Crystal structure of tetra(4-methylpyridine)copper(II) diperchlorate, $[\text{Cu}(\text{C}_6\text{H}_7\text{N})_4][\text{ClO}_4]_2$

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Abstract

$\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{CuN}_4\text{O}_8$, monoclinic, $C12/c1$ (no. 15), $a = 18.778(8) \text{ \AA}$, $b = 10.214(4) \text{ \AA}$, $c = 16.128(7) \text{ \AA}$, $\beta = 108.760(8)^\circ$, $V = 2929.0 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.056$, $wR_{\text{ref}}(F^2) = 0.172$, $T = 294 \text{ K}$.

Source of material

A methanol solution (5 ml) of $[\text{Cu}(\text{MeCN})_4][\text{ClO}_4]$ (1 mmol, 0.240 g) was added dropwise to a methanol solution of 4-methylpyridine (4 mmol, 0.381 g). The reaction mixture was refluxed for 4 h and filtered, the filtrate was kept in a CaCl_2 desiccator. During the preparation, Cu(I) is oxidized to Cu(II) by air oxygen. After a few days, blue crystals suitable for X-ray analysis were obtained.

Experimental details

While the H atoms bonded to aromatic C atoms were added geometrically and treated as riding, the methyl groups were rotated to fit the electron density. At the same time, the oxygen atoms of perchlorate anions are disordered and split into two positions each.

Discussion

During the past two decades, considerable attention has been paid to the chemistry of heterocyclic compounds and complexes with metal ions due to their chelating ability and their potentially beneficial chemical and biological activities [1,2].

The formula unit of the title crystal structure consists of one Cu(II) cation, four 4-methylpyridine molecules, and two perchlorate anions. The Cu(II) atom is tetra-coordinated by four nitrogen atoms of four 4-methylpyridine ligands in a square-planar fashion, which is similar to the isotopic tetrakis(4-methylpyridine)nickel(II) perchlorate, $[\text{Ni}(\text{II})(\text{C}_6\text{H}_7\text{N})_4][\text{ClO}_4]_2$ [3]. The Cu—N bond lengths are in the range $2.015(4) \text{ \AA}$ – $2.016(4) \text{ \AA}$, which is similar to the compound previously reported [4]. The distances of $2.669 \text{ \AA}$ for Cu...O1 and $2.933 \text{ \AA}$ for Cu and O1' of the perchlorate anions is very long, which indicates the existence of only very weak interactions, and this is very common in copper(II) complex systems due to the Jahn-Teller effect. The CH groups donate the hydrogen atoms to O1 of the perchlorate anion to form weak intermolecular C—H...O hydrogen bonds ($d(\text{C}\cdots\text{O}) = 3.235 \text{ \AA}$, $\angle \text{C—H}\cdots\text{O} = 132.6^\circ$). The O3 atom of another neighboring perchlorate anion also accept hydrogen atoms from the ligand to generate intermolecular hydrogen bonds ($d(\text{H}\cdots\text{O}) = 2.514 \text{ \AA}$, $\angle \text{C—H}\cdots\text{O} = 148.3^\circ$), which are responsible for the supermolecular assembly in form of 1D chains along [010] direction.

Table 1. Data collection and handling.

Crystal:	blue block, size $0.18 \times 0.20 \times 0.24 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71073 \text{ \AA}$)
μ :	9.79 cm^{-1}
Diffraction, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	7235, 2577
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1427
$N(\text{param})_{\text{refined}}$:	217
Programs:	SHELXS-97 [5], SHELXL-97 [6]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	8f	1.0945	1.0273	0.1892	0.099
H(2)	8f	1.1479	0.8994	0.3073	0.106
H(4)	8f	1.0492	0.5940	0.1703	0.087
H(5)	8f	1.0009	0.7276	0.0529	0.086
H(6A)	8f	1.1091	0.5676	0.3285	0.152
H(6B)	8f	1.1462	0.6903	0.3839	0.152
H(6C)	8f	1.1890	0.6142	0.3300	0.152
H(7)	8f	0.8396	0.9417	−0.0312	0.072
H(8)	8f	0.7414	1.0044	0.0127	0.073
H(10)	8f	0.8751	1.2676	0.1681	0.087
H(11)	8f	0.9698	1.1939	0.1227	0.090
H(12A)	8f	0.6862	1.1723	0.0831	0.124
H(12B)	8f	0.7391	1.2765	0.1441	0.124
H(12C)	8f	0.7346	1.1343	0.1788	0.124

