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Poly[aqua(μ_2-4,4′-bipyridyl-κ^2N:N')-(μ_2-3-phosphonatobenzenesulfonato-κ^2O:O')copper(II)]

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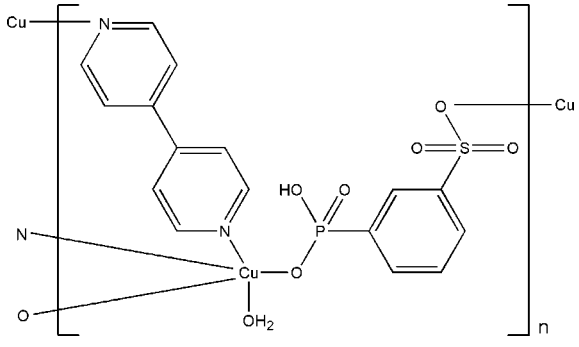
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.047; wR factor = 0.105; data-to-parameter ratio = 12.8.

The title polymer, $[Cu(C_6H_5O_6PS)(C_{10}H_8N_2)(H_2O)]_n$, was synthesized by a hydrothermal method. The Cu^{II} ion is five-coordinated by one phosphonate O atom, one sulfonate O atom, two N atoms of the bipyridyl ligand and one water molecule. The coordination geometry around the metal centre can be described as slightly distorted square-pyramidal. The Cu^{II} ions are connected by bidentate bridging phosphonatobenzenesulfonate ligands, forming one-dimensional helical chains along [010], which are further bridged by bidentate 4,4′-bipyridyl ligands, generating a two-dimensional layered crystal structure. The layered structure features an eight-membered ring including four Cu^{II} ions, two $[O_3S–C_6H_4–PO_3H]^{2-}$ anions and two 4,4′-bipyridyl ligands. Hydrogen bonds involving aqua ligands, phosphonate O and sulfonate O atoms are observed between the layers,

Related literature

For related literature on metal phosphonate chemistry, see: Clearfield (1998); Maeda (2004); Mao (2007). A related chemistry using two bridging ligands has been developed: Du *et al.* (2006*a*, 2006*b*); Du, Li, Liu & Mao (2007); Du, Xu, Li & Mao (2007). For complexes structurally related to the title compound, see: Drumel *et al.* (1996); Zhong *et al.* (2005).



Experimental

Crystal data

$[Cu(C_6H_5O_6PS)(C_{10}H_8N_2)(H_2O)]$
M_r = 473.87
Monoclinic, $P2_1/c$
a = 10.9824 (2) Å
b = 11.2924 (3) Å
c = 15.1189 (3) Å
β = 110.331 (1)°
V = 1758.20 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.50 mm^{-1}
T = 293 (2) K
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.645, T_{max} = 0.741
9468 measured reflections
3351 independent reflections
2413 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.106
S = 1.09
3351 reflections
261 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.82 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WB···O3^{i}	0.87 (5)	1.74 (6)	2.595 (4)	166 (5)
O1W—H1WA···O5^{ii}	0.90 (6)	1.82 (6)	2.701 (5)	163 (5)
O2—H2B···O6^{iii}	0.82	1.86	2.631 (5)	156

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2004) and *DIAMOND* (Brandenburg, 1999); 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: BH2137).

References

Brandenburg, K. (1999). *DIAMOND*. Version 2.1c. Crystal Impact GbR, Bonn, Germany.
Bruker (2004). *APEX2* (Version 1.22), *SAINT* (Version 6.0) and *SHELXTL* (Version 5.1). Bruker AXS Inc., Madison, Wisconsin, USA.
Clearfield, A. (1998). *Metal phosphonate chemistry*. In *Progress in Inorganic Chemistry*, Vol. 47, edited by K. D. Karlin, pp. 371–510. New York: John Wiley & Sons.
Drumel, S., Janvier, P., Bujoli-Doeuff, M. & Bujoli, B. (1996). *Inorg. Chem.* **35**, 5786–5790.
Du, Z.-Y., Li, X.-L., Liu, Q.-Y. & Mao, J.-G. (2007). *Cryst. Growth Des.* **7**, 1501–1507.
Du, Z.-Y., Xu, H.-B., Li, X.-L. & Mao, J.-G. (2007). *Eur. J. Inorg. Chem.* 4520–4529.
Du, Z.-Y., Xu, H.-B. & Mao, J.-G. (2006*a*). *Inorg. Chem.* **45**, 6424–6430.

