

## catena-Poly[potassium-di- $\mu$ -aqua- $\mu$ -4-(5-tetrazolio)pyridine]

Li-Jing Cui

Ordered Matter Science Research Center, College of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, People's Republic of China  
Correspondence e-mail: fudavid88@yahoo.com.cn

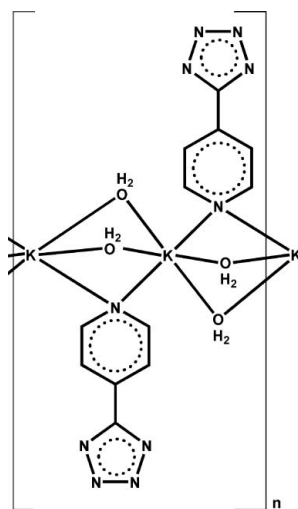
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.037;  $wR$  factor = 0.096; data-to-parameter ratio = 16.9.

The title compound,  $[\text{K}(\text{C}_6\text{H}_4\text{N}_5)(\text{H}_2\text{O})_2]_n$ , was synthesized by hydrothermal reaction of KOH with 4-(5-tetrazolio)pyridine. The K atom has a distorted octahedral coordination environment and is coordinated by two axial N atoms from the organic ligand and by four water molecules in the equatorial plane. The molecules as a whole are located on crystallographic mirror planes; the K atom is also located on an inversion center. Both the water molecules and the organic ligands act as bridges to link symmetrically the adjacent K atoms into polymeric chains parallel to the  $c$  axis. O—H...N hydrogen bonds involving the water O atoms and aromatic  $\pi$ – $\pi$  interactions [centroid–centroid distance 3.80 (2) Å] between the pyridine and tetrazole rings build up an infinite three-dimensional network.

### Related literature

For applications of tetrazole derivatives in coordination chemistry, see: Xiong *et al.* (2002); Wang *et al.* (2005). For the crystal structure of a related compound, see: Dai & Fu (2008).



### Experimental

#### Crystal data

$[\text{K}(\text{C}_6\text{H}_4\text{N}_5)(\text{H}_2\text{O})_2]$   
 $M_r = 221.27$   
Monoclinic,  $C2/c$   
 $a = 12.361$  (3) Å  
 $b = 12.281$  (3) Å  
 $c = 7.3431$  (15) Å  
 $\beta = 117.25$  (3)°

$V = 991.1$  (3) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 0.52$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.25 \times 0.15 \times 0.10$  mm

#### Data collection

Rigaku Mercury2 diffractometer  
Absorption correction: multi-scan  
(*CrystalClear*; Rigaku, 2005)  
 $T_{\min} = 0.913$ ,  $T_{\max} = 1.000$   
(expected range = 0.867–0.949)

5056 measured reflections  
1134 independent reflections  
928 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.096$   
 $S = 1.07$   
1134 reflections  
67 parameters

2 restraints  
H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.32$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.19$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA...N2 <sup>i</sup>	0.84	2.01	2.852 (2)	177
O1W—H1WB...N3 <sup>ii</sup>	0.88	1.97	2.831 (2)	169

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2195).

### References

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Wang, X.-S., Tang, Y.-Z., Huang, X.-F., Qu, Z.-R., Che, C.-M., Chan, C. W. H. & Xiong, R.-G. (2005). *Inorg. Chem.* **44**, 5278–5285.  
Xiong, R.-G., Xue, X., Zhao, H., You, X.-Z., Abrahams, B. F. & Xue, Z.-L. (2002). *Angew. Chem. Int. Ed.* **41**, 3800–3803.

**supplementary materials**

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## **catena-Poly[potassium-di- $\mu$ -aqua- $\mu$ -4-(5-tetrazolio)pyridine]**

**L.-J. Cui**

### **Comment**

In the past few years, more and more people have focused on the chemistry of tetrazole derivatives because of their multiple coordination modes as ligands to metal ions and for the construction of novel metal-organic frameworks (Wang, *et al.* 2005; Xiong, *et al.* 2002). We report here the crystal structure of the title compound, tetra-aqua-bis[4-(2*H*-tetrazol-5-yl)pyridine]potassium(I).

