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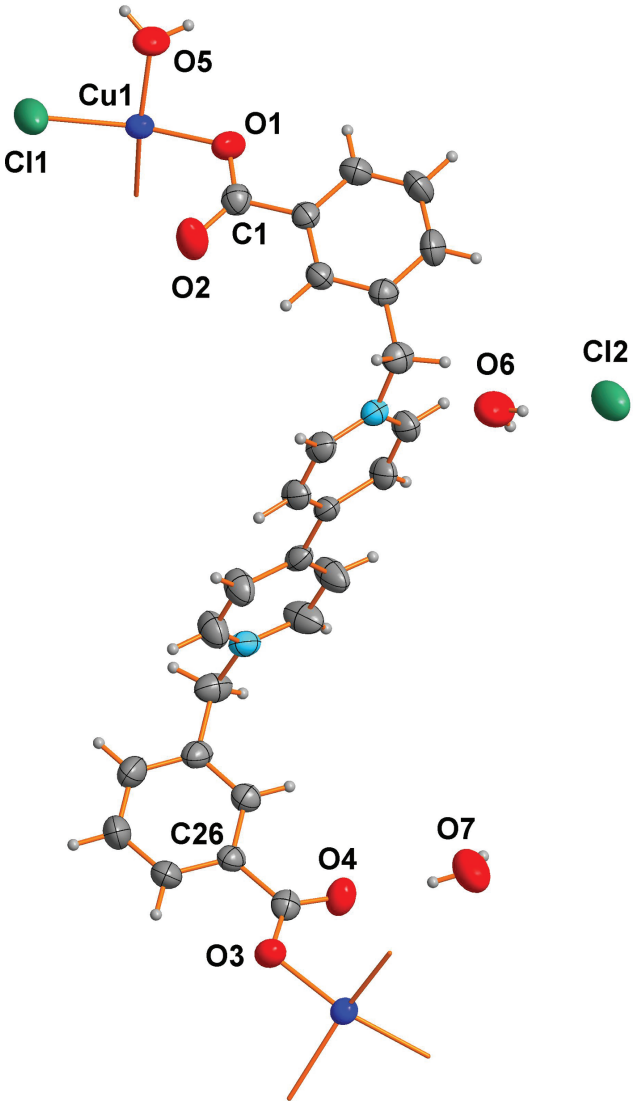
The crystal structure of *catena*-poly[aquachlorido(3,3′-([4,4′-bipyridine]-1,1′-diium-1,1′-diylbis(methylene))dibenzoato-κ²*O*:*O*′)copper(II)] chloride dihydrate, $C_{26}H_{26}Cl_2CuN_2O_7$



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Abstract

$\{[Cu(C_{26}H_{20}N_2O_4)Cl(H_2O)]^+ \cdot Cl^- \cdot 2H_2O\}_n$, monoclinic, *Cc* (no. 9), $a = 17.225(4)$, $b = 14.918(3)$, $c = 11.589(3)$ Å, $\beta = 118.957(3)°$, $V = 2605.6(10)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0334$, $\omega R_{ref}(F^2) = 0.0819$, $T = 293$ K.

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A representative part of the polymeric title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Block, blue
Size:	0.40 × 0.30 × 0.20 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.09 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
$2\theta_{max}$, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11350, 4799, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4420
$N(param)_{refined}$:	344
Programs:	Bruker programs [1], SHELX [2, 3], DIAMOND [4]

Source of materials

A mixture of 1,1′-bis(3-carboxylatobenzyl)-4,4′-bipyridium dichloride (0.2487 g, 0.50 mmol) and 2,2′-diimidazoleimidazole (0.2487 g, 0.50 mmol) were stirred in 20 mL of distilled water. After that HCl (0.5 mL, 3 mol/L) was added to make the pH = 3. $CuCl_2 \cdot 4H_2O$ (0.3524 g, 5 mmol) in 10 mL distilled water was added dropwise with constant stirring. Then, the mixture was stirred for 5 h. The resulting mixture was filtered and the filtrate was kept for slow evaporation at room temperature. After 2 weeks, blue block crystals were obtained.

Experimental details

Hydrogen atoms attached to C and O atoms were placed geometrically and refined using a riding model approximation, with C—H = 0.93–0.96 Å and O—H = 0.82 Å. Hydrogen

