Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Dipotassium [*N*,*N*′-(propane-1,3-diyl)-dioxamato-κ^4O,N,N',O']copper(II) trihydrate: redetermination at 100 K

Daniel J. Price* and Marta Martinez-Belmonte

WestCHEM, Department of Chemistry, University of Glasgow, University Avenue, Glasgow G12 8QQ, Scotland
Correspondence e-mail: d.price@chem.gla.ac.uk

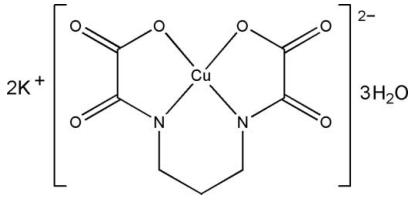
Received 3 October 2007; accepted 19 November 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.032; wR factor = 0.083; data-to-parameter ratio = 18.8.

Redetermination of the structure of the title compound, $K_2[Cu(C_7H_6N_2O_6)]\cdot 3H_2O$, at 100 K reveals conformational disorder in the almost planar copper-containing molecular dianions and clarifies the complex hydrogen-bonded network involving the water molecules. The asymmetric unit contains two independent formula units. In one of the $[Cu(C_7H_6N_2O_6)]^{2-}$ dianions, the propyl chain is disordered over two orientiations, with site-occupancy factors of 0.852 (5) and 0.148 (5).

Related literature

The structure of the title compound at room temperature has been reported previously, see: Zhu *et al.* (1999). A related monohydrate structure has been reported, see: Fritsky *et al.* (1999). For other related structures, see: Rodríguez-Romero *et al.* (1996); Cervera *et al.* (1998); Pei *et al.* (1986). For synthetic details, see: Nonoyama *et al.* (1976).



Experimental

Crystal data

$K_2[Cu(C_7H_6N_2O_6)]\cdot 3H_2O$
M_r = 409.98
Triclinic, $P\overline{1}$
a = 10.4738 (17) Å
b = 10.5498 (15) Å
c = 12.940 (2) Å
α = 72.322 (6)°
β = 78.691 (7)°
γ = 87.622 (6)°
V = 1335.6 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.31 mm^{-1}
T = 100 (2) K
0.4 × 0.2 × 0.2 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.408, T_{max} = 0.631
19933 measured reflections
7887 independent reflections
6530 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.084
S = 1.05
7887 reflections
419 parameters
18 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O13—H13B···O16^{i}	0.83 (2)	2.05 (2)	2.884 (3)	177 (2)
O13—H13A···O5	0.82 (2)	2.00 (2)	2.800 (2)	166 (3)
O14—H14A···O2	0.82 (2)	2.13 (2)	2.918 (2)	163 (2)
O14—H14B···O3^{ii}	0.82 (2)	1.99 (2)	2.806 (2)	169 (2)
O15—H15A···O14^{iii}	0.82 (2)	1.98 (2)	2.795 (2)	171 (2)
O15—H15B···O18^{iv}	0.84 (2)	2.05 (2)	2.870 (3)	167 (2)
O16—H16A···O12^{v}	0.80 (3)	2.00 (3)	2.701 (2)	147 (2)
O16—H16B···O2^{iii}	0.80 (3)	1.97 (3)	2.740 (2)	162 (2)
O17—H17A···O9	0.83 (2)	2.00 (3)	2.654 (2)	136 (2)
O17—H17B···O4^{vi}	0.84 (2)	2.01 (3)	2.807 (2)	163 (2)
O18—H18A···O16^{vii}	0.84 (2)	2.24 (3)	2.953 (3)	144 (2)
O18—H18B···O17	0.83 (2)	2.02 (2)	2.842 (3)	173 (2)

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We are grateful to the University of Glasgow for funding to MMB.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2246).

References

Brandenburg, K. (1999). *DIAMOND*. Release 2.1c. Crystal Impact GbR, Bonn, Germany.
Bruker (2006). *APEX2*. Version 2.1-4. Bruker AXS Inc., Madison, Wisconsin, USA.
Cervera, B., Sanz, J. L., Ibanez, M. J., Vila, G., Lloret, F., Julve, M., Ruiz, R., Ottenwaelder, X., Aukaullo, A., Poussereau, S., Journaux, Y. & Munoz, M. C. (1998). *J. Chem. Soc. Dalton Trans.* pp. 781–790.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Fritsky, I. O., Dudarenko, M. M., Efetova, O. P. & Kalibabchuk, V. O. (1999). *Bull. Nat. Acad. Sci. Ukraine: Geol. Chem. Biol. Sci.* pp. 144–147.
Nonoyama, K., Oijma, H. & Nonoyama, M. (1976). *Inorg. Chim. Acta*, **20**, 127–133.
Pei, Y., Kahn, O. & Sletten, J. (1986). *J. Am. Chem. Soc.* **108**, 3143–3145.
Rodríguez-Romero, F. V., Ruiz-Pérez, C. & Solans, X. (1996). *Acta Cryst.* C**52**, 1415–1417.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
Zhu, Z.-C., Xu, Z. & Huang, X.-Y. (1999). *Chin. J. Struct. Chem.* **18**, 131–135.

  doi:10.1107/S1600536807060837

supplementary materials

Acta Cryst. (2007). E**63**, m3158 [**doi:10.1107/S1600536807060837**]

Dipotassium [*N*,*N*'-(propane-1,3-diyl)dioxamato-κ^4*O*,*N*,*N*',*O*']copper(II) trihydrate: redetermination at 100 K

D. J. Price and M. Martinez-Belmonte

Comment

The asymmetric unit (Fig. 1) of the title compound contains two independent formula units. Both $[Cu(C_7H_6N_2O_6)]^{2-}$ anions have similar geometric parameters with Cu^{II} ions in square-planar CuO_2N_2 environments. Each ligand adopts a tetradentate coordination forming 5–6-5 membered chelate rings around the Cu^{II} ion (Fig. 1). The four K^+ ions in the asymmetric unit show a variety of coordination geometries with coordination numbers in the range six to eight, all being coordinated by carbonyl oxygen atoms from the $[Cu(C_7H_6N_2O_6)]^{2-}$ ion and water of crystallization. The crystal packing is shown in Fig. 2.