The K atom has a distorted octahedral geometry and is coordinated by two axial pyridyl N atoms from the organic ligand and four water molecules ligands in the equatorial plane. The molecules as a whole are located on crystallographic mirror planes, the potassium ion is also located on an inversion center. Both the water molecules and the organic ligands act as bridges linking adjacent K ions into polymeric chains parallel to the *c* axis by covalent bonds (K—N, and K—O). The pyridine and tetrazole rings are nearly coplanar and are twisted from each other by a dihedral angle of only 12.99 (0.13) ° (Fig. 1). The bond distances and bond angles of the tetrazole rings are in the usual ranges (Wang, *et al.* 2005; Dai & Fu 2008).

The crystal packing (Fig. 2) is stabilized by aromatic  $\pi$ - $\pi$  interactions between the pyridine and tetrazole rings of the neighbouring ligand systems. The centroid...centroid distance is 3.80 (2) Å (symmetry code: *x*, *y*, *z*+1 and *x*, *y*, *z*). The molecular packing is further stabilized by intermolecular O—H...N hydrogen bonds involving the aqueous O atoms. The  $\pi$ - $\pi$  and hydrogen bonding interactions build up an infinite three-dimensional network. (Fig. 2 and Table 1).

### **Experimental**

A mixture of 4-(2*H*-tetrazol-5-yl)pyridine (0.4 mmol) and KOH (0.4 mmol), ethanol (1 ml) and a few drops of water sealed in a glass tube was maintained at 373 K. Colorless needle crystals suitable for X-ray analysis were obtained after 3 days.

### **Refinement**

All H atoms attached to C atoms were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic) with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The H atoms of water molecules were located in difference Fourier maps and the O—H distances were restrained in the subsequent refinements to 0.85 Å with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . In the last stage of the refinement they were treated as riding on the O atom.

## Figures

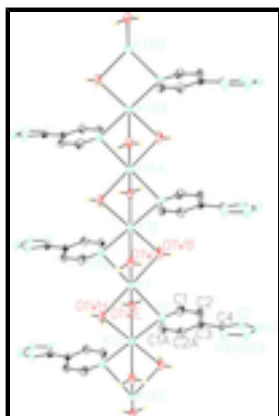


Fig. 1. A view of the title compound with the atomic numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

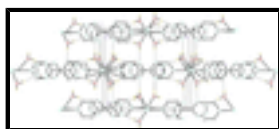


Fig. 2. The crystal packing of the title compound viewed along the *c* axis showing the three dimensional network (dashed lines). Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

## catena-Poly[potassium(I)-di-μ-aqua-μ-4-(5-tetrazolio)pyridine]

### Crystal data

[K(C<sub>6</sub>H<sub>4</sub>N<sub>5</sub>)(H<sub>2</sub>O)<sub>2</sub>]

*M<sub>r</sub>* = 221.27

Monoclinic, *C*2/*c*

Hall symbol: -*C* 2yc

*a* = 12.361 (3) Å

*b* = 12.281 (3) Å

*c* = 7.3431 (15) Å

β = 117.25 (3)°

*V* = 991.1 (3) Å<sup>3</sup>

*Z* = 4

*F*<sub>000</sub> = 456

*D<sub>x</sub>* = 1.483 Mg m<sup>-3</sup>

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 1134 reflections

θ = 3.3–27.5°

μ = 0.52 mm<sup>-1</sup>

*T* = 298 K

Needle, colorless

0.25 × 0.15 × 0.10 mm

### Data collection

Rigaku Mercury2 (2 × 2 bin mode) diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 13.6612 pixels mm<sup>-1</sup>

*T* = 298 K

ω scans

Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)

*T*<sub>min</sub> = 0.913, *T*<sub>max</sub> = 1.000

1134 independent reflections

928 reflections with *I* > 2σ(*I*)

*R*<sub>int</sub> = 0.027

θ<sub>max</sub> = 27.5°

θ<sub>min</sub> = 3.3°

*h* = -16 → 16

*k* = -15 → 15

*l* = -9 → 9

5056 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
$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.096$	$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 0.7641P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
1134 reflections	$(\Delta/\sigma)_{\max} < 0.001$
67 parameters	$\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$
2 restraints	$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$
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  $F^2 > \sigma(F^2)$  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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.5000	0.0000	0.5000	0.0467 (2)
C4	0.5000	0.5325 (2)	0.7500	0.0365 (6)
C3	0.5000	0.4124 (2)	0.7500	0.0358 (5)
N2	0.60000 (14)	0.59305 (13)	0.8162 (3)	0.0468 (4)
C2	0.60283 (18)	0.35391 (16)	0.7821 (3)	0.0459 (5)
H2	0.6742	0.3897	0.8050	0.055*
N3	0.55965 (15)	0.69599 (13)	0.7896 (3)	0.0530 (5)
N1	0.5000	0.18446 (19)	0.7500	0.0522 (6)
C1	0.5980 (2)	0.24208 (17)	0.7797 (4)	0.0534 (5)
H1	0.6678	0.2041	0.8000	0.064*
O1W	0.34559 (12)	0.08972 (11)	0.1308 (2)	0.0516 (4)
H1WA	0.2731	0.0885	0.0381	0.077*
H1WB	0.3654	0.1588	0.1421	0.077*