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cu(1)	4a		0	0	0	0.0579(7)	0.1022(9)	0.0480(6)	0.0312(6)	0.0250(5)	0.0076(6)
N(1)	8f		1.0421(3)	0.8910(5)	0.1090(3)	0.050(3)	0.069(3)	0.050(3)	0.008(2)	0.022(2)	−0.005(2)
N(2)	8f		0.9148(3)	1.0614(5)	0.0407(3)	0.052(3)	0.069(3)	0.048(3)	0.013(2)	0.020(2)	−0.001(2)
C(1)	8f		1.0853(4)	0.9376(7)	0.1845(4)	0.119(6)	0.059(4)	0.060(4)	−0.007(4)	0.015(4)	−0.005(3)
C(2)	8f		1.1172(4)	0.8611(7)	0.2559(4)	0.125(7)	0.074(5)	0.045(3)	−0.007(4)	−0.001(4)	−0.005(3)
C(3)	8f		1.1051(4)	0.7293(6)	0.2534(4)	0.067(4)	0.060(4)	0.062(4)	0.010(3)	0.029(3)	0.004(3)
C(4)	8f		1.0603(4)	0.6829(6)	0.1760(5)	0.081(5)	0.053(4)	0.087(5)	−0.003(3)	0.032(4)	−0.011(4)
C(5)	8f		1.0305(4)	0.7642(7)	0.1055(4)	0.062(4)	0.087(5)	0.060(4)	−0.008(4)	0.013(3)	−0.018(4)
C(6)	8f		1.1406(5)	0.6425(7)	0.3310(4)	0.116(6)	0.098(6)	0.090(5)	0.029(5)	0.032(5)	0.033(4)
C(7)	8f		0.8471(3)	1.0082(6)	0.0101(4)	0.062(4)	0.061(4)	0.058(3)	0.013(3)	0.021(3)	−0.011(3)
C(8)	8f		0.7878(3)	1.0456(6)	0.0360(4)	0.050(3)	0.067(4)	0.069(4)	−0.002(3)	0.023(3)	−0.007(3)
C(9)	8f		0.7963(3)	1.1439(5)	0.0962(4)	0.055(4)	0.056(3)	0.060(3)	0.009(3)	0.031(3)	0.008(3)
C(10)	8f		0.8663(4)	1.1997(6)	0.1276(4)	0.078(5)	0.070(4)	0.084(4)	−0.012(4)	0.047(4)	−0.029(3)
C(11)	8f		0.9227(4)	1.1556(7)	0.0994(4)	0.055(4)	0.097(5)	0.080(4)	−0.015(4)	0.032(3)	−0.028(4)
C(12)	8f		0.7334(4)	1.1855(7)	0.1285(5)	0.073(4)	0.095(5)	0.099(5)	0.016(4)	0.056(4)	0.007(4)
Cl(1)	8f		0.8745(1)	0.6771(2)	0.8868(1)	0.078(1)	0.062(1)	0.074(1)	−0.0131(9)	0.0134(9)	−0.0071(9)
O(1)	8f	0.61(1)	0.9163(5)	0.7950(6)	0.9237(6)	0.074(5)	0.044(4)	0.070(6)	−0.011(3)	0.023(4)	−0.005(3)
O(2)	8f	0.61	0.8916(6)	0.5830(7)	0.9551(4)	0.114(7)	0.084(5)	0.070(5)	−0.032(5)	0.023(5)	0.026(4)
O(3)	8f	0.61	0.9037(7)	0.6379(9)	0.8188(6)	0.20(1)	0.103(6)	0.103(6)	0.008(6)	0.066(7)	−0.025(5)
O(4)	8f	0.61	0.7980(4)	0.709(1)	0.8548(9)	0.104(7)	0.21(1)	0.19(1)	−0.002(7)	0.000(7)	0.015(8)
O(1')	8f	0.39	0.9053(9)	0.801(1)	0.885(1)	0.12(1)	0.083(9)	0.08(1)	−0.023(7)	0.039(8)	−0.001(6)
O(2')	8f	0.39	0.9313(9)	0.586(1)	0.936(1)	0.15(1)	0.12(1)	0.17(1)	0.016(9)	0.016(9)	−0.009(9)
O(3')	8f	0.39	0.8355(8)	0.624(1)	0.8044(5)	0.105(9)	0.097(8)	0.058(6)	0.006(7)	0.000(6)	−0.011(6)
O(4')	8f	0.39	0.8190(9)	0.687(2)	0.934(1)	0.14(1)	0.15(1)	0.16(1)	−0.051(8)	0.081(9)	0.002(8)

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