

Poly[(μ_2 -1,4-benzenedicarboxylato)-aquadipyridinecopper(II) 0.25-hydrate]

Ming-Sheng Wang, Guo-Wei Zhou, Guo-Cong Guo* and Jin-Shun Huang

Fujian Institute for the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China
Correspondence e-mail: gcuo@fjirsm.ac.cn

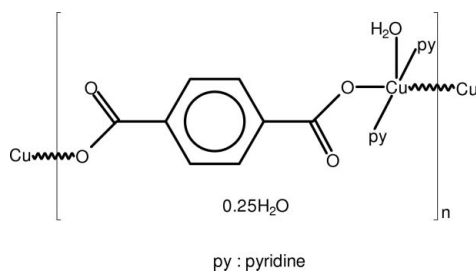
Received 21 August 2007; accepted 7 September 2007

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; H-atom completeness 97%; disorder in solvent or counterion; R factor = 0.065; wR factor = 0.141; data-to-parameter ratio = 15.3.

The title compound, $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})]_n \cdot 0.25n\text{H}_2\text{O}$, was obtained unintentionally as the product of an attempted synthesis of a 4-cyanobenzoate-bridged network complex of copper(II) using pyridine as a base to deprotonate the organic acid. Its crystal structure is built up by one-dimensional helical chains along the c direction and uncoordinated water molecules through intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds and van der Waals interactions. The investigated crystal was a partial inversion twin.

Related literature

For related literature, see: Bu *et al.* (2002); Cutland *et al.* (2001); Evans & Lin (2000); Evans *et al.* (1999); Gutschke *et al.* (2000); Lin *et al.* (1998, 2000); Ma *et al.* (1999); Ohmura *et al.* (2003); Seo *et al.* (2000); Sun *et al.* (2001); Tao *et al.* (2002); Xiong *et al.* (1998).



Experimental

Crystal data

$[\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})]_n \cdot 0.25\text{H}_2\text{O}$

$M_r = 408.37$

Orthorhombic, $P2_12_12_1$

$a = 5.9896$ (7) Å

$b = 15.2593$ (18) Å

$c = 21.581$ (2) Å

$V = 1972.4$ (4) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 1.14$ mm⁻¹

$T = 293$ (2) K

$0.48 \times 0.24 \times 0.14$ mm

Data collection

Siemens SMART CCD diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.874$, $T_{\max} = 1.000$
(expected range = 0.745–0.853)

5908 measured reflections
2927 independent reflections
1689 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.073$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$

$wR(F^2) = 0.141$

$S = 1.01$

2927 reflections

191 parameters

9 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.71$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Absolute structure: Flack (1983), with 876 Friedel pairs

Flack parameter: 0.31 (2)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1W}-\text{H1WA}\cdots\text{O21}^{\text{i}}$	0.850 (4)	2.078 (7)	2.735 (4)	133.7 (6)
$\text{O1W}-\text{H1WB}\cdots\text{O23}^{\text{ii}}$	0.850 (4)	1.889 (5)	2.719 (3)	164.9 (10)

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

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1994); data reduction: SAINT and XPREP in SHELXTL (Siemens, 1995); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

The authors gratefully acknowledge financial support from the NSF of Fujian Province (grant Nos. 2004J039 and 2006J0275).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2383).

References

- Bu, X.-H., Liu, H., Du, M., Zhang, L. & Guo, Y.-M. (2002). *Inorg. Chem.* **41**, 1855–1861.
- Cutland, A. D., Halfen, J. A., Kampf, J. W. & Pecoraro, V. L. (2001). *J. Am. Chem. Soc.* **123**, 6211–6212.
- Evans, O. R. & Lin, W. (2000). *Inorg. Chem.* **39**, 2189–2198.
- Evans, O. R., Wang, Z., Xiong, R.-G., Foxman, B. M. & Lin, W. (1999). *Inorg. Chem.* **38**, 2969–2973.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gutschke, S. O. H., Price, D. J., Powell, A. K. & Wood, P. T. (2000). *Inorg. Chem.* **39**, 3705–3707.
- Lin, W., Chapman, M. E., Wang, Z. & Yee, G. T. (2000). *Inorg. Chem.* **39**, 4169–4173.
- Lin, W., Evans, O. R., Xiong, R.-G. & Wang, Z. (1998). *J. Am. Chem. Soc.* **120**, 13272–13273.
- Ma, L., Evans, O. R., Foxman, B. M. & Lin, W. (1999). *Inorg. Chem.* **38**, 5837–5840.
- Ohmura, T., Mori, W., Hasegawa, M., Takei, T., Ikeda, T. & Hasegawa, E. (2003). *Bull. Chem. Soc. Jpn.* **76**, 1387–1395.
- Seo, J. S., Whang, D., Lee, H., Jun, S. I., Oh, J., Jeon, Y. J. & Kim, K. (2000). *Nature*, **404**, 982–986.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Siemens (1994). *SAINTE*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

- Siemens (1996). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sun, D., Cao, R., Liang, Y., Shi, Q., Su, W. & Hong, M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2335–2340.
- Tao, J., Zhang, Y., Tong, M.-L., Chen, X. M., Yuen, T., Lin, C. L., Huang, X. & Li, J. (2002). *Chem. Commun.* pp. 1342–1343.
- Xiong, R.-G., Wilson, S. R. & Lin, W. (1998). *J. Chem. Soc. Dalton Trans.* pp. 4089–4090.

supplementary materials

Acta Cryst. (2007). E63, m2524-m2525 [doi:10.1107/S1600536807043942]

Poly[(μ_2 -1,4-benzenedicarboxylato)aquadipyridinecopper(II) 0.25-hydrate]

M.-S. Wang, G.-W. Zhou, G.-C. Guo and J.-S. Huang

Comment

Many interesting *in situ* reactions such as hydrolysis (Lin *et al.*, 1998; Evans *et al.*, 1999; Lin *et al.*, 2000; Sun *et al.*, 2001), redox (Xiong *et al.*, 1998; Ma *et al.*, 1999; Evans *et al.*, 2000; Tao *et al.*, 2002), and dehydration (Gutschke *et al.*, 2000) can occur under solvothermal environment. It has been found that cyano substituted aromatic compound can be hydrolyzed and the cyano group would be changed to carboxylic acid. For example, Lin's group reported that 3-cyanopyridine or 4-cyanopyridine undergoes a hydrolysis reaction to form 3-pyridinecarboxylic acid (Lin *et al.*, 2000) and 4-pyridinecarboxylic acid (Evans *et al.*, 1999), respectively; Hong's group revealed that the hydrolysis of 1,4-dicyanobenzene gives rise to 1,4-benzenedicarboxylate acid (Sun *et al.*, 2001). The present example shows that 4-cyanobenzoic acid also undergoes a similar hydrolysis procedure.

The hydrothermal reaction of 4-cyanobenzoic acid, CuO, pyridine (py) and water under weak basified conditions gave rise to the title compound (**1**) as blue prismatic crystals, which were very easy to be efflorescent and become opaque when out of the mother liquid. The IR spectrum of (**1**) exhibits strong bands at 1605 and 1390 cm^{-1} , which are attributed to the Vas and Vas peaks of COO^- group, respectively. The absence of peaks in the range of 2240—2220 cm^{-1} shows that there exists no cyano group in (**1**).