The structure at room temperature been reported previously by Zhu *et al.* (1999). Improved crystallographic data, collected at 100 K, allows us to see structural disorder in the ligand backbone of one $[Cu(C_7H_6N_2O_6)]^{2-}$ unit, with the minor component present at about 15%. We are also able to locate all H atoms in Fourier difference maps, enabling a good description of the important hydrogen bonded network formed by the six water molecules in the asymmetric unit (Fig. 3).

Experimental

The synthesis of the sodium salt of $[Cu(C_7H_6N_2O_6]^{2-}$ has been previously described Nonoyama *et al.* (1976). The title compound was obtained after a partial hydrolysis of the polyamide formed from 1,3-diaminopropane and diethyloxalate. A solution of 1,2-diaminopropane (0.31 g, 4.2 mmol) in absolute ethanol (10 ml) was slowly added to a refluxing solution of diethyloxalate (1.01 g, 6.9 mmol) in absolute ethanol (30 ml). The reaction was refluxed for a further 3 h, then cooled and the white solid was collected by filtration and washed with ethanol (3 *x* 10 ml). To a warm (323 K) suspension of this solid amide (0.251 g) in distilled water (20 ml) an aqueous solution of KOH (1.0 *M*) was added drop-wise until the amide had all dissolved, giving a clear solution with pH 12. A solution of $CuCl_2{\cdot}2H_2O$ (0.65 g, 3.8 mmol) in distilled water (10 ml) was added to the basic amide solution, giving at first a purple then brown solution. After 24 h a fine blue solid is precipitated which is removed by filtration. Brown needle shaped crystals of the product were then obtained by slow vapour diffusion of acetone into the aqueous phase.

Refinement

H atoms bound to C atoms were placed geometrically and allowed to ride during refinement with C—H = 0.97 Å and with U_{iso}(H) = 1.2 U_{eq}(C). In one of the complex anions conformational disorder is observed for the propyl chain of the ligand, which was modelled in two orientiations with site occupancy factors 0.852 (5) and 0.148 (5), respectively. H atoms on the water molecules were found in difference Fourier maps, and refined with the O—H and H···H distances restrained to 0.82 (3) and 1.30 (3) Å, respectively. Their displacement parameters were constrained to be 1.2 U_{eq} for the parent O atom.

Figures

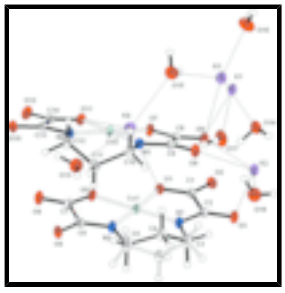


Fig. 1. The asymmetric unit of the title compound, showing the anionic molecular unit and the potassium counter ions. Displacement ellipsoids drawn at the 70% probability level.

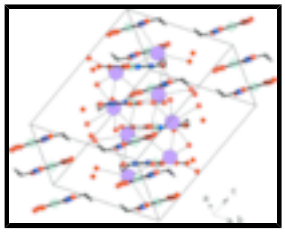


Fig. 2. A packing diagram showing the relative arangements of the complex anion and the potassium cations. Cu: cyan, K: purple, O: red, N: blue C: black, H: not shown.

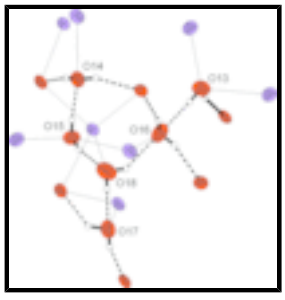


Fig. 3. The coordination spheres of the water molecules and the hydrogen bonding network that they form. Displacement ellipsoids drawn at the 90% probability level. K: purple, O: red, H: white.

Dipotassium [*N*,*N*'-(propane-1,3-diyl)dioxamato-κ^4*O*,*N*,*N*',*O*']copper(II) trihydrate

Crystal data

$K_2[Cu(C_7H_6N_2O_6)]\cdot 3H_2O$	$Z = 4$
$M_r = 409.98$	$F_{000} = 828$
Triclinic, $P\overline{1}$	$D_x = 2.039$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 10.4738$ (17) Å	Cell parameters from 6896 reflections
$b = 10.5498$ (15) Å	$\theta = 2.3$–$30.6°$
$c = 12.940$ (2) Å	$\mu = 2.31$ mm^{-1}
$\alpha = 72.322$ (6)°	$T = 100$ (2) K
$\beta = 78.691$ (7)°	Needle, brown
$\gamma = 87.622$ (6)°	0.4 × 0.2 × 0.2 mm
$V = 1335.6$ (4) Å^3	

Data collection

Bruker APEXII CCD diffractometer	7887 independent reflections

Radiation source: fine-focus sealed tube	6530 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.031$
$T = 100(2)$ K	$\theta_{max} = 30.6°$
φ and ω–scans	$\theta_{min} = 1.7°$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$h = -14 \rightarrow 14$
$T_{min} = 0.408$, $T_{max} = 0.631$	$k = -7 \rightarrow 14$
19933 measured reflections	$l = -17 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.084$	$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 1.1147P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
7887 reflections	$\Delta\rho_{max} = 1.14$ e Å^{-3}
419 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}
18 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.00614 (2)	0.61853 (2)	0.377692 (19)	0.00882 (6)	
O1	−0.11603 (14)	0.70645 (14)	0.46968 (12)	0.0114 (3)	
C1	−0.2262 (2)	0.6448 (2)	0.50706 (16)	0.0099 (4)	
C2	−0.2405 (2)	0.5175 (2)	0.47506 (16)	0.0104 (4)	
O2	−0.31996 (15)	0.67950 (15)	0.56729 (12)	0.0126 (3)	
O3	−0.34651 (15)	0.45298 (15)	0.50764 (12)	0.0132 (3)	
N1	−0.13270 (17)	0.49092 (17)	0.41369 (14)	0.0117 (3)	
C3	−0.1314 (2)	0.3744 (2)	0.37447 (19)	0.0171 (4)	