## supplementary materials

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### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
K1	0.0545 (4)	0.0460 (4)	0.0403 (3)	-0.0005 (3)	0.0221 (3)	-0.0025 (3)
C4	0.0345 (13)	0.0344 (12)	0.0323 (13)	0.000	0.0080 (11)	0.000
C3	0.0381 (13)	0.0334 (13)	0.0296 (12)	0.000	0.0102 (10)	0.000
N2	0.0383 (9)	0.0337 (8)	0.0522 (10)	-0.0025 (7)	0.0067 (7)	-0.0016 (7)
C2	0.0392 (10)	0.0406 (10)	0.0536 (12)	-0.0008 (8)	0.0176 (9)	-0.0029 (9)
N3	0.0503 (9)	0.0340 (8)	0.0541 (11)	-0.0042 (7)	0.0062 (8)	-0.0020 (7)
N1	0.0602 (16)	0.0343 (12)	0.0524 (15)	0.000	0.0174 (13)	0.000
C1	0.0514 (12)	0.0416 (11)	0.0596 (13)	0.0090 (9)	0.0189 (10)	-0.0026 (9)
O1W	0.0341 (7)	0.0376 (7)	0.0667 (10)	0.0014 (6)	0.0088 (7)	0.0026 (6)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

K1—O1W <sup>i</sup>	2.7309 (16)	C3—C2 <sup>iv</sup>	1.383 (2)
K1—O1W <sup>ii</sup>	2.7309 (16)	C3—C2	1.383 (2)
K1—O1W	2.7330 (17)	N2—N3	1.340 (2)
K1—O1W <sup>iii</sup>	2.7330 (17)	C2—C1	1.375 (3)
K1—N1 <sup>iii</sup>	2.9159 (18)	C2—H2	0.9300
K1—N1	2.9159 (18)	N3—N3 <sup>iv</sup>	1.314 (3)
K1—C1 <sup>iii</sup>	3.499 (2)	N1—C1	1.332 (3)
K1—C1	3.499 (2)	N1—C1 <sup>iv</sup>	1.332 (3)
K1—K1 <sup>ii</sup>	3.6716 (7)	N1—K1 <sup>iv</sup>	2.9159 (18)
K1—K1 <sup>iv</sup>	3.6716 (8)	C1—H1	0.9300
K1—H1WB	3.0780	O1W—K1 <sup>ii</sup>	2.7309 (16)
C4—N2	1.329 (2)	O1W—H1WA	0.8412
C4—N2 <sup>iv</sup>	1.329 (2)	O1W—H1WB	0.8765
C4—C3	1.475 (3)		
O1W <sup>i</sup> —K1—O1W <sup>ii</sup>	180.00 (3)	C1 <sup>iii</sup> —K1—K1 <sup>iv</sup>	115.36 (4)
O1W <sup>i</sup> —K1—O1W	103.20 (5)	C1—K1—K1 <sup>iv</sup>	64.64 (4)
O1W <sup>ii</sup> —K1—O1W	76.80 (5)	K1 <sup>ii</sup> —K1—K1 <sup>iv</sup>	180.0
O1W <sup>i</sup> —K1—O1W <sup>iii</sup>	76.80 (5)	O1W <sup>i</sup> —K1—H1WB	111.4
O1W <sup>ii</sup> —K1—O1W <sup>iii</sup>	103.20 (5)	O1W <sup>ii</sup> —K1—H1WB	68.6
O1W—K1—O1W <sup>iii</sup>	180.0	O1W—K1—H1WB	16.0
O1W <sup>i</sup> —K1—N1 <sup>iii</sup>	96.28 (4)	O1W <sup>iii</sup> —K1—H1WB	164.0
O1W <sup>ii</sup> —K1—N1 <sup>iii</sup>	83.72 (4)	N1 <sup>iii</sup> —K1—H1WB	96.4
O1W—K1—N1 <sup>iii</sup>	83.68 (4)	N1—K1—H1WB	83.6
O1W <sup>iii</sup> —K1—N1 <sup>iii</sup>	96.32 (4)	C1 <sup>iii</sup> —K1—H1WB	97.5
O1W <sup>i</sup> —K1—N1	83.72 (4)	C1—K1—H1WB	82.5
O1W <sup>ii</sup> —K1—N1	96.28 (4)	K1 <sup>ii</sup> —K1—H1WB	52.7
O1W—K1—N1	96.32 (4)	K1 <sup>iv</sup> —K1—H1WB	127.3
O1W <sup>iii</sup> —K1—N1	83.68 (4)	N2—C4—N2 <sup>iv</sup>	112.0 (2)

N1 <sup>iii</sup> —K1—N1	180.0	N2—C4—C3	124.01 (11)
O1W <sup>i</sup> —K1—C1 <sup>iii</sup>	75.74 (5)	N2 <sup>iv</sup> —C4—C3	124.01 (11)
O1W <sup>ii</sup> —K1—C1 <sup>iii</sup>	104.26 (5)	C2 <sup>iv</sup> —C3—C2	117.4 (2)
O1W—K1—C1 <sup>iii</sup>	82.15 (5)	C2 <sup>iv</sup> —C3—C4	121.30 (12)
O1W <sup>iii</sup> —K1—C1 <sup>iii</sup>	97.85 (5)	C2—C3—C4	121.30 (12)
N1 <sup>iii</sup> —K1—C1 <sup>iii</sup>	21.60 (4)	C4—N2—N3	104.64 (16)
N1—K1—C1 <sup>iii</sup>	158.40 (4)	C1—C2—C3	119.1 (2)
O1W <sup>i</sup> —K1—C1	104.26 (5)	C1—C2—H2	120.5
O1W <sup>ii</sup> —K1—C1	75.74 (5)	C3—C2—H2	120.5
O1W—K1—C1	97.85 (5)	N3 <sup>iv</sup> —N3—N2	109.38 (10)
O1W <sup>iii</sup> —K1—C1	82.15 (5)	C1—N1—C1 <sup>iv</sup>	115.8 (2)
N1 <sup>iii</sup> —K1—C1	158.40 (4)	C1—N1—K1	104.69 (11)
N1—K1—C1	21.60 (4)	C1 <sup>iv</sup> —N1—K1	124.89 (11)
C1 <sup>iii</sup> —K1—C1	180.00 (9)	C1—N1—K1 <sup>iv</sup>	124.89 (11)
O1W <sup>i</sup> —K1—K1 <sup>ii</sup>	132.19 (4)	C1 <sup>iv</sup> —N1—K1 <sup>iv</sup>	104.69 (11)
O1W <sup>ii</sup> —K1—K1 <sup>ii</sup>	47.81 (4)	K1—N1—K1 <sup>iv</sup>	78.04 (6)
O1W—K1—K1 <sup>ii</sup>	47.76 (3)	N1—C1—C2	124.3 (2)
O1W <sup>iii</sup> —K1—K1 <sup>ii</sup>	132.24 (3)	N1—C1—K1	53.71 (10)
N1 <sup>iii</sup> —K1—K1 <sup>ii</sup>	50.98 (3)	C2—C1—K1	149.08 (16)
N1—K1—K1 <sup>ii</sup>	129.02 (3)	N1—C1—H1	117.8
C1 <sup>iii</sup> —K1—K1 <sup>ii</sup>	64.64 (4)	C2—C1—H1	117.8
C1—K1—K1 <sup>ii</sup>	115.36 (4)	K1—C1—H1	73.4
O1W <sup>i</sup> —K1—K1 <sup>iv</sup>	47.81 (4)	K1 <sup>ii</sup> —O1W—K1	84.44 (4)
O1W <sup>ii</sup> —K1—K1 <sup>iv</sup>	132.19 (4)	K1 <sup>ii</sup> —O1W—H1WA	111.4
O1W—K1—K1 <sup>iv</sup>	132.24 (3)	K1—O1W—H1WA	142.8
O1W <sup>iii</sup> —K1—K1 <sup>iv</sup>	47.76 (3)	K1 <sup>ii</sup> —O1W—H1WB	102.4
N1 <sup>iii</sup> —K1—K1 <sup>iv</sup>	129.02 (3)	K1—O1W—H1WB	105.0
N1—K1—K1 <sup>iv</sup>	50.98 (3)	H1WA—O1W—H1WB	104.0