  doi:10.1107/S1600536807050763

Du, Z.-Y., Xu, H.-B. & Mao, J.-G. (2006*b*). *Inorg. Chem.* **45**, 9780–9788.
Maeda, K. (2004). *Microporous Mesoporous Mater.* **73**, 47–55.
Mao, J.-G. (2007). *Coord. Chem. Rev.* **251**, 1493–1520.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Zhong, Z., Postnikova, B. J., Hanes, R. E., Lynch, V. M. & Anslyn, E. V. (2005). *Chem. Eur. J.* **11**, 2385–2394.

supplementary materials

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Poly[aqua(μ_2-4,4'-bipyridyl-κ^2N:N')(μ_2-3-phosphonatobenzenesulfonato-κ^2O:O')copper(II)]

Z.-Y. Du, Y.-R. Xie and H.-R. Wen

Comment

The chemistry of metal phosphonates has been a research field of rapid expansion in recent years, mainly due to their potential applications in the area of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry (Clearfield, 1998; Maeda, 2004; Mao, 2007). The strategy of attaching functional groups such as amine, hydroxyl or carboxylate groups to the phosphonic acid can lead to a number of new metal phosphonates with micro-porous or open-framework structures. However, reports on the use of sulfonate group as a functional group to build metal phosphonate open frameworks are almost unknown to date. Recently, our increasing attention has been devoted to the metal coordination chemistry of phenylphosphonic acid ligand bonded to a sulfonate group, which can adopt a variety of coordination modes and form a variety of metal cluster compounds when an ancillary ligand, such as 1,10-phenanthroline or 4,4'-bipyridyl (4,4'-bipy), is also applied (Du *et al.*, 2006*a*, 2006*b*; Du, Li, Liu & Mao, 2007; Du, Xu, Li & Mao, 2007). As an expansion of our previous work, we have also obtained a Cu^{II} sulfonate-phosphonate by applying this synthetic route. Herein, we report its synthesis and crystal structure.

The structure of the title compound features a layered architecture. The asymmetric unit contains one Cu^{II} ion, one $[O_3S—C_6H_4—PO_3H]^{2-}$ dianion, one 4,4'-bipy molecule, and one coordinated water molecule. Cu^{II} ion is five-coordinated with one phosphonate O atom from one $[O_3S—C_6H_4—PO_3H]^{2-}$ anion, one sulfonate O atom from a symmetry related $[O_3S—C_6H_4—PO_3H]^{2-}$ anion, two N atoms from two symmetry related 4,4'-bipy ligands, and one water molecule (Fig. 1). The coordination geometry around Cu can be described as a slightly distorted square-pyramid. The square plane is formed by one phosphonate O atom, two N atoms and the water molecule. The apical position is occupied by a sulfonate O atom. The Cu—O [1.964 (3)–2.234 (3) Å] and Cu—N [1.992 (3)–1.994 (3) Å] bond lengths are comparable to those reported for other Cu^{II} sulfonate/phosphonates complexes (Drumel *et al.*, 1996; Zhong *et al.*, 2005).

The phosphonate group is not completely deprotonated, as required for charge balance. The $[O_3S—C_6H_4—PO_3H]^{2-}$ ligand is bidentate and bridges two Cu^{II} ions *via* one phosphonate O atom and one sulfonate O atom. These bridges result in the formation of a one-dimensional helical chain along [010] (Fig. 2). These helical chains are further connected by bidentate bridging 4,4'-bipy ligands, to form a layered architecture (Fig. 3). The layered structure features an eight-membered ring including four Cu^{II} ions, two $[O_3S—C_6H_4—PO_3H]^{2-}$ anions and two 4,4'-bipy ligands. Between the layers, hydrogen bonds are formed, involving phosphonate O atom O2, sulfonate O atom O6 and the water molecule O1W (Fig. 4; Table 2). The O···O contacts range from 2.595 (4) to 2.701 (5) Å. Such a complex hydrogen-bond network is likely to contribute to the overall stability of the crystal structure and prevents guest molecules entering into the interstitial voids between the layers.