H3A	−0.2191	0.3554	0.3688	0.020*	0.852 (5)
H3B	−0.1027	0.2979	0.4279	0.020*	0.852 (5)
H3A'	−0.1665	0.2994	0.4375	0.020*	0.148 (5)
H3B'	−0.1912	0.3905	0.3236	0.020*	0.148 (5)
C4	−0.0429 (2)	0.3955 (2)	0.26375 (19)	0.0116 (5)	0.852 (5)
H4A	−0.0736	0.4718	0.2115	0.014*	0.852 (5)
H4B	−0.0522	0.3186	0.2394	0.014*	0.852 (5)
C5	0.0999 (2)	0.4176 (2)	0.25727 (19)	0.0176 (4)	
H5A	0.1324	0.3420	0.3089	0.021*	0.852 (5)
H5B	0.1468	0.4230	0.1835	0.021*	0.852 (5)
H5A'	0.0908	0.4434	0.1805	0.021*	0.148 (5)
H5B'	0.1772	0.3640	0.2628	0.021*	0.148 (5)
C4'	−0.0081 (14)	0.3338 (14)	0.3198 (11)	0.0116 (5)	0.148 (5)
H4A'	0.0254	0.2666	0.3773	0.014*	0.148 (5)
H4B'	−0.0308	0.2880	0.2711	0.014*	0.148 (5)
N2	0.12531 (17)	0.53890 (17)	0.28247 (14)	0.0114 (3)	
C6	0.2387 (2)	0.6010 (2)	0.24114 (16)	0.0105 (4)	
C7	0.2481 (2)	0.7263 (2)	0.27828 (16)	0.0101 (4)	
O4	0.33547 (14)	0.57099 (15)	0.17878 (12)	0.0131 (3)	
O5	0.14623 (14)	0.75018 (14)	0.34315 (12)	0.0121 (3)	
O6	0.34929 (15)	0.79414 (16)	0.24447 (13)	0.0152 (3)	
Cu2	0.00607 (2)	0.87837 (2)	0.118918 (19)	0.00887 (6)	
O7	−0.14892 (15)	0.86329 (15)	0.23306 (12)	0.0124 (3)	
C8	−0.2332 (2)	0.7783 (2)	0.23232 (16)	0.0097 (4)	
O8	−0.33757 (15)	0.74967 (15)	0.29780 (12)	0.0130 (3)	
C9	−0.1965 (2)	0.7087 (2)	0.14147 (16)	0.0102 (4)	
O9	−0.27554 (15)	0.62825 (15)	0.13377 (12)	0.0139 (3)	
N3	−0.07932 (17)	0.74530 (17)	0.08150 (14)	0.0104 (3)	
C10	−0.0265 (2)	0.6857 (2)	−0.00552 (16)	0.0110 (4)	
H10A	−0.0533	0.7364	−0.0736	0.013*	
H10B	−0.0610	0.5957	0.0149	0.013*	
C11	0.1224 (2)	0.6827 (2)	−0.02428 (17)	0.0120 (4)	
H11A	0.1480	0.6356	0.0453	0.014*	
H11B	0.1532	0.6325	−0.0757	0.014*	
C12	0.1896 (2)	0.8194 (2)	−0.06914 (17)	0.0132 (4)	
H12A	0.2829	0.8086	−0.0876	0.016*	
H12B	0.1603	0.8695	−0.1363	0.016*	
N4	0.16214 (17)	0.89388 (17)	0.01087 (14)	0.0107 (3)	
C13	0.2501 (2)	0.97875 (19)	0.01224 (16)	0.0092 (4)	
O10	0.36044 (14)	1.00638 (15)	−0.04981 (12)	0.0129 (3)	
C14	0.2045 (2)	1.0457 (2)	0.10437 (16)	0.0110 (4)	
O11	0.08988 (15)	1.01213 (14)	0.16221 (12)	0.0117 (3)	
O12	0.27828 (16)	1.12601 (15)	0.11610 (12)	0.0148 (3)	
K1	−0.49090 (4)	0.77624 (4)	0.04661 (4)	0.01255 (9)	
K2	−0.47340 (4)	0.52166 (5)	0.31974 (4)	0.01281 (9)	
K3	−0.48490 (5)	0.96678 (4)	0.27047 (4)	0.01381 (9)	
K4	−0.08998 (5)	0.98287 (5)	0.37159 (4)	0.01467 (10)	
O13	0.15400 (17)	0.96010 (17)	0.43218 (13)	0.0190 (3)	
H13B	0.208 (2)	1.018 (2)	0.391 (2)	0.023*	

