Xuan Feng, Zhannan Yang and Xin-Hua Li*

Crystal structure of dichlorido-([2,2':6',2''-terpyridine]-4'-carboxylic acid- $\kappa^3 N, N', N''$)copper(II) monohydrate, $C_{16}H_{13}Cl_2CuN_3O_3$

Table 1: Data collection and handling.

Crystal:	Blue prism
Size:	0.17 × 0.10 × 0.08 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.64 mm ⁻¹
Diffractometer, scan mode:	Xcalibur, ω
$\theta_{\max}$, completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14547, 3839, 0.016
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3463
$N(\text{param})_{\text{refined}}$:	235
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Diamond [4]

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Abstract

$C_{16}H_{13}Cl_2CuN_3O_3$, monoclinic, $P2_1/c$ (no. 14), $a = 11.2656(9)$ Å, $b = 17.1737(14)$ Å, $c = 8.7774(7)$ Å, $\beta = 98.1940(10)^\circ$, $V = 1680.8(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0270$, $wR_{\text{ref}}(F^2) = 0.0852$, $T = 298(2)$ K.

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The 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.

Source of material

Copper dichloride dihydrate (0.34 g, 2 mmol) and 4'-carboxy-2,2':6',2''-terpyridine (0.55 g, 2 mmol) were suspended in water (15 mL), 2 mL HCl (1 mol/L) was added dropwisely and stirred on a constant temperature magnetic stirrer for half an

hour at 27 °C. Then the solution was poured into a 30 mL Teflon-lined stainless-steel reactor, sealed, and allowed to react at 150 °C for 96 hours. The reactor was allowed to cool to 27 °C. The blue schistose shaped crystals were collected by filtration, washed several times using deionized water and ethanol in a sequential manner, and finally dried in an electric blast oven at 90 °C to obtain the product (yield ca. 62% based on Cu (II)). The substance is insoluble in water and common organic solvents.

Experimental details

H atoms of the organic ligand were positioned geometrically and their U_{iso} values were set to $1.2U_{\text{eq}}$ of the parent atoms.

Comment

Terpyridine (tpy) is ubiquitous as a tridentate, chelating ligand [5]. In particular, polypyridyl-based metal-organic complexes and coordination polymers exhibit an extensive range of technological application [6–8]. The pseudo-octahedral htpy-CM^{2+} -Ctpyi moieties are thus the favorite monomers for diverse metallodendrimers, racks, and grids, as well as macrocycles, cages and diverse polyhedra [9–11].

Herein, we report the crystal structure of $[\text{CuCl}_2(\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_2)] \cdot \text{H}_2\text{O}$. The title crystal structure consists of a copper(II) complex and a water solvent. The Cu atom is pentacoordinated, and its environment is a slight distorted square-pyramidal geometry arising from coordination by three N atoms from a 4'-carboxy-2,2':6',2''-terpyridine and two chlorido ligands and one chlorido ligand occupies the axial position (the Figure). The title copper(II) complex and water

*Corresponding author: Xin-Hua Li, College of Chemistry and Materials Engineering, Wenzhou University, Zhejiang Wenzhou 325035, P.R. China, e-mail: lixinhua01@126.com