Experimental

A mixture of $Cu(OAc)_2$ (65 mg, 0.36 mmol), 3-phosphono-benzenesulfonic acid (86 mg, 0.36 mmol) and 4,4'-bipy (50 mg, 0.32 mmol) in 10 ml distilled water with an initial pH value of *ca*. 3.5, was put into a Parr Teflon-lined autoclave (23 ml) and heated at 413 K for 4 days. Blue brick-shaped crystals of the title polymer were collected in a *ca*. 12% yield based on Cu. Analysis calculated for $C_{16}H_{15}O_7N_2P_1S_1Cu_1$: C 40.55, H 3.19, N 5.91%; found: C 40.64, H 3.30, N 5.82%.

Refinement

H atoms bonded to C atoms were positioned geometrically and included in the refinement using a riding-model approximation, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(carrier C). Water H atoms were located in a difference map and refined with O—H and H···H distances restrained to 0.85 (1) and 1.39 (1) Å, respectively, and U_{iso}(H) = 1.5U_{eq}(O1W). H atom of protonated HPO_3 group was positioned geometrically (O—H = 0.82 Å) and included in the refinement in the riding-model approximation, with U_{iso}(H) = 1.5U_{eq}(O2).

Figures

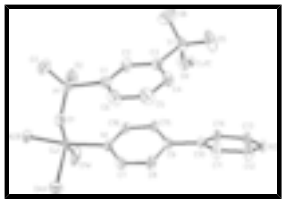

Fig. 1. A view of the structure of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Atoms labeled with the suffixes A, B and C are generated by symmetry codes (−*x*, 1/2 + *y*, 1/2 − *z*), (−1 + *x*, 1/2 − *y*, −1/2 + *z*) and (−*x*, −1/2 + *y*, 1/2 − *z*), respectively.

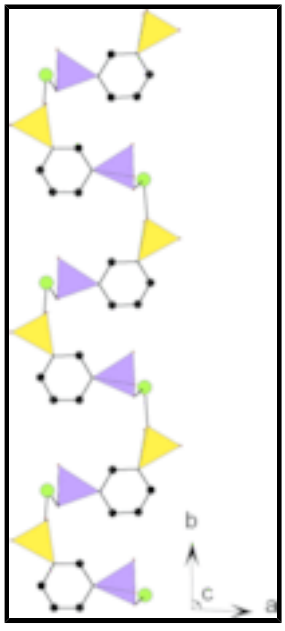

Fig. 2. A one-dimensional helical chain of Cu^{II} sulfonate-phosphonate in the title compound. Cu and C atoms are drawn as green and black circles, respectively. The CPO_3 and CSO_3 groups are shaded in pink and yellow, respectively. H atoms have been omitted for clarity.

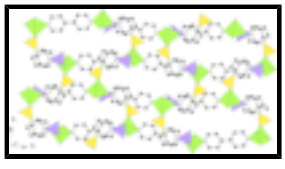

Fig. 3. View of the layer structure of the title compound down [001]. The CuO_3N_2 polyhedra, CPO_3 and CSO_3 groups are shaded in green, pink and yellow, respectively. C atoms are drawn as black circles and H atoms have been omitted for clarity.

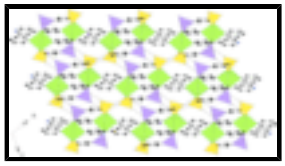

Fig. 4. View of the three-dimensional supramolecular structure of the title compound down [010]. The CuO_3N_2 polyhedra, CPO_3 and CSO_3 groups are shaded in green, pink and yellow, respectively. C atoms are drawn as black circles and H atoms have been omitted for clarity. Hydrogen bonds are represented by dashed lines.

Poly[aqua(μ$_2$-4,4'-bipyridyl-κ^2*N*:*N*')(μ$_2$-3-\ phosphonatobenzenesulfonato-κ^2*O*:*O*')copper(II)]

Crystal data

$[Cu(C_6H_5O_6PS)(C_{10}H_8N_2)(H_2O)]$	$F_{000} = 964$
$M_r = 473.87$	$D_x = 1.790$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 3426 reflections
$a = 10.9824$ (2) Å	$\theta = 2.3$–25.7º
$b = 11.2924$ (3) Å	$\mu = 1.50$ mm^{-1}
$c = 15.1189$ (3) Å	$T = 293$ (2) K
$\beta = 110.3310$ (10)º	Brick, blue
$V = 1758.20$ (7) Å^3	0.30 × 0.25 × 0.20 mm
$Z = 4$	

Data collection

Bruker SMART APEXII CCD diffractometer	3351 independent reflections
Radiation source: fine-focus sealed tube	2413 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.052$
$T = 293$(2) K	$\theta_{max} = 25.7$º
narrow frame method scans	$\theta_{min} = 2.3$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -13\rightarrow12$
$T_{min} = 0.645$, $T_{max} = 0.741$	$k = -13\rightarrow10$
9468 measured reflections	$l = -18\rightarrow18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.047$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.106$	$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 2.653P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} < 0.001$
3351 reflections	$\Delta\rho_{max} = 0.82$ e Å^{-3}
261 parameters	$\Delta\rho_{min} = -0.52$ e Å^{-3}

Primary atom site location: structure-invariant direct methods

Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	−0.25750 (5)	0.30566 (5)	0.18344 (3)	0.02307 (16)
P1	−0.12583 (11)	0.29056 (10)	0.03360 (7)	0.0269 (3)
S1	0.33196 (10)	0.04087 (10)	0.19138 (8)	0.0301 (3)
N1	−0.0778 (3)	0.2833 (3)	0.2746 (2)	0.0218 (8)
N2	0.5660 (3)	0.2033 (3)	0.5851 (2)	0.0266 (8)
C1	0.0481 (4)	0.2855 (4)	0.0959 (3)	0.0250 (10)
C2	0.1169 (4)	0.1801 (4)	0.1125 (3)	0.0260 (10)
H2A	0.0747	0.1098	0.0877	0.031*
C3	0.2487 (4)	0.1789 (4)	0.1661 (3)	0.0229 (9)
C4	0.3123 (4)	0.2822 (4)	0.2027 (3)	0.0310 (11)
H4A	0.3997	0.2807	0.2400	0.037*
C5	0.2458 (5)	0.3879 (4)	0.1837 (4)	0.0413 (12)
H5A	0.2893	0.4582	0.2070	0.050*
C6	0.1144 (4)	0.3905 (4)	0.1301 (3)	0.0362 (11)
H6A	0.0705	0.4624	0.1170	0.043*
C7	−0.0052 (4)	0.3733 (4)	0.3224 (3)	0.0309 (10)
H7A	−0.0419	0.4484	0.3162	0.037*
C8	0.1217 (4)	0.3587 (4)	0.3804 (3)	0.0332 (11)
H8A	0.1693	0.4237	0.4118	0.040*
C14	0.4058 (4)	0.3201 (4)	0.4718 (3)	0.0390 (12)
H11A	0.3841	0.3917	0.4398	0.047*
C13	0.5286 (4)	0.3021 (5)	0.5364 (3)	0.0416 (12)
H12A	0.5887	0.3631	0.5463	0.050*
C12	0.4804 (4)	0.1147 (4)	0.5676 (3)	0.0319 (11)
H13A	0.5055	0.0437	0.6000	0.038*
C11	0.3556 (4)	0.1246 (4)	0.5027 (3)	0.0305 (10)
H14A	0.2994	0.0603	0.4913	0.037*
C10	0.3146 (4)	0.2293 (4)	0.4552 (3)	0.0243 (10)
C9	0.1792 (4)	0.2478 (4)	0.3922 (3)	0.0234 (9)
C15	0.1028 (4)	0.1546 (4)	0.3436 (3)	0.0258 (10)
H17A	0.1362	0.0781	0.3496	0.031*
C16	−0.0228 (4)	0.1768 (4)	0.2864 (3)	0.0277 (10)
H18A	−0.0725	0.1135	0.2539	0.033*
O1	−0.1830 (3)	0.3664 (3)	0.09164 (19)	0.0294 (7)