H13A	0.166 (3)	0.899 (2)	0.405 (2)	0.023*
O14	−0.55355 (16)	0.79251 (16)	0.48618 (13)	0.0158 (3)
H14A	−0.4804 (17)	0.767 (3)	0.495 (2)	0.019*
H14B	−0.586 (2)	0.726 (2)	0.480 (2)	0.019*
O15	−0.31804 (17)	1.12393 (17)	0.33581 (13)	0.0174 (3)
H15A	−0.351 (3)	1.142 (3)	0.3924 (14)	0.021*
H15B	−0.338 (3)	1.191 (2)	0.2876 (16)	0.021*
O16	−0.65571 (17)	1.16255 (17)	0.29677 (14)	0.0204 (4)
H16A	−0.693 (3)	1.177 (3)	0.2463 (18)	0.024*
H16B	−0.679 (3)	1.212 (3)	0.333 (2)	0.024*
O17	−0.37629 (17)	0.55354 (18)	−0.01201 (15)	0.0206 (3)
H17A	−0.311 (2)	0.572 (3)	0.008 (2)	0.025*
H17B	−0.350 (3)	0.527 (3)	−0.0664 (18)	0.025*
O18	−0.42834 (18)	0.34400 (19)	0.19062 (15)	0.0243 (4)
H18A	−0.499 (2)	0.309 (3)	0.191 (2)	0.029*
H18B	−0.411 (3)	0.400 (2)	0.1284 (17)	0.029*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.00652 (12)	0.00991 (12)	0.00891 (11)	−0.00154 (9)	0.00108 (8)	−0.00260 (9)
O1	0.0095 (7)	0.0121 (7)	0.0115 (7)	−0.0012 (5)	0.0008 (5)	−0.0035 (5)
C1	0.0085 (9)	0.0134 (9)	0.0065 (8)	0.0000 (7)	−0.0023 (7)	−0.0003 (7)
C2	0.0084 (9)	0.0121 (9)	0.0097 (9)	−0.0001 (7)	−0.0016 (7)	−0.0017 (7)
O2	0.0101 (7)	0.0164 (7)	0.0114 (7)	0.0009 (6)	−0.0003 (5)	−0.0053 (6)
O3	0.0090 (7)	0.0157 (7)	0.0139 (7)	−0.0040 (6)	0.0011 (5)	−0.0048 (6)
N1	0.0080 (8)	0.0122 (8)	0.0141 (8)	−0.0024 (6)	0.0022 (6)	−0.0053 (6)
C3	0.0127 (11)	0.0148 (10)	0.0234 (11)	−0.0039 (8)	0.0048 (8)	−0.0100 (8)
C4	0.0120 (12)	0.0135 (11)	0.0109 (11)	−0.0007 (8)	−0.0018 (8)	−0.0062 (8)
C5	0.0139 (11)	0.0164 (10)	0.0230 (11)	−0.0037 (8)	0.0039 (8)	−0.0110 (9)
C4'	0.0120 (12)	0.0135 (11)	0.0109 (11)	−0.0007 (8)	−0.0018 (8)	−0.0062 (8)
N2	0.0087 (8)	0.0126 (8)	0.0127 (8)	−0.0026 (6)	0.0021 (6)	−0.0060 (6)
C6	0.0094 (9)	0.0125 (9)	0.0092 (9)	0.0002 (7)	−0.0021 (7)	−0.0023 (7)
C7	0.0095 (9)	0.0121 (9)	0.0080 (8)	−0.0014 (7)	−0.0024 (7)	−0.0014 (7)
O4	0.0076 (7)	0.0173 (7)	0.0137 (7)	−0.0016 (6)	0.0017 (5)	−0.0058 (6)
O5	0.0092 (7)	0.0126 (7)	0.0130 (7)	−0.0032 (5)	0.0020 (5)	−0.0040 (5)
O6	0.0110 (7)	0.0193 (8)	0.0148 (7)	−0.0055 (6)	0.0008 (6)	−0.0055 (6)
Cu2	0.00750 (12)	0.01079 (12)	0.00748 (11)	−0.00203 (9)	0.00116 (9)	−0.00287 (9)
O7	0.0102 (7)	0.0154 (7)	0.0106 (7)	−0.0036 (6)	0.0026 (5)	−0.0048 (5)
C8	0.0084 (9)	0.0107 (9)	0.0082 (8)	0.0005 (7)	−0.0011 (7)	−0.0007 (7)
O8	0.0094 (7)	0.0148 (7)	0.0126 (7)	−0.0007 (6)	0.0012 (5)	−0.0030 (6)
C9	0.0099 (9)	0.0111 (9)	0.0086 (8)	0.0002 (7)	−0.0015 (7)	−0.0016 (7)
O9	0.0106 (7)	0.0174 (7)	0.0141 (7)	−0.0040 (6)	−0.0005 (6)	−0.0060 (6)
N3	0.0101 (8)	0.0117 (8)	0.0090 (7)	−0.0006 (6)	0.0007 (6)	−0.0038 (6)
C10	0.0102 (10)	0.0137 (9)	0.0100 (9)	−0.0012 (7)	0.0001 (7)	−0.0057 (7)
C11	0.0106 (10)	0.0122 (9)	0.0139 (9)	−0.0002 (7)	0.0000 (7)	−0.0062 (7)
C12	0.0107 (10)	0.0166 (10)	0.0128 (9)	−0.0028 (8)	0.0022 (7)	−0.0074 (8)
N4	0.0087 (8)	0.0131 (8)	0.0105 (8)	−0.0019 (6)	0.0016 (6)	−0.0055 (6)

C13	0.0084 (9)	0.0096 (9)	0.0084 (8)	0.0005 (7)	−0.0016 (7)	−0.0012 (7)
O10	0.0078 (7)	0.0161 (7)	0.0138 (7)	−0.0019 (5)	0.0010 (5)	−0.0044 (6)
C14	0.0118 (10)	0.0122 (9)	0.0075 (8)	−0.0014 (7)	−0.0015 (7)	−0.0008 (7)
O11	0.0117 (7)	0.0134 (7)	0.0094 (7)	−0.0031 (5)	0.0006 (5)	−0.0036 (5)
O12	0.0157 (8)	0.0163 (7)	0.0124 (7)	−0.0060 (6)	−0.0006 (6)	−0.0047 (6)
K1	0.0095 (2)	0.0138 (2)	0.0122 (2)	−0.00217 (15)	0.00079 (15)	−0.00224 (15)
K2	0.0096 (2)	0.0169 (2)	0.01092 (19)	−0.00272 (16)	−0.00020 (15)	−0.00333 (16)
K3	0.0124 (2)	0.0141 (2)	0.0147 (2)	−0.00086 (16)	−0.00016 (16)	−0.00532 (16)
K4	0.0165 (2)	0.0160 (2)	0.0129 (2)	−0.00074 (17)	−0.00389 (17)	−0.00549 (16)
O13	0.0205 (9)	0.0201 (8)	0.0172 (8)	−0.0005 (7)	−0.0001 (6)	−0.0091 (6)
O14	0.0123 (8)	0.0182 (8)	0.0176 (8)	−0.0001 (6)	−0.0019 (6)	−0.0069 (6)
O15	0.0183 (8)	0.0209 (8)	0.0140 (7)	0.0029 (6)	−0.0021 (6)	−0.0076 (6)
O16	0.0217 (9)	0.0240 (9)	0.0229 (9)	0.0084 (7)	−0.0108 (7)	−0.0149 (7)
O17	0.0146 (9)	0.0279 (9)	0.0236 (9)	−0.0017 (7)	−0.0023 (7)	−0.0149 (7)
O18	0.0201 (9)	0.0256 (9)	0.0222 (9)	0.0027 (7)	0.0012 (7)	−0.0035 (7)

Geometric parameters (Å, °)

Cu1—N1	1.9131 (18)	C8—C9	1.546 (3)
Cu1—N2	1.9287 (17)	O8—K3	2.6797 (16)
Cu1—O5	1.9536 (15)	O8—K2	2.7571 (16)
Cu1—O1	1.9721 (15)	C9—O9	1.248 (2)
O1—C1	1.281 (2)	C9—N3	1.320 (3)
O1—K4	2.8057 (16)	O9—K2	2.8185 (16)
C1—O2	1.244 (2)	O9—K1	2.9041 (16)
C1—C2	1.542 (3)	N3—C10	1.459 (3)
C2—O3	1.257 (3)	C10—C11	1.530 (3)
C2—N1	1.319 (3)	C10—H10A	0.970
O2—K2^{i}	2.9294 (16)	C10—H10B	0.970
O3—K2^{i}	2.6995 (16)	C11—C12	1.527 (3)
O3—K2	2.8844 (16)	C11—H11A	0.970
N1—C3	1.464 (3)	C11—H11B	0.970
C3—C4'	1.460 (14)	C12—N4	1.459 (3)
C3—C4	1.504 (3)	C12—H12A	0.970
C3—H3A	0.970	C12—H12B	0.970
C3—H3B	0.970	N4—C13	1.317 (3)
C3—H3A'	0.970	C13—O10	1.260 (2)
C3—H3B'	0.970	C13—C14	1.552 (3)
C4—C5	1.506 (3)	O10—K1^{iii}	2.7329 (16)
C4—H4A	0.970	O10—K3^{iii}	2.8305 (16)
C4—H4B	0.970	O10—K1^{ii}	2.9128 (16)
C5—C4'	1.416 (14)	C14—O12	1.232 (3)
C5—N2	1.460 (3)	C14—O11	1.284 (3)
C5—H5A	0.970	O11—K4	2.9194 (16)
C5—H5B	0.970	O12—K1^{iii}	2.7365 (16)
C5—H5A'	0.970	K1—O17	2.8332 (18)
C5—H5B'	0.970	K2—O18	2.837 (2)
C4'—H4A'	0.970	K3—O16	2.7320 (17)

C4'—H4B'	0.970	K3—O14	2.8096 (17)
N2—C6	1.314 (3)	K3—O15	2.8617 (18)
C6—O4	1.259 (2)	K4—O13^{iv}	2.7360 (17)
C6—C7	1.551 (3)	K4—O13	2.7969 (19)
C7—O6	1.231 (3)	K4—O15	2.8027 (17)
C7—O5	1.289 (2)	O13—H13B	0.83 (2)
O4—K1^{ii}	2.7890 (16)	O13—H13A	0.82 (2)
O4—K2^{ii}	2.8939 (16)	O14—H14A	0.82 (2)
O6—K3^{ii}	2.7037 (16)	O14—H14B	0.83 (3)
O6—K1^{ii}	2.8247 (16)	O15—H15A	0.83 (3)
O6—K2^{ii}	3.3506 (17)	O15—H15B	0.84 (3)
Cu2—N4	1.9080 (18)	O16—H16A	0.80 (3)
Cu2—N3	1.9214 (18)	O16—H16B	0.81 (2)
Cu2—O7	1.9443 (15)	O17—H17A	0.82 (2)
Cu2—O11	1.9625 (15)	O17—H17B	0.83 (2)
O7—C8	1.287 (2)	O18—H18A	0.83 (2)
O7—K4	2.6567 (16)	O18—H18B	0.83 (2)
C8—O8	1.230 (2)		
N1—Cu1—N2	96.64 (8)	C11—C12—H12B	109.3
N1—Cu1—O5	178.92 (7)	H12A—C12—H12B	107.9
N2—Cu1—O5	84.42 (7)	C13—N4—C12	119.52 (17)
N1—Cu1—O1	84.37 (7)	C13—N4—Cu2	115.16 (14)
N2—Cu1—O1	177.61 (7)	C12—N4—Cu2	125.31 (14)
O5—Cu1—O1	94.58 (6)	O10—C13—N4	127.39 (19)
C1—O1—Cu1	112.10 (13)	O10—C13—C14	120.66 (18)
C1—O1—K4	123.41 (12)	N4—C13—C14	111.95 (17)
Cu1—O1—K4	108.76 (6)	C13—O10—K1^{iii}	117.31 (13)
O2—C1—O1	124.89 (19)	C13—O10—K3^{iii}	140.13 (13)
O2—C1—C2	118.74 (18)	K1^{iii}—O10—K3^{iii}	92.13 (5)
O1—C1—C2	116.37 (17)	C13—O10—K1^{ii}	101.51 (12)
O3—C2—N1	128.1 (2)	K1^{iii}—O10—K1^{ii}	105.99 (5)
O3—C2—C1	119.79 (18)	K3^{iii}—O10—K1^{ii}	94.69 (5)
N1—C2—C1	112.15 (18)	O12—C14—O11	125.32 (19)
C1—O2—K2^{i}	115.85 (13)	O12—C14—C13	118.82 (18)
C2—O3—K2^{i}	122.56 (13)	O11—C14—C13	115.86 (17)
C2—O3—K2	105.64 (12)	C14—O11—Cu2	112.40 (13)
K2^{i}—O3—K2	106.34 (5)	C14—O11—K4	147.63 (13)
C2—N1—C3	118.80 (18)	Cu2—O11—K4	96.76 (6)
C2—N1—Cu1	114.97 (14)	C14—O12—K1^{iii}	119.12 (13)
C3—N1—Cu1	126.13 (14)	O10^{iii}—K1—O12^{iii}	61.29 (5)
C4'—C3—N1	119.0 (6)	O10^{iii}—K1—O4^{v}	142.77 (5)
N1—C3—C4	111.94 (18)	O12^{iii}—K1—O4^{v}	152.08 (5)
C4'—C3—H3A	128.5	O10^{iii}—K1—O6^{v}	85.83 (5)
N1—C3—H3A	109.2	O12^{iii}—K1—O6^{v}	147.06 (5)