A single-crystal X-ray diffraction analysis revealed that compound (**1**) has a similar 1-D chain structure as that of $\text{CuL}^1(\text{py})_2(\text{H}_2\text{O})\cdot\text{py}\cdot\text{H}_2\text{O}$ ($L^1 = 1,4\text{-benzenedicarboxylate}$ ligand; Ohmura *et al.*, 2003). The crystallographically independent unit of (**1**) consists of one L^1 ligand, two py ligands, one copper(II) atom, one coordination water molecule and hemisemi lattice water molecule. As show in Fig. 1, each copper(II) atom is almost in a square-based pyramidal environment, of which the axial position is occupied by coordination water molecule O1w ($\text{Cu1—O1w} = 2.243(3) \text{ \AA}$) and the square plane is defined by two nitrogen atoms from two py ligands ($\text{Cu—N} = 1.996(3)$ and $2.010(3) \text{ \AA}$), two oxygen atoms from two L^1 ligands ($\text{Cu—O} = 1.931(2)$ and $1.934(2) \text{ \AA}$) with an O24—Cu1—O22 bond angle of $178.3(1)^\circ$. The bond angles of O1w—Cu1—X ($X =$ the atoms in the square plane) vary from $89.4(1)$ to $96.2(1)^\circ$, which indicates that O1w is approximately perpendicular to the square plane. In this way, each L^1 ligand links two symmetry-related copper(II) atoms ($\text{Cu}\cdots\text{Cu}$, *ca* 10.901 \AA) into a 1-D chain along the *c* direction. Compound **1** crystallizes in space group $P2_12_12_1$, and the 1-D chain perfectly lies in the 2_1 axis. Hence, the 1-D chain is in a helical mode as the case found in the structure of $[\text{Cu}(L^2)(\text{NO}_3)_2]_8$ ($L^2 = 2,5\text{-bis}(2\text{-pyridyl})\text{-}1,3,4\text{-oxodiazole}$) (Bu *et al.*, 2002). To the best of our knowledge, 1-D helical chiral compound with bridging L^1 ligands has only a reported example in the literature (Cutland *et al.*, 2001).

Considering the short contacts shows that the neighboring parallel chains are interconnected by $\text{O—H}\cdots\text{O}$ hydrogen bonds [$\text{O1W}\cdots\text{O21}^i = 2.735(4) \text{ \AA}$, $\text{O1w—Hw1}\cdots\text{O21}^i = 133.7(6)^\circ$; $\text{O1W}\cdots\text{O23}^{ii} = 2.719(3) \text{ \AA}$, $\text{O1w—Hw2}\cdots\text{O23}^{ii} = 165(1)^\circ$; (*i*) $x - 1, y, z$; (*ii*) $-0.5 - x, 1 - y, -1/2 + z$. (Table 1)] to form a layer (Fig. 1). Each of these hydrogen bonds is established from an axially coordinated water molecule to one of the carboxylate group of a neighboring L^1 ligand. The

supplementary materials

distance of two adjacent chains agrees with the Cu1...Cu1a separation of *ca* 5.990 Å, which is shorter than the L^1 -bridged Cu...Cu separation. However, considering the short contacts between two adjacent layers, only van der Waals interactions can be found (Fig. 2). The layers are crosswise arranged along the *b* direction to form a self-complementary structure (Seo *et al.*, 2000) that apparently stabilizes the whole crystal structure. Uncoordinated water molecules locate in the channels along the *a* direction.

Experimental

A mixture of 4-cyanobenzoic acid (147 mg, 1 mmol), CuO (40 mg, 0.5 mmol), pyrimidine (1 ml) and H₂O (9 ml) was loaded into a 25-ml sealed Teflon-lined autoclave, and heated at 160 °C for 5 d, after which it was cooled to room temperature. Blue pismatic crystals of **1** were obtained by filtration of the result solution, and washed by ethanol and diethyl ether successively. IR peaks (cm⁻¹): 3363 (*m*), 3273 (*m*), 1605 (*versus*), 1502 (*m*), 1448 (*s*), 1390 (*versus*), 1356 (*versus*), 1219 (*m*), 1147 (*m*), 1070 (*m*), 1024 (*w*), 889 (*w*), 849 (*m*), 754 (*s*), 698 (*s*), 652 (*m*), 571 (*m*), 509 (*w*).

Refinement

H atoms of coordination water molecules (O1W) were located in a difference Fourier map and refined as riding in their as-found relative positions, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The *DFIX* commands were used to restrain the O—H bond distances of water molecules (Table 1). The H atoms of uncoordinated water molecules (O2W) were not included. Other H atoms were allowed to ride on their respective parent atoms with C—H distances of 0.93 Å, and were included in the refinement with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. ISOR was applied to O2W atom to avoid large adp.

Figures

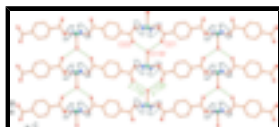


Fig. 1. 2-D hydrogen-bonding network in the *ac* plane built upon 1-D helical chains with green dash lines showing the O1w—H...O (O21 or O23) hydrogen bonds. Hydrogen atoms are omitted for clarity.

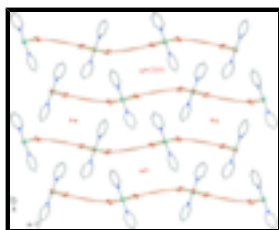


Fig. 2. 3-D packing diagram viewed along the *a* direction. Hydrogen atoms are omitted for clarity.

Poly[(μ_2 -1,4-benzenedicarboxylato)aquadipyridinecopper(II) 0.25-hydrate]

Crystal data

[Cu(C₈H₄O₄)(C₅H₅N)₂(H₂O)]·0.25H₂O

$M_r = 408.37$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$F_{000} = 838$

$D_x = 1.375 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1986 reflections

$a = 5.9896 (7) \text{ \AA}$
 $b = 15.2593 (18) \text{ \AA}$
 $c = 21.581 (2) \text{ \AA}$
 $V = 1972.4 (4) \text{ \AA}^3$
 $Z = 4$

$\theta = 2.3\text{--}25.1^\circ$
 $\mu = 1.14 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Prismatic, blue
 $0.48 \times 0.24 \times 0.14 \text{ mm}$

Data collection

Siemens SMART CCD diffractometer
 Radiation source: fine-focus sealed tube
 Monochromator: graphite
 $T = 293(2) \text{ K}$
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.874, T_{\max} = 1.000$
 5908 measured reflections

2927 independent reflections
 1689 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.073$
 $\theta_{\max} = 25.1^\circ$
 $\theta_{\min} = 2.3^\circ$
 $h = -6 \rightarrow 7$
 $k = -11 \rightarrow 18$
 $l = -23 \rightarrow 25$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.141$
 $S = 1.01$
 2927 reflections
 191 parameters
 9 restraints
 Primary atom site location: structure-invariant direct methods
 Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.032P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.71 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e \AA}^{-3}$
 Extinction correction: none
 Absolute structure: Flack (1983), 876 Friedel pairs
 Flack parameter: 0.31 (2)

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.16689 (10)	0.53883 (4)	0.34904 (2)	0.03936 (14)	
O21	0.5303 (6)	0.5146 (3)	0.45248 (14)	0.0864 (16)	
O22	0.1645 (6)	0.49792 (18)	0.43385 (11)	0.0459 (10)	
O23	-0.0356 (5)	0.4486 (3)	0.74787 (12)	0.0625 (12)	
O24	0.3310 (6)	0.42383 (19)	0.76355 (11)	0.0486 (10)	
C21	0.1555 (9)	0.4372 (3)	0.72974 (17)	0.0406 (15)	
C22	0.2054 (7)	0.4467 (3)	0.66137 (15)	0.0368 (14)	
C23	0.4192 (7)	0.4528 (5)	0.63920 (18)	0.068 (2)	
H23A	0.5386	0.4453	0.6662	0.082*	

supplementary materials

C24	0.4604 (9)	0.4698 (5)	0.5775 (2)	0.090 (2)	
H24A	0.6068	0.4770	0.5640	0.107*	
C25	0.2899 (8)	0.4763 (3)	0.53580 (16)	0.0410 (15)	
C26	0.0789 (7)	0.4670 (4)	0.55662 (18)	0.0547 (17)	
H26A	-0.0401	0.4706	0.5291	0.066*	
C27	0.0384 (8)	0.4517 (4)	0.62017 (18)	0.0632 (19)	
H27A	-0.1079	0.4449	0.6338	0.076*	
C28	0.3415 (11)	0.4975 (3)	0.46790 (19)	0.0523 (17)	
N11	0.1812 (5)	0.41556 (16)	0.31642 (10)	0.0500 (9)	
C11	0.3632 (5)	0.3621 (2)	0.32926 (15)	0.0810 (16)	
H11A	0.4814	0.3834	0.3528	0.097*	
C12	0.3685 (8)	0.2766 (2)	0.3070 (2)	0.103 (2)	
H12A	0.4903	0.2408	0.3156	0.124*	
C13	0.1918 (9)	0.24467 (19)	0.27188 (19)	0.111 (2)	
H13A	0.1953	0.1875	0.2570	0.133*	
C14	0.0097 (8)	0.2982 (2)	0.25904 (18)	0.128 (2)	
H14A	-0.1085	0.2768	0.2355	0.154*	
C15	0.0044 (6)	0.3836 (2)	0.28131 (15)	0.0891 (17)	
H15A	-0.1173	0.4194	0.2727	0.107*	
N31	0.2070 (5)	0.66163 (17)	0.37881 (11)	0.0500 (9)	
C31	0.3862 (5)	0.7127 (2)	0.35951 (16)	0.0810 (16)	
H31A	0.4865	0.6908	0.3305	0.097*	
C32	0.4155 (7)	0.7964 (2)	0.3836 (2)	0.103 (2)	
H32A	0.5354	0.8305	0.3707	0.124*	
C33	0.2655 (9)	0.8290 (2)	0.4270 (2)	0.111 (2)	
H33A	0.2851	0.8850	0.4431	0.133*	
C34	0.0863 (8)	0.7780 (2)	0.44630 (18)	0.128 (2)	
H34A	-0.0140	0.7999	0.4753	0.154*	
C35	0.0571 (6)	0.6943 (2)	0.42221 (15)	0.0891 (17)	
H35A	-0.0628	0.6602	0.4351	0.107*	
O1W	-0.2068 (4)	0.54786 (18)	0.35159 (9)	0.0553 (10)	
H1WA	-0.2573 (15)	0.5095 (3)	0.37645 (16)	0.083*	
H1WB	-0.2802 (11)	0.5393 (6)	0.31842 (15)	0.083*	
O2W	0.026 (4)	0.2549 (17)	0.4836 (10)	0.178 (5)	0.25

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0449 (3)	0.0560 (3)	0.01714 (19)	0.0003 (4)	-0.0009 (3)	0.0010 (3)
O21	0.040 (2)	0.178 (4)	0.0409 (18)	-0.022 (3)	0.0112 (19)	0.033 (2)
O22	0.050 (2)	0.068 (2)	0.0196 (13)	0.0003 (19)	0.0030 (19)	0.0028 (13)
O23	0.034 (2)	0.126 (3)	0.0277 (15)	-0.010 (3)	0.0127 (16)	0.005 (2)
O24	0.047 (2)	0.079 (2)	0.0201 (14)	0.000 (2)	-0.0019 (19)	0.0022 (14)
C21	0.042 (3)	0.053 (3)	0.027 (2)	-0.025 (3)	-0.007 (3)	-0.0031 (19)
C22	0.037 (3)	0.058 (3)	0.0153 (19)	0.004 (3)	-0.004 (2)	-0.004 (2)
C23	0.021 (3)	0.162 (5)	0.022 (2)	-0.006 (4)	-0.008 (2)	0.013 (3)
C24	0.034 (3)	0.206 (7)	0.029 (2)	0.004 (5)	0.004 (3)	0.028 (4)
C25	0.038 (3)	0.068 (3)	0.0175 (19)	0.006 (3)	-0.003 (2)	0.006 (2)

C26	0.028 (3)	0.117 (4)	0.019 (2)	-0.002 (3)	0.000 (2)	0.003 (3)
C27	0.026 (3)	0.133 (5)	0.030 (2)	-0.001 (4)	0.007 (2)	-0.005 (3)
C28	0.054 (3)	0.076 (4)	0.028 (2)	-0.006 (3)	0.001 (3)	0.005 (2)
N11	0.0537 (19)	0.0574 (18)	0.0388 (13)	0.0086 (17)	-0.0068 (17)	0.0085 (12)
C11	0.084 (3)	0.068 (3)	0.091 (3)	-0.009 (3)	-0.012 (3)	-0.002 (2)
C12	0.115 (5)	0.052 (3)	0.143 (4)	-0.015 (3)	0.010 (3)	-0.016 (3)
C13	0.144 (5)	0.071 (3)	0.118 (3)	-0.002 (3)	0.004 (4)	-0.040 (3)
C14	0.140 (5)	0.105 (4)	0.140 (4)	0.009 (4)	0.018 (4)	-0.062 (3)
C15	0.093 (4)	0.096 (4)	0.078 (3)	0.015 (3)	-0.004 (3)	-0.030 (2)
N31	0.0537 (19)	0.0574 (18)	0.0388 (13)	0.0086 (17)	-0.0068 (17)	0.0085 (12)
C31	0.084 (3)	0.068 (3)	0.091 (3)	-0.009 (3)	-0.012 (3)	-0.002 (2)
C32	0.115 (5)	0.052 (3)	0.143 (4)	-0.015 (3)	0.010 (3)	-0.016 (3)
C33	0.144 (5)	0.071 (3)	0.118 (3)	-0.002 (3)	0.004 (4)	-0.040 (3)
C34	0.140 (5)	0.105 (4)	0.140 (4)	0.009 (4)	0.018 (4)	-0.062 (3)
C35	0.093 (4)	0.096 (4)	0.078 (3)	0.015 (3)	-0.004 (3)	-0.030 (2)
O1W	0.051 (2)	0.086 (2)	0.0287 (13)	-0.003 (2)	-0.0029 (19)	0.008 (2)
O2W	0.193 (7)	0.164 (7)	0.178 (7)	-0.005 (6)	-0.013 (6)	-0.022 (6)

Geometric parameters (Å, °)

Cu1—O24 ⁱ	1.931 (2)	N11—C15	1.3900
Cu1—O22	1.934 (2)	C11—C12	1.3900
Cu1—N31	1.996 (3)	C11—H11A	0.9300
Cu1—N11	2.010 (3)	C12—C13	1.3900
Cu1—O1W	2.243 (3)	C12—H12A	0.9300
O21—C28	1.208 (7)	C13—C14	1.3900
O22—C28	1.290 (6)	C13—H13A	0.9300
O23—C21	1.222 (6)	C14—C15	1.3900
O24—C21	1.296 (6)	C14—H14A	0.9300
O24—Cu1 ⁱⁱ	1.931 (2)	C15—H15A	0.9300
C21—C22	1.513 (5)	N31—C31	1.3900
C22—C27	1.341 (6)	N31—C35	1.3900
C22—C23	1.370 (6)	C31—C32	1.3900
C23—C24	1.380 (6)	C31—H31A	0.9300
C23—H23A	0.9300	C32—C33	1.3900
C24—C25	1.364 (6)	C32—H32A	0.9300
C24—H24A	0.9300	C33—C34	1.3900
C25—C26	1.349 (6)	C33—H33A	0.9300
C25—C28	1.532 (6)	C34—C35	1.3900
C26—C27	1.412 (6)	C34—H34A	0.9300
C26—H26A	0.9300	C35—H35A	0.9300
C27—H27A	0.9300	O1W—H1WA	0.850 (4)
N11—C11	1.3900	O1W—H1WB	0.850 (4)
O24 ⁱ —Cu1—O22	178.33 (13)	C15—N11—Cu1	119.12 (15)
O24 ⁱ —Cu1—N31	91.70 (12)	C12—C11—N11	120.0
O22—Cu1—N31	89.96 (11)	C12—C11—H11A	120.0
O24 ⁱ —Cu1—N11	86.63 (11)	N11—C11—H11A	120.0
O22—Cu1—N11	91.70 (11)	C11—C12—C13	120.0

supplementary materials

N31—Cu1—N11	170.51 (13)	C11—C12—H12A	120.0
O24 ⁱ —Cu1—O1W	90.68 (12)	C13—C12—H12A	120.0
O22—Cu1—O1W	89.38 (12)	C14—C13—C12	120.0
N31—Cu1—O1W	93.13 (11)	C14—C13—H13A	120.0
N11—Cu1—O1W	96.23 (12)	C12—C13—H13A	120.0
C28—O22—Cu1	122.3 (3)	C15—C14—C13	120.0
C21—O24—Cu1 ⁱⁱ	119.8 (3)	C15—C14—H14A	120.0
O23—C21—O24	127.0 (4)	C13—C14—H14A	120.0
O23—C21—C22	118.9 (4)	C14—C15—N11	120.0
O24—C21—C22	113.8 (4)	C14—C15—H15A	120.0
C27—C22—C23	117.5 (4)	N11—C15—H15A	120.0
C27—C22—C21	120.3 (4)	C31—N31—C35	120.0
C23—C22—C21	122.1 (4)	C31—N31—Cu1	121.51 (15)
C22—C23—C24	121.2 (4)	C35—N31—Cu1	118.41 (15)
C22—C23—H23A	119.4	C32—C31—N31	120.0
C24—C23—H23A	119.4	C32—C31—H31A	120.0
C25—C24—C23	121.1 (5)	N31—C31—H31A	120.0
C25—C24—H24A	119.5	C31—C32—C33	120.0
C23—C24—H24A	119.5	C31—C32—H32A	120.0
C26—C25—C24	118.3 (4)	C33—C32—H32A	120.0
C26—C25—C28	122.0 (4)	C32—C33—C34	120.0
C24—C25—C28	119.7 (4)	C32—C33—H33A	120.0
C25—C26—C27	120.1 (4)	C34—C33—H33A	120.0
C25—C26—H26A	119.9	C33—C34—C35	120.0
C27—C26—H26A	119.9	C33—C34—H34A	120.0
C22—C27—C26	121.7 (4)	C35—C34—H34A	120.0
C22—C27—H27A	119.2	C34—C35—N31	120.0
C26—C27—H27A	119.2	C34—C35—H35A	120.0
O21—C28—O22	127.7 (4)	N31—C35—H35A	120.0
O21—C28—C25	119.9 (5)	Cu1—O1W—H1WA	109.2 (7)
O22—C28—C25	112.4 (5)	Cu1—O1W—H1WB	119.1 (5)
C11—N11—C15	120.0	H1WA—O1W—H1WB	103.9 (6)
C11—N11—Cu1	120.88 (15)		

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

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 O21 ⁱⁱⁱ	0.850 (4)	2.078 (7)	2.735 (4)	133.7 (6)
O1W—H1WB \cdots O23 ^{iv}	0.850 (4)	1.889 (5)	2.719 (3)	164.9 (10)

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

Fig. 1

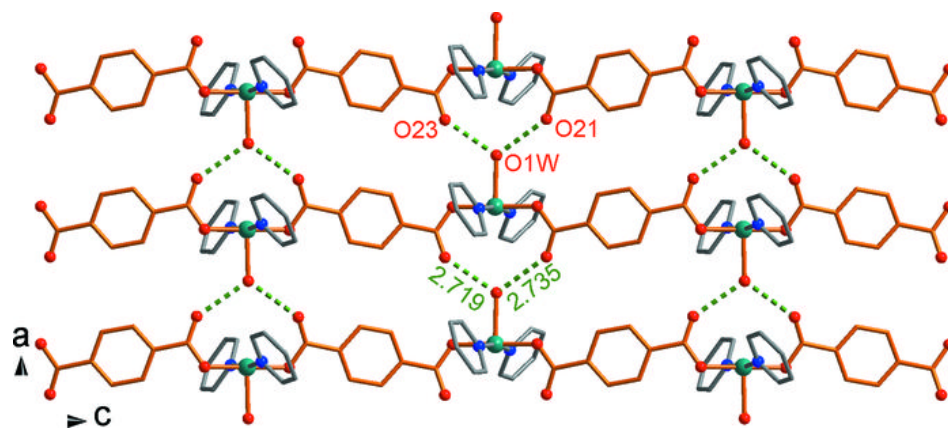


Fig. 2