O2	−0.1690 (3)	0.1599 (3)	0.0405 (2)	0.0424 (9)
H2B	−0.2074	0.1342	−0.0126	0.064*
O3	−0.1557 (3)	0.3310 (3)	−0.0648 (2)	0.0389 (8)
O4	0.2841 (3)	−0.0182 (3)	0.2586 (2)	0.0396 (8)
O5	0.4693 (3)	0.0663 (3)	0.2314 (3)	0.0547 (10)
O6	0.2960 (4)	−0.0212 (3)	0.1014 (2)	0.0618 (11)
O1W	−0.3168 (3)	0.2021 (4)	0.2649 (2)	0.0486 (10)
H1WB	−0.273 (5)	0.185 (5)	0.324 (4)	0.054 (17)*
H1WA	−0.397 (6)	0.170 (5)	0.251 (4)	0.063 (18)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0101 (2)	0.0324 (3)	0.0205 (3)	−0.0011 (2)	−0.00244 (19)	0.0020 (2)
P1	0.0194 (6)	0.0349 (7)	0.0226 (6)	0.0000 (5)	0.0025 (5)	0.0020 (5)
S1	0.0210 (6)	0.0277 (6)	0.0382 (6)	−0.0018 (4)	0.0059 (5)	0.0023 (5)
N1	0.0148 (17)	0.033 (2)	0.0160 (16)	−0.0025 (15)	0.0030 (14)	0.0025 (15)
N2	0.0147 (18)	0.033 (2)	0.0252 (18)	0.0031 (16)	−0.0021 (15)	−0.0043 (17)
C1	0.022 (2)	0.030 (3)	0.023 (2)	−0.0005 (18)	0.0080 (18)	0.0015 (18)
C2	0.021 (2)	0.025 (2)	0.029 (2)	−0.0062 (18)	0.0053 (18)	0.0022 (19)
C3	0.020 (2)	0.027 (2)	0.021 (2)	−0.0010 (18)	0.0071 (17)	0.0046 (18)
C4	0.015 (2)	0.039 (3)	0.037 (3)	−0.0042 (19)	0.0058 (19)	−0.004 (2)
C5	0.028 (3)	0.029 (3)	0.062 (3)	−0.008 (2)	0.010 (2)	−0.013 (2)
C6	0.027 (3)	0.030 (3)	0.049 (3)	0.002 (2)	0.011 (2)	0.001 (2)
C7	0.020 (2)	0.029 (3)	0.036 (3)	0.0048 (19)	0.0006 (19)	−0.002 (2)
C8	0.017 (2)	0.036 (3)	0.037 (3)	−0.0040 (19)	−0.004 (2)	−0.005 (2)
C14	0.021 (2)	0.036 (3)	0.047 (3)	−0.002 (2)	−0.004 (2)	0.012 (2)
C13	0.019 (2)	0.045 (3)	0.050 (3)	−0.006 (2)	−0.003 (2)	0.004 (3)
C12	0.022 (2)	0.035 (3)	0.029 (2)	0.006 (2)	−0.0031 (19)	0.002 (2)
C11	0.020 (2)	0.033 (3)	0.030 (2)	−0.0035 (19)	−0.0018 (19)	−0.003 (2)
C10	0.014 (2)	0.032 (3)	0.021 (2)	0.0032 (17)	−0.0010 (17)	−0.0025 (18)
C9	0.014 (2)	0.033 (2)	0.020 (2)	0.0025 (18)	0.0029 (17)	0.0034 (19)
C15	0.021 (2)	0.024 (2)	0.024 (2)	0.0040 (17)	−0.0022 (18)	0.0002 (18)
C16	0.022 (2)	0.032 (3)	0.023 (2)	−0.0041 (19)	0.0001 (18)	−0.0043 (19)
O1	0.0221 (16)	0.0367 (18)	0.0262 (16)	0.0022 (13)	0.0045 (13)	0.0057 (13)
O2	0.0341 (19)	0.037 (2)	0.046 (2)	−0.0052 (15)	0.0014 (16)	0.0017 (15)
O3	0.038 (2)	0.053 (2)	0.0217 (16)	−0.0008 (16)	0.0048 (14)	0.0050 (14)
O4	0.0273 (18)	0.043 (2)	0.048 (2)	0.0022 (15)	0.0118 (15)	0.0174 (16)
O5	0.0181 (18)	0.044 (2)	0.095 (3)	−0.0030 (15)	0.0114 (19)	0.012 (2)
O6	0.094 (3)	0.039 (2)	0.042 (2)	0.009 (2)	0.012 (2)	−0.0112 (18)
O1W	0.0240 (19)	0.075 (3)	0.035 (2)	−0.0198 (18)	−0.0045 (16)	0.021 (2)