C4—C3—H3A	109.2	$O4^{v}$—K1—$O6^{v}$	58.72 (4)
C4'—C3—H3B	73.0	$O10^{iii}$—K1—O17	125.98 (5)
N1—C3—H3B	109.2	$O12^{iii}$—K1—O17	74.14 (5)
C4—C3—H3B	109.2	$O4^{v}$—K1—O17	78.11 (5)
H3A—C3—H3B	107.9	$O6^{v}$—K1—O17	130.91 (5)
C4'—C3—H3A'	107.6	$O10^{iii}$—K1—O9	84.50 (5)
N1—C3—H3A'	107.6	$O12^{iii}$—K1—O9	76.14 (5)
C4—C3—H3A'	137.1	$O4^{v}$—K1—O9	90.53 (5)
C4'—C3—H3B'	107.6	$O6^{v}$—K1—O9	100.13 (5)
N1—C3—H3B'	107.6	O17—K1—O9	55.10 (5)
C4—C3—H3B'	76.5	$O10^{iii}$—K1—$O10^{v}$	74.01 (5)
H3A'—C3—H3B'	107.0	$O12^{iii}$—K1—$O10^{v}$	90.17 (5)
C3—C4—C5	117.3 (2)	$O4^{v}$—K1—$O10^{v}$	108.66 (5)
C3—C4—H4A	108.0	$O6^{v}$—K1—$O10^{v}$	82.08 (5)
C5—C4—H4A	108.0	O17—K1—$O10^{v}$	137.51 (5)
C3—C4—H4B	108.0	O9—K1—$O10^{v}$	158.22 (5)
C5—C4—H4B	108.0	$O3^{i}$—K2—O8	93.93 (5)
H4A—C4—H4B	107.2	$O3^{i}$—K2—O9	151.45 (5)
C4'—C5—N2	120.2 (6)	O8—K2—O9	59.29 (4)
N2—C5—C4	112.26 (19)	$O3^{i}$—K2—O18	136.49 (5)
C4'—C5—H5A	72.3	O8—K2—O18	129.53 (5)
N2—C5—H5A	109.2	O9—K2—O18	70.65 (5)
C4—C5—H5A	109.2	$O3^{i}$—K2—O3	73.66 (5)
C4'—C5—H5B	127.7	O8—K2—O3	75.51 (4)
N2—C5—H5B	109.2	O9—K2—O3	105.64 (5)
C4—C5—H5B	109.2	O18—K2—O3	114.72 (5)
H5A—C5—H5B	107.9	$O3^{i}$—K2—$O4^{v}$	91.61 (5)
C4'—C5—H5A'	107.3	O8—K2—$O4^{v}$	112.26 (5)
N2—C5—H5A'	107.3	O9—K2—$O4^{v}$	90.16 (5)
C4—C5—H5A'	76.2	O18—K2—$O4^{v}$	71.87 (5)
C4'—C5—H5B'	107.3	O3—K2—$O4^{v}$	164.10 (4)
N2—C5—H5B'	107.3	$O3^{i}$—K2—$O2^{i}$	58.66 (4)
C4—C5—H5B'	137.4	O8—K2—$O2^{i}$	152.46 (5)
H5A'—C5—H5B'	106.9	O9—K2—$O2^{i}$	148.07 (4)
C5—C4'—C3	126.7 (10)	O18—K2—$O2^{i}$	77.98 (5)
C5—C4'—H4A'	105.6	O3—K2—$O2^{i}$	92.55 (4)
C3—C4'—H4A'	105.6	$O4^{v}$—K2—$O2^{i}$	74.27 (4)
C5—C4'—H4B'	105.6	$O3^{i}$—K2—$O6^{v}$	68.82 (4)
C3—C4'—H4B'	105.6	O8—K2—$O6^{v}$	68.37 (4)
H4A'—C4'—H4B'	106.1	O9—K2—$O6^{v}$	90.39 (4)
C6—N2—C5	119.85 (18)	O18—K2—$O6^{v}$	120.48 (5)
C6—N2—Cu1	114.65 (14)	O3—K2—$O6^{v}$	124.74 (4)

C5—N2—Cu1	125.48 (14)	O4^{v}—K2—O6^{v}	51.68 (4)
O4—C6—N2	128.8 (2)	O2^{i}—K2—O6^{v}	100.65 (4)
O4—C6—C7	118.82 (18)	O8—K3—O6^{v}	80.17 (5)
N2—C6—C7	112.39 (17)	O8—K3—O16	166.04 (5)
O6—C7—O5	125.6 (2)	O6^{v}—K3—O16	99.19 (5)
O6—C7—C6	118.86 (18)	O8—K3—O14	69.03 (5)
O5—C7—C6	115.55 (18)	O6^{v}—K3—O14	77.95 (5)
C6—O4—K1^{ii}	117.31 (13)	O16—K3—O14	97.13 (5)
C6—O4—K2^{ii}	100.63 (12)	O8—K3—O10^{iii}	78.67 (5)
K1^{ii}—O4—K2^{ii}	83.00 (4)	O6^{v}—K3—O10^{iii}	86.26 (5)
C7—O5—Cu1	112.98 (13)	O16—K3—O10^{iii}	115.27 (5)
C7—O6—K3^{ii}	149.85 (14)	O14—K3—O10^{iii}	145.90 (5)
C7—O6—K1^{ii}	117.26 (13)	O8—K3—O15	96.70 (5)
K3^{ii}—O6—K1^{ii}	92.87 (5)	O6^{v}—K3—O15	170.50 (5)
C7—O6—K2^{ii}	90.70 (12)	O16—K3—O15	81.66 (5)
K3^{ii}—O6—K2^{ii}	96.66 (5)	O14—K3—O15	92.55 (5)
K1^{ii}—O6—K2^{ii}	74.62 (4)	O10^{iii}—K3—O15	102.00 (5)
N4—Cu2—N3	97.12 (7)	O7—K4—O13^{iv}	149.28 (5)
N4—Cu2—O7	177.77 (7)	O7—K4—O13	122.30 (5)
N3—Cu2—O7	84.63 (7)	O13^{iv}—K4—O13	79.99 (6)
N4—Cu2—O11	84.61 (7)	O7—K4—O15	84.01 (5)
N3—Cu2—O11	178.08 (6)	O13^{iv}—K4—O15	81.34 (5)
O7—Cu2—O11	93.63 (6)	O13—K4—O15	150.97 (5)
C8—O7—Cu2	112.87 (13)	O7—K4—O1	68.72 (5)
C8—O7—K4	138.61 (13)	O13^{iv}—K4—O1	94.44 (5)
Cu2—O7—K4	106.22 (6)	O13—K4—O1	86.35 (5)
O8—C8—O7	124.83 (19)	O15—K4—O1	117.16 (5)
O8—C8—C9	119.32 (18)	O7—K4—O11	61.23 (4)
O7—C8—C9	115.85 (17)	O13^{iv}—K4—O11	149.49 (5)
C8—O8—K3	108.63 (12)	O13—K4—O11	77.03 (5)
C8—O8—K2	120.21 (13)	O15—K4—O11	110.54 (5)
K3—O8—K2	113.34 (6)	O1—K4—O11	103.79 (4)
O9—C9—N3	128.80 (19)	K4^{iv}—O13—K4	100.01 (6)
O9—C9—C8	119.22 (18)	K4^{iv}—O13—H13B	106.5 (18)
N3—C9—C8	111.97 (18)	K4—O13—H13B	114 (2)
C9—O9—K2	117.15 (13)	K4^{iv}—O13—H13A	143.5 (19)
C9—O9—K1	108.51 (12)	K4—O13—H13A	86 (2)
K2—O9—K1	82.31 (4)	H13B—O13—H13A	104 (2)
C9—N3—C10	119.53 (17)	K3—O14—H14A	98.1 (19)
C9—N3—Cu2	114.60 (14)	K3—O14—H14B	105.8 (19)
C10—N3—Cu2	125.86 (14)	H14A—O14—H14B	102 (2)
N3—C10—C11	111.04 (16)	K4—O15—K3	108.62 (6)
N3—C10—H10A	109.4	K4—O15—H15A	108.3 (19)
C11—C10—H10A	109.4	K3—O15—H15A	114 (2)

N3—C10—H10B	109.4	K4—O15—H15B	135.9 (19)
C11—C10—H10B	109.4	K3—O15—H15B	88.7 (19)
H10A—C10—H10B	108.0	H15A—O15—H15B	101 (2)
C12—C11—C10	114.65 (17)	K3—O16—H16A	105.0 (19)
C12—C11—H11A	108.6	K3—O16—H16B	144.0 (19)
C10—C11—H11A	108.6	H16A—O16—H16B	111 (2)
C12—C11—H11B	108.6	K1—O17—H17A	86 (2)
C10—C11—H11B	108.6	K1—O17—H17B	142 (2)
H11A—C11—H11B	107.6	H17A—O17—H17B	107 (2)
N4—C12—C11	111.76 (17)	K2—O18—H18A	110 (2)
N4—C12—H12A	109.3	K2—O18—H18B	98 (2)
C11—C12—H12A	109.3	H18A—O18—H18B	104 (2)
N4—C12—H12B	109.3		

Symmetry codes: (i) −*x*−1, −*y*+1, −*z*+1; (ii) *x*+1, *y*, *z*; (iii) −*x*, −*y*+2, −*z*; (iv) −*x*, −*y*+2, −*z*+1; (v) *x*−1, *y*, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O13—H13B···O16^{ii}	0.83 (2)	2.05 (2)	2.884 (3)	177 (2)
O13—H13A···O5	0.82 (2)	2.00 (2)	2.800 (2)	166 (3)
O14—H14A···O2	0.82 (2)	2.13 (2)	2.918 (2)	163 (2)
O14—H14B···O3^{i}	0.82 (2)	1.99 (2)	2.806 (2)	169 (2)
O15—H15A···O14^{vi}	0.82 (2)	1.98 (2)	2.795 (2)	171 (2)
O15—H15B···O18^{vii}	0.84 (2)	2.05 (2)	2.870 (3)	167 (2)
O16—H16A···O12^{v}	0.80 (3)	2.00 (3)	2.701 (2)	147 (2)
O16—H16B···O2^{vi}	0.80 (3)	1.97 (3)	2.740 (2)	162 (2)
O17—H17A···O9	0.83 (2)	2.00 (3)	2.654 (2)	136 (2)
O17—H17B···O4^{viii}	0.84 (2)	2.01 (3)	2.807 (2)	163 (2)
O18—H18A···O16^{ix}	0.84 (2)	2.24 (3)	2.953 (3)	144 (2)
O18—H18B···O17	0.83 (2)	2.02 (2)	2.842 (3)	173 (2)

Symmetry codes: (ii) *x*+1, *y*, *z*; (i) −*x*−1, −*y*+1, −*z*+1; (vi) −*x*−1, −*y*+2, −*z*+1; (vii) *x*, *y*+1, *z*; (v) *x*−1, *y*, *z*; (viii) −*x*, −*y*+1, −*z*; (ix) *x*, *y*−1, *z*.

Fig. 1

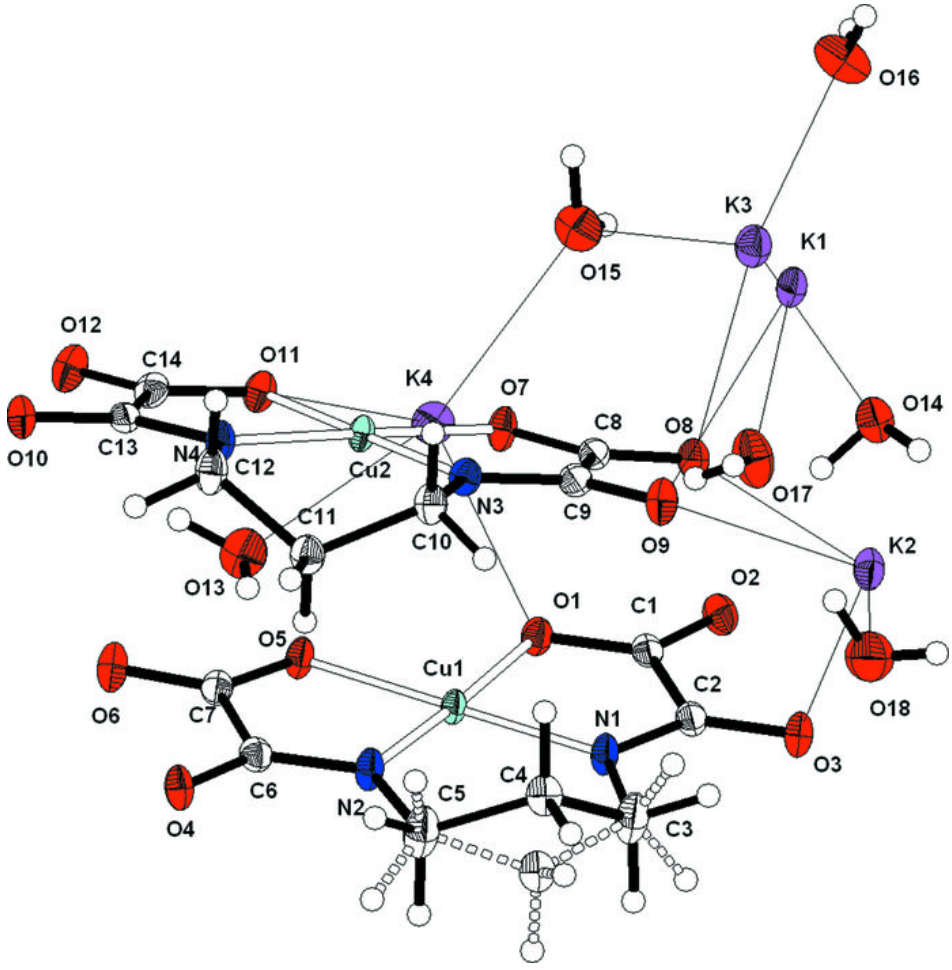

O16
K3
K1
O15
O12
C14
O11
K4
O7
C8
O8
O14
O10
C13
N4
C12
Cu2
N3
C9
O17
C11
C10
O9
K2
O13
O1
C1
O2
O5
Cu1
C2
O6
C7
N1
O18
O3
C6
C5
C4
N2
O4
C3

Fig. 2

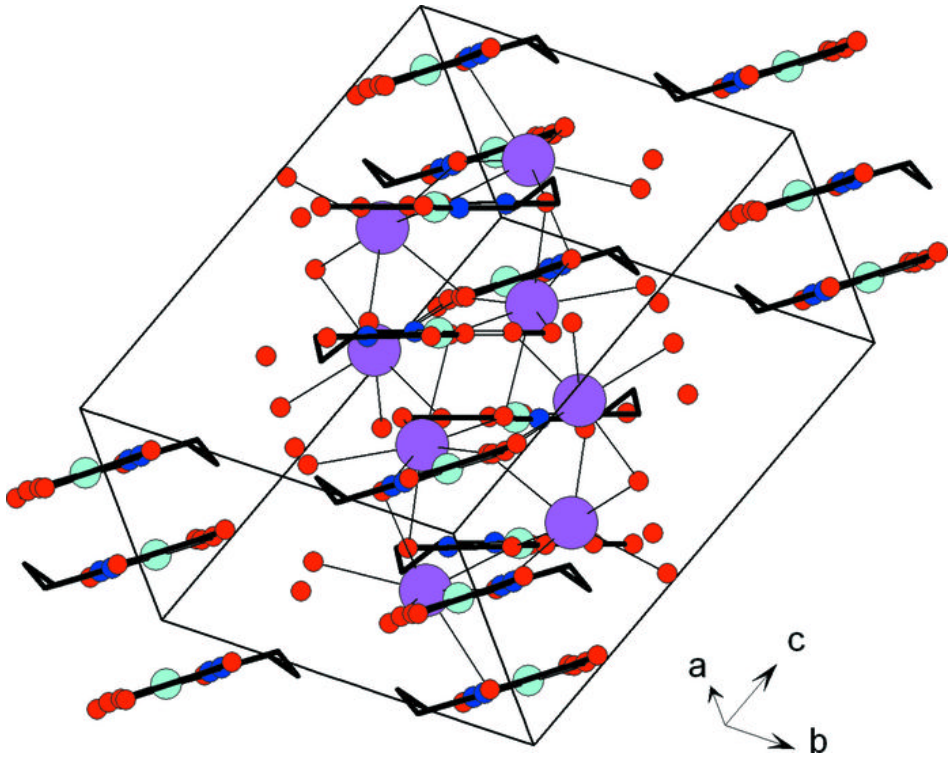


Fig. 3