Xuan Feng and Zhannan Yang: Key Laboratory for Information System of Mountainous Area and Protection of Ecological Environment of Guizhou Province, Guizhou Normal University, Guizhou Guiyang 550001, P.R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Cu1	0.16672(2)	1.09262(2)	0.13287(2)	0.03103(9)
Cl1	0.33574(5)	1.08193(4)	0.36544(6)	0.05482(16)
Cl2	0.08334(5)	1.20762(3)	0.14948(8)	0.05512(15)
C1	0.31522(18)	0.76387(11)	−0.0491(3)	0.0440(4)
C2	0.27113(16)	0.84287(10)	−0.0093(2)	0.0370(4)
C3	0.32586(17)	0.90745(10)	−0.0662(2)	0.0364(4)
H3	0.3847	0.9014	−0.1296	0.044*
C4	0.28999(15)	0.98094(10)	−0.02534(19)	0.0314(3)
C5	0.18234(15)	0.85196(10)	0.0826(2)	0.0361(4)
H5	0.1452	0.8089	0.1195	0.043*
C6	0.14975(15)	0.92735(10)	0.11862(19)	0.0316(3)
C7	0.05494(15)	0.94975(10)	0.20985(19)	0.0326(3)
C8	−0.01780(18)	0.89724(12)	0.2720(2)	0.0423(4)
H8	−0.0072	0.8439	0.2610	0.051*
C9	−0.10668(18)	0.92542(14)	0.3510(2)	0.0463(4)
H9	−0.1564	0.8912	0.3944	0.056*
C10	−0.12060(17)	1.00401(14)	0.3645(2)	0.0448(4)
H10	−0.1807	1.0239	0.4158	0.054*
C11	−0.04455(16)	1.05368(12)	0.3014(2)	0.0387(4)
H11	−0.0540	1.1071	0.3120	0.046*
C12	0.33389(15)	1.05633(10)	−0.07503(19)	0.0325(3)
C13	0.41556(18)	1.06408(12)	−0.1771(2)	0.0416(4)
H13	0.4512	1.0204	−0.2141	0.050*
C14	0.4437(2)	1.13852(13)	−0.2238(2)	0.0488(5)
H14	0.4980	1.1452	−0.2932	0.059*
C15	0.3906(2)	1.20191(12)	−0.1665(2)	0.0483(5)
H15	0.4082	1.2520	−0.1968	0.058*
C16	0.31058(19)	1.19028(11)	−0.0629(2)	0.0421(4)
H16	0.2752	1.2334	−0.0236	0.050*
H3A	0.371(3)	0.5439(19)	−0.029(4)	0.070(10)*
H3B	0.452(3)	0.5885(16)	0.048(4)	0.070(10)*
N1	0.28235(13)	1.11922(8)	−0.01741(16)	0.0336(3)
N2	0.20448(12)	0.98849(8)	0.06516(16)	0.0296(3)
N3	0.04220(13)	1.02771(8)	0.22544(16)	0.0324(3)
O1	0.39360(19)	0.75584(10)	−0.1263(3)	0.0760(6)
O2	0.26117(15)	0.70681(8)	0.0120(2)	0.0638(5)
H2	0.3000	0.6666	0.0084	0.096*
O3	0.38436(18)	0.57925(10)	0.0222(3)	0.0667(6)

solvents interact through O—H...O and O—H...Cl hydrogen bonds to generate a three-dimensional network.

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References

1. Oxford Diffraction Ltd: CrysAlis^{PRO}. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England (2006).
2. Sheldrick, G. M.: SHELXT – integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Brandenburg K.: DIAMOND. Visual Crystal Structure Information System. Ver. 4.0., Crystal Impact, Bonn, Germany (2015).
5. Chakraborty, S.; Newkome G. R.: Terpyridine-based metal-losupramolecular constructs: tailored monomers to precise 2D-motifs and 3D-metallocages. *Chem. Soc. Rev.* **47** (2018) 3991–4016.
6. Indumathy, R.; Weyhermüller, T.; Rajapandian, V.; Subramanian, V.; Nair, B. U.: An unusual oxidation of the imidazolyl ring in a cobalt terpyridyl complex: crystal structure and photolysis activity of the transformed cobalt terpyridyl complex. *Polyhedron* **43** (2012) 159–169.
7. Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C.: Visible light photoredox catalysis with transition metal complexes: applications in organic synthesis. *Chem. Rev.* **113** (2013) 5322–5363.
8. Sakamoto, R.; Katagiri, S.; Maeda, H.; Nishihara, H.: Bis(terpyridine) metal complex wires: excellent long-range electron transfer ability and controllable intrawire redox conduction on silicon electrode. *Coord. Chem. Rev.* **257** (2013) 1493–1506.
9. Czerwińska, K.; Machura, B.; Kula, S.; Krompiec, S.; Erfurt, K.; Roma-Rodrigues, C.; Fernandes, A. R.; Shul'pina, L. S.; Ikonnikov, N. S.; Shul'pin, G. B.: Copper(II) complexes of functionalized 2,2':6',2''-terpyridines and 2,6-di(thiazol-2-yl)pyridine: structure, spectroscopy, cytotoxicity and catalytic activity. *Dalton Trans.* **46** (2017) 9591–9604.
10. Zhang, G.; Liu, E.; Yang, C.; Li, L.; Golen, J. A.; Rheingold, A. L.: Copper(II) complexes of 2,2':6',2''-terpyridine derivatives for catