5)	-0.0257 (6)
O3	0.0316 (6)	0.0372 (7)	0.0555 (8)	-0.0072 (5)	-0.0149 (5)	-0.0206 (6)
O4	0.0308 (6)	0.0333 (6)	0.0824 (10)	-0.0118 (5)	-0.0192 (6)	-0.0174 (6)
O5	0.0297 (6)	0.0743 (9)	0.0417 (7)	-0.0057 (6)	-0.0116 (5)	-0.0282 (6)
K1	0.0338 (3)	0.0339 (3)	0.0456 (3)	-0.0005 (2)	-0.0012 (2)	0.0006 (2)

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

C1—N1	1.327 (2)	N1—K1	2.8655 (15)
C1—C2	1.383 (2)	O1—K1	2.8995 (12)
C1—H1A	0.9300	O1—H1	0.80 (4)
C2—N2	1.331 (2)	O3—K1	2.8771 (15)
C2—H2	0.9300	O3—H3A	0.85 (2)
C3—N2	1.3381 (19)	O3—H3B	0.848 (9)
C3—C4	1.392 (2)	O5—H5	0.86 (3)
C3—C6	1.5097 (19)	K1—N1 ⁱ	2.8655 (15)
C4—N1	1.3397 (18)	K1—O3 ⁱ	2.8771 (15)
C4—C5	1.507 (2)	K1—O1 ⁱ	2.8995 (12)
C5—O4	1.2248 (18)	K1—O2 ⁱⁱ	3.0897 (13)
C5—O1	1.2760 (19)	K1—O2 ⁱⁱⁱ	3.0897 (13)
C6—O2	1.1983 (19)	K1—H3A	3.09 (2)
C6—O5	1.3073 (19)		
N1—C1—C2	121.91 (13)	N1 ⁱ —K1—O3	72.84 (4)

N1—C1—H1A	119.0	N1—K1—O3	107.16 (4)
C2—C1—H1A	119.0	O3 ⁱ —K1—O3	180.0
N2—C2—C1	121.64 (14)	N1 ⁱ —K1—O1 ⁱ	55.92 (4)
N2—C2—H2	119.2	N1—K1—O1 ⁱ	124.08 (4)
C1—C2—H2	119.2	O3 ⁱ —K1—O1 ⁱ	76.02 (4)
N2—C3—C4	121.58 (13)	O3—K1—O1 ⁱ	103.98 (4)
N2—C3—C6	113.19 (12)	N1 ⁱ —K1—O1	124.08 (4)
C4—C3—C6	125.20 (13)	N1—K1—O1	55.92 (4)
N1—C4—C3	121.03 (13)	O3 ⁱ —K1—O1	103.98 (4)
N1—C4—C5	118.15 (13)	O3—K1—O1	76.02 (4)
C3—C4—C5	120.76 (13)	O1 ⁱ —K1—O1	180.000 (1)
O4—C5—O1	125.67 (14)	N1 ⁱ —K1—O2 ⁱⁱ	107.44 (4)
O4—C5—C4	118.05 (13)	N1—K1—O2 ⁱⁱ	72.56 (4)
O1—C5—C4	116.21 (13)	O3 ⁱ —K1—O2 ⁱⁱ	116.00 (3)
O2—C6—O5	126.25 (14)	O3—K1—O2 ⁱⁱ	64.00 (3)
O2—C6—C3	121.86 (13)	O1 ⁱ —K1—O2 ⁱⁱ	81.35 (3)
O5—C6—C3	111.63 (13)	O1—K1—O2 ⁱⁱ	98.65 (4)
C1—N1—C4	117.01 (13)	N1 ⁱ —K1—O2 ⁱⁱⁱ	72.56 (4)
C1—N1—K1	119.50 (9)	N1—K1—O2 ⁱⁱⁱ	107.44 (4)
C4—N1—K1	123.12 (9)	O3 ⁱ —K1—O2 ⁱⁱⁱ	64.00 (3)
C2—N2—C3	116.78 (13)	O3—K1—O2 ⁱⁱⁱ	116.00 (3)
C5—O1—K1	125.42 (10)	O1 ⁱ —K1—O2 ⁱⁱⁱ	98.65 (4)
C5—O1—H1	109 (3)	O1—K1—O2 ⁱⁱⁱ	81.35 (4)
K1—O1—H1	126 (3)	O2 ⁱⁱ —K1—O2 ⁱⁱⁱ	180.00 (2)
C6—O2—K1 ^{iv}	132.38 (10)	N1 ⁱ —K1—H3A	70.6 (3)
K1—O3—H3A	96.3 (15)	N1—K1—H3A	109.4 (3)
K1—O3—H3B	99.8 (15)	O3 ⁱ —K1—H3A	164.1 (2)
H3A—O3—H3B	106.6 (13)	O3—K1—H3A	15.9 (2)
C6—O5—H5	111.0 (16)	O1 ⁱ —K1—H3A	112.9 (3)
N1 ⁱ —K1—N1	180.0	O1—K1—H3A	67.1 (3)
N1 ⁱ —K1—O3 ⁱ	107.16 (4)	O2 ⁱⁱ —K1—H3A	79.1 (2)
N1—K1—O3 ⁱ	72.84 (4)	O2 ⁱⁱⁱ —K1—H3A	100.9 (2)
N1—C1—C2—N2	1.9 (2)	O4—C5—O1—K1	-175.29 (12)
N2—C3—C4—N1	2.1 (2)	C4—C5—O1—K1	7.78 (19)
C6—C3—C4—N1	179.87 (13)	O5—C6—O2—K1 ^{iv}	154.68 (13)
N2—C3—C4—C5	-174.99 (13)	C3—C6—O2—K1 ^{iv}	-19.1 (2)
C6—C3—C4—C5	2.8 (2)	C1—N1—K1—O3 ⁱ	61.01 (11)
N1—C4—C5—O4	-175.63 (14)	C4—N1—K1—O3 ⁱ	-111.76 (11)
C3—C4—C5—O4	1.5 (2)	C1—N1—K1—O3	-118.99 (11)
N1—C4—C5—O1	1.5 (2)	C4—N1—K1—O3	68.24 (11)
C3—C4—C5—O1	178.67 (13)	C1—N1—K1—O1 ⁱ	1.94 (12)
N2—C3—C6—O2	74.92 (18)	C4—N1—K1—O1 ⁱ	-170.83 (10)

supplementary materials

C4—C3—C6—O2	-103.06 (18)	C1—N1—K1—O1	-178.06 (12)
N2—C3—C6—O5	-99.65 (16)	C4—N1—K1—O1	9.17 (10)
C4—C3—C6—O5	82.37 (18)	C1—N1—K1—O2 ⁱⁱ	-64.29 (11)
C2—C1—N1—C4	-1.8 (2)	C4—N1—K1—O2 ⁱⁱ	122.94 (11)
C2—C1—N1—K1	-174.99 (12)	C1—N1—K1—O2 ⁱⁱⁱ	115.71 (11)
C3—C4—N1—C1	-0.1 (2)	C4—N1—K1—O2 ⁱⁱⁱ	-57.06 (11)
C5—C4—N1—C1	177.00 (12)	C5—O1—K1—N1 ⁱ	171.23 (11)
C3—C4—N1—K1	172.82 (10)	C5—O1—K1—N1	-8.77 (11)
C5—C4—N1—K1	-10.06 (17)	C5—O1—K1—O3 ⁱ	48.85 (13)
C1—C2—N2—C3	0.0 (2)	C5—O1—K1—O3	-131.15 (13)
C4—C3—N2—C2	-1.9 (2)	C5—O1—K1—O2 ⁱⁱ	-70.80 (13)
C6—C3—N2—C2	-179.99 (12)	C5—O1—K1—O2 ⁱⁱⁱ	109.20 (13)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3A \cdots O4 ^v	0.85 (2)	1.899 (10)	2.7334 (17)	167 (2)
O3—H3B \cdots N2 ⁱⁱ	0.848 (9)	2.035 (10)	2.8701 (19)	168 (2)
O5—H5 \cdots O3 ^{vi}	0.86 (3)	1.76 (3)	2.5994 (17)	168 (2)
O1—H1 \cdots O1 ^v	0.80 (4)	1.68 (4)	2.480 (2)	171 (5)

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

Fig. 1

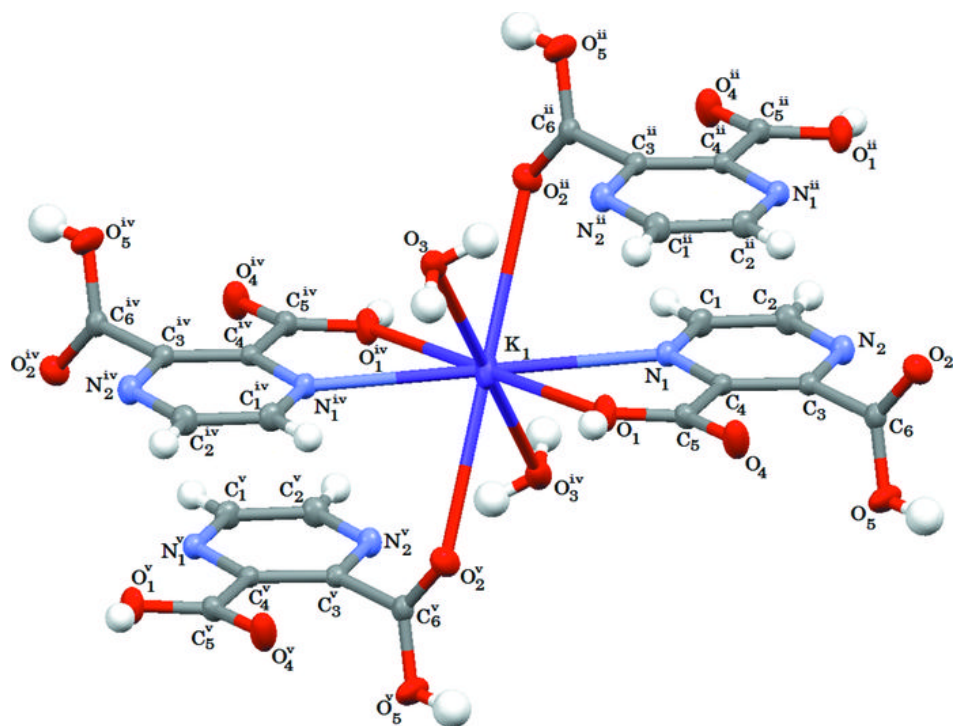


Fig. 2