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA $\cdots$ N2 <sup>v</sup>	0.84	2.01	2.852 (2)	177
O1W—H1WB $\cdots$ N3 <sup>vi</sup>	0.88	1.97	2.831 (2)	169

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

Fig. 1

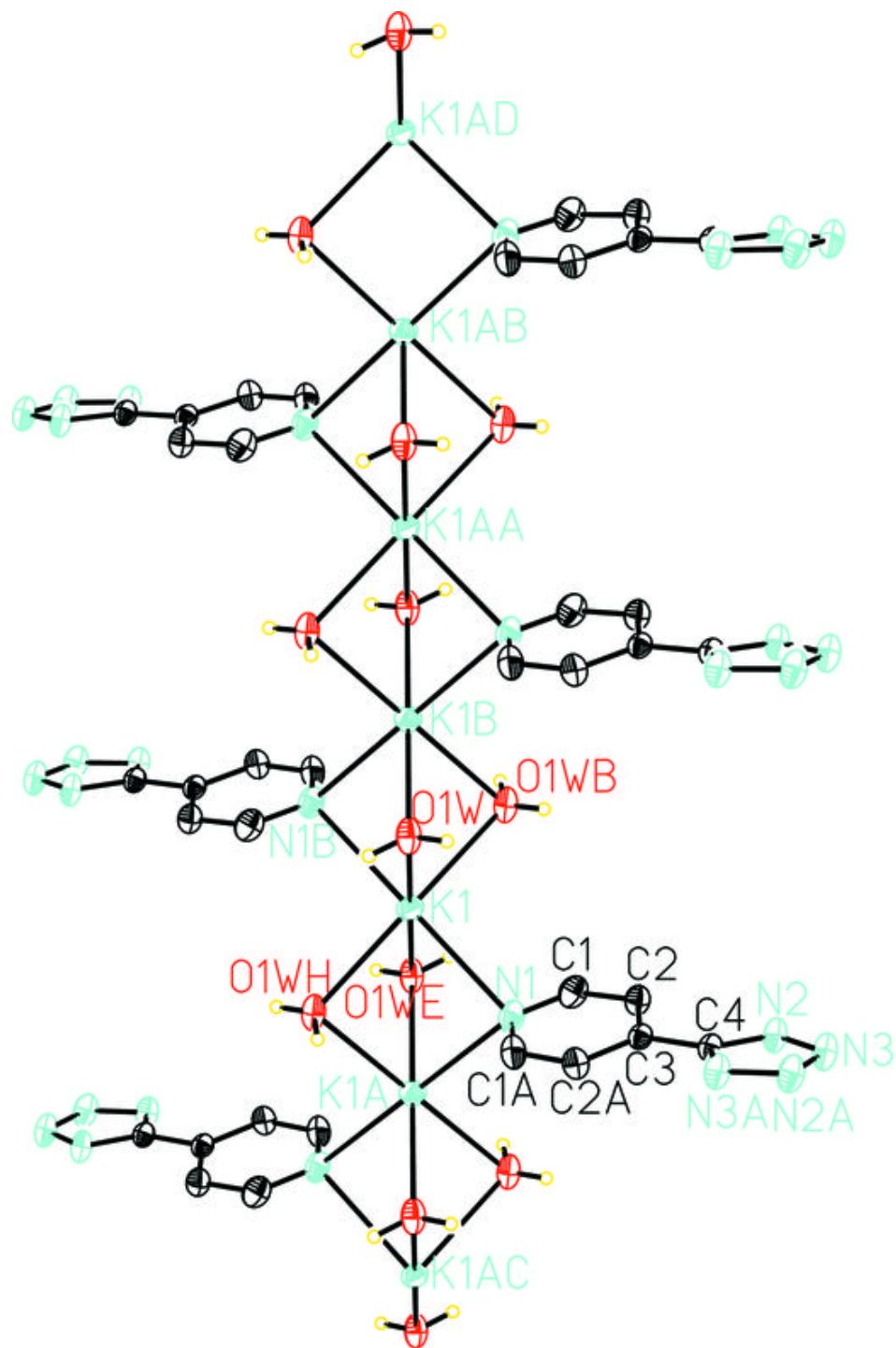




Fig. 2