Geometric parameters (Å, °)

Cu1—O1	1.964 (3)	C5—H5A	0.9300
Cu1—O1W	1.966 (3)	C6—H6A	0.9300
Cu1—N1	1.992 (3)	C7—C8	1.374 (6)
Cu1—N2^{i}	1.994 (3)	C7—H7A	0.9300
Cu1—O4^{ii}	2.234 (3)	C8—C9	1.386 (6)
P1—O3	1.480 (3)	C8—H8A	0.9300
P1—O1	1.510 (3)	C14—C13	1.378 (6)
P1—O2	1.564 (3)	C14—C10	1.394 (6)
P1—C1	1.813 (4)	C14—H11A	0.9300
S1—O5	1.446 (3)	C13—H12A	0.9300
S1—O4	1.457 (3)	C12—C11	1.385 (5)
S1—O6	1.458 (4)	C12—H13A	0.9300
S1—C3	1.780 (4)	C11—C10	1.375 (6)

N1—C16	1.329 (5)	C11—H14A	0.9300
N1—C7	1.338 (5)	C10—C9	1.476 (5)
N2—C13	1.321 (6)	C9—C15	1.387 (6)
N2—C12	1.335 (6)	C15—C16	1.372 (5)
N2—Cu1^{iii}	1.994 (3)	C15—H17A	0.9300
C1—C2	1.385 (6)	C16—H18A	0.9300
C1—C6	1.393 (6)	O2—O6^{iv}	2.631 (5)
C2—C3	1.392 (6)	O2—H2B	0.8200
C2—H2A	0.9300	O4—Cu1^{v}	2.234 (3)
C3—C4	1.373 (6)	O1W—O3^{vi}	2.595 (4)
C4—C5	1.377 (6)	O1W—O5^{vii}	2.701 (5)
C4—H4A	0.9300	O1W—H1WB	0.87 (5)
C5—C6	1.389 (6)	O1W—H1WA	0.90 (6)
O1—Cu1—O1W	163.85 (15)	C5—C6—H6A	119.9
O1—Cu1—N1	88.69 (12)	C1—C6—H6A	119.9
O1W—Cu1—N1	87.45 (14)	N1—C7—C8	122.4 (4)
O1—Cu1—N2^{i}	91.53 (13)	N1—C7—H7A	118.8
O1W—Cu1—N2^{i}	89.36 (14)	C8—C7—H7A	118.8
N1—Cu1—N2^{i}	169.20 (15)	C7—C8—C9	120.4 (4)
O1—Cu1—O4^{ii}	96.31 (12)	C7—C8—H8A	119.8
O1W—Cu1—O4^{ii}	99.62 (15)	C9—C8—H8A	119.8
N1—Cu1—O4^{ii}	94.27 (12)	C13—C14—C10	119.0 (4)
N2^{i}—Cu1—O4^{ii}	96.43 (13)	C13—C14—H11A	120.5
O3—P1—O1	114.69 (18)	C10—C14—H11A	120.5
O3—P1—O2	113.07 (19)	N2—C13—C14	123.9 (4)
O1—P1—O2	107.39 (18)	N2—C13—H12A	118.1
O3—P1—C1	110.94 (18)	C14—C13—H12A	118.1
O1—P1—C1	106.94 (17)	N2—C12—C11	122.3 (4)
O2—P1—C1	102.99 (19)	N2—C12—H13A	118.8
O5—S1—O4	112.1 (2)	C11—C12—H13A	118.8
O5—S1—O6	113.0 (2)	C10—C11—C12	120.2 (4)
O4—S1—O6	112.6 (2)	C10—C11—H14A	119.9
O5—S1—C3	107.4 (2)	C12—C11—H14A	119.9
O4—S1—C3	105.49 (19)	C11—C10—C14	117.0 (4)
O6—S1—C3	105.6 (2)	C11—C10—C9	122.2 (4)
C16—N1—C7	117.2 (3)	C14—C10—C9	120.8 (4)
C16—N1—Cu1	120.2 (3)	C8—C9—C15	116.9 (4)
C7—N1—Cu1	122.6 (3)	C8—C9—C10	121.5 (4)
C13—N2—C12	117.5 (4)	C15—C9—C10	121.5 (4)
C13—N2—Cu1^{iii}	119.4 (3)	C16—C15—C9	119.0 (4)
C12—N2—Cu1^{iii}	123.0 (3)	C16—C15—H17A	120.5
C2—C1—C6	118.8 (4)	C9—C15—H17A	120.5
C2—C1—P1	122.1 (3)	N1—C16—C15	124.1 (4)
C6—C1—P1	119.1 (3)	N1—C16—H18A	118.0
C1—C2—C3	120.4 (4)	C15—C16—H18A	118.0
C1—C2—H2A	119.8	P1—O1—Cu1	124.93 (18)

C3—C2—H2A	119.8	P1—O2—O6^{iv}	126.43 (19)
C4—C3—C2	120.4 (4)	P1—O2—H2B	109.5
C4—C3—S1	120.4 (3)	S1—O4—Cu1^{v}	144.0 (2)
C2—C3—S1	119.1 (3)	Cu1—O1W—O3^{vi}	116.55 (17)
C3—C4—C5	119.6 (4)	Cu1—O1W—O5^{vii}	132.54 (18)
C3—C4—H4A	120.2	O3^{vi}—O1W—O5^{vii}	110.66 (16)
C5—C4—H4A	120.2	Cu1—O1W—H1WB	126 (3)
C4—C5—C6	120.5 (4)	O5^{vii}—O1W—H1WB	101 (3)
C4—C5—H5A	119.7	Cu1—O1W—H1WA	127 (3)
C6—C5—H5A	119.7	O3^{vi}—O1W—H1WA	117 (3)
C5—C6—C1	120.1 (4)	H1WB—O1W—H1WA	107 (5)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1WB···O3^{vi}	0.87 (5)	1.74 (6)	2.595 (4)	166 (5)
O1W—H1WA···O5^{vii}	0.90 (6)	1.82 (6)	2.701 (5)	163 (5)
O2—H2B···O6^{iv}	0.82	1.86	2.631 (5)	156

Symmetry codes: (vi) *x*, −*y*+1/2, *z*+1/2; (vii) *x*−1, *y*, *z*; (iv) −*x*, −*y*, −*z*.

Fig. 1

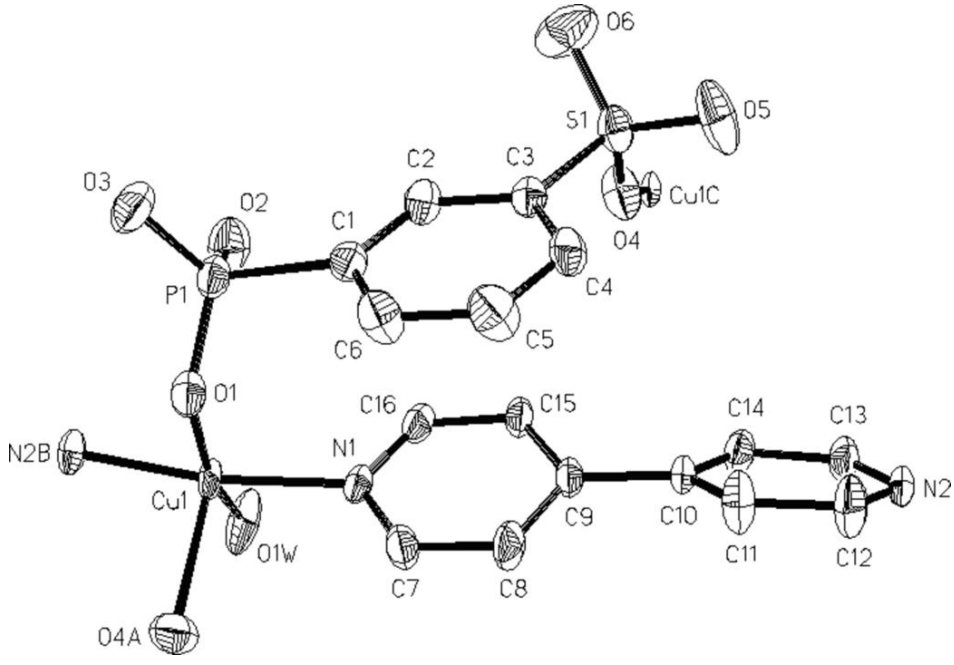
O6
S1
O5
C2
C3
O3
O2
Cu1C
C1
O4
P1
C4
C6
C5
O1
C16
C15
C14
C13
N2B
N1
N2
Cu1
C9
C10
O1W
C11
C12
C7
C8
O4A

Fig. 2

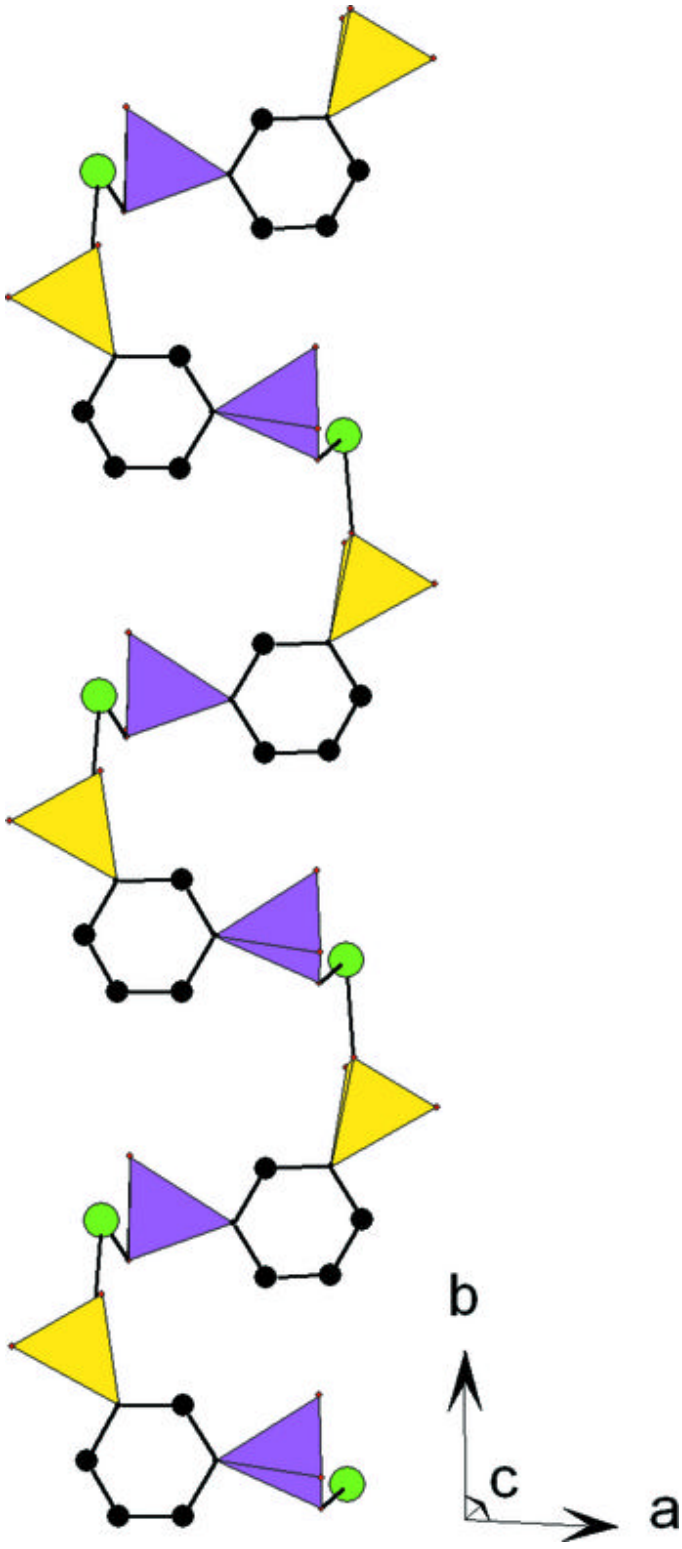

Fig. 3

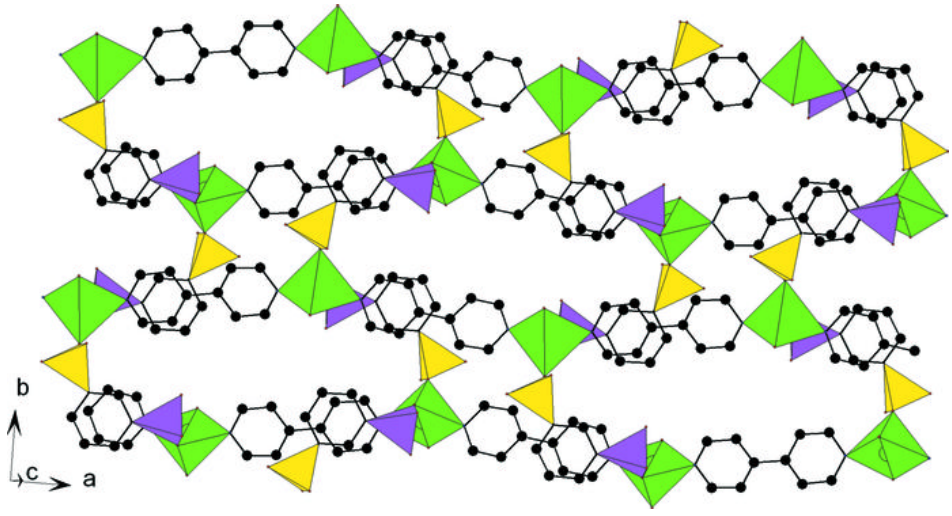

Fig. 4