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.75077(4)	1.31429(3)	0.24947(4)	0.03834(16)
Cl1	0.71116(13)	1.39479(10)	0.06779(15)	0.0741(5)
O1	0.7418(3)	1.2499(2)	0.3876(4)	0.0557(10)
O2	0.6202(3)	1.1867(3)	0.2343(5)	0.0736(15)
O3	0.2760(2)	0.2906(2)	−0.3243(4)	0.0491(9)
O4	0.4073(2)	0.2824(3)	−0.1465(4)	0.0550(9)
O5	0.7655(3)	1.4224(3)	0.3535(4)	0.0599(10)
H5A	0.7784	1.4717	0.3362	0.090*
H5B	0.7925	1.4164	0.4339	0.090*
N1	0.5237(3)	0.8986(2)	0.3872(4)	0.0380(9)
N2	0.5587(3)	0.6186(3)	−0.0709(4)	0.0395(9)
C1	0.6772(3)	1.1976(3)	0.3498(5)	0.0431(11)
C2	0.6707(3)	1.1459(3)	0.4570(5)	0.0373(10)
C3	0.7302(4)	1.1599(4)	0.5883(5)	0.0486(12)
H3	0.7747	1.2026	0.6121	0.058*
C4	0.7242(4)	1.1115(4)	0.6833(5)	0.0619(16)
H4	0.7644	1.1220	0.7716	0.074*
C5	0.6589(4)	1.0469(4)	0.6503(5)	0.0535(13)
H5	0.6568	1.0131	0.7162	0.064*
C6	0.5972(3)	1.0327(3)	0.5205(5)	0.0380(10)
C7	0.6033(3)	1.0828(3)	0.4236(5)	0.0379(10)
H7	0.5617	1.0742	0.3354	0.045*
C8	0.5241(3)	0.9647(3)	0.4829(5)	0.0439(11)
H8A	0.5321	0.9337	0.5615	0.053*
H8B	0.4674	0.9954	0.4445	0.053*
C9	0.5890(3)	0.8375(3)	0.4280(5)	0.0439(11)
H9	0.6312	0.8349	0.5169	0.053*
C10	0.5946(3)	0.7794(3)	0.3416(5)	0.0421(11)
H10	0.6406	0.7378	0.3719	0.051*
C11	0.5317(3)	0.7820(3)	0.2079(5)	0.0350(10)
C12	0.4634(3)	0.8446(3)	0.1693(5)	0.0411(11)
H12	0.4193	0.8479	0.0816	0.049*
C13	0.4611(3)	0.9009(3)	0.2599(5)	0.0425(11)
H13	0.4149	0.9420	0.2329	0.051*
C14	0.5386(3)	0.7226(3)	0.1101(5)	0.0373(10)
C15	0.4840(4)	0.7321(4)	−0.0232(5)	0.0546(14)
H15	0.4391	0.7749	−0.0539	0.066*
C16	0.4943(4)	0.6803(4)	−0.1110(6)	0.0550(14)
H16	0.4560	0.6877	−0.2008	0.066*
C17	0.6118(4)	0.6063(4)	0.0583(6)	0.0589(15)
H17	0.6554	0.5622	0.0862	0.071*
C18	0.6040(4)	0.6565(4)	0.1502(6)	0.0607(16)
H18	0.6420	0.6468	0.2395	0.073*
C19	0.5713(4)	0.5659(4)	−0.1701(6)	0.0508(13)
H19A	0.6200	0.5242	−0.1245	0.061*
H19B	0.5871	0.6064	−0.2209	0.061*
C20	0.4891(3)	0.5144(3)	−0.2628(5)	0.0420(11)
C21	0.4411(4)	0.5399(4)	−0.3936(6)	0.0548(14)
H21	0.4600	0.5882	−0.4244	0.066*
C22	0.3652(4)	0.4937(4)	−0.4785(5)	0.0638(17)
H22	0.3341	0.5097	−0.5671	0.077*
C23	0.3357(4)	0.4239(3)	−0.4321(5)	0.0473(12)
H23	0.2830	0.3948	−0.4887	0.057*
C24	0.3835(3)	0.3967(3)	−0.3023(4)	0.0355(10)
C25	0.4612(3)	0.4427(3)	−0.2182(5)	0.0389(10)
H25	0.4945	0.4245	−0.1309	0.047*
C26	0.3546(4)	0.3182(3)	−0.2513(5)	0.0390(12)
Cl2	0.32101(10)	0.89165(10)	0.82117(14)	0.0651(4)
O6	0.3709(4)	0.9124(3)	0.6061(5)	0.0896(15)
H6C	0.4020	0.8682	0.6165	0.134*
H6D	0.3491	0.9061	0.6546	0.134*
O7	0.4503(3)	0.2405(3)	0.1085(4)	0.0845(15)
H7A	0.4327	0.2497	0.0300	0.127*
H7B	0.5041	0.2330	0.1427	0.127*

atoms attached water were located from difference Fourier maps, but we didn't refine their coordinates nor their U_{iso} parameters. The title structure was refined as an inversion twin (0.146(16)/0.854(16)).

Comment

Metal-organic frameworks have attracted great attention due to their particular structural diversity and potential application as functional materials [5, 6]. The aromatic multicarboxylate ligands have been extensively employed in the preparations of metal-organic coordination polymers. The ligand has a rigid conformation and would therefore facilitate the construction of the resulting coordination networks with regular shapes that can be reasonably predicted [7–9].

In this study, we choosed a flexible viologen derivative 1,1′-bis(3-carboxybenzyl)-4,4′-bipyridinium dichloride ($BpybcCl_2$) as educt to get a coordination polymer $\{[Cu(Bpybc)Cl(H_2O)]^+ \cdot Cl^- \cdot 2H_2O\}n$. The asymmetric unit contains one Cu(II) cation, one Bpybc, one coordinated water, one chlorido ligand, one chloride counter anion and two not coordinating water molecules (*cf.* the figure). Each Cu center is coordinated by one water molecule, one chlorido ligand and two oxygen atoms of two distinct Bpybc ligands. The Cu—O and Cu—Cl bond lengths are in the expected ranges (1.931–1.955 Å for Cu–O and 2.225 Å for Cu–Cl). In addition, Cu1···O2 and Cu1···O4A distances are 2.886 Å and 2.767 Å respectively, suggesting non-negligible interactions between the copper atoms and the uncoordinated carboxylate oxygen atoms, which can be described as a semi-chelating coordination mode [10].

Because the methylene groups are used as knots to link together the pyridine rings and phenyl rings, the whole Bpybc ligand is not linear and exhibits a zigzag conformation. Each Bpybc ligand bridges two metal ions through terminal carboxylate groups in a monodentate coordination mode with a Cu···Cu distance of 18.51(7) Å (*cf.* the figure). Thus the title structure exhibits a one-dimensional zigzag chain along the c-axis.

The most intriguing structural feature is an infinite two-dimensional water-chloride network by O—H···O and O—H···Cl hydrogen bonds between carboxylate oxygen atoms, coordinated water molecules, one independent chloride ion and two independent lattice water molecules in the crystal structures.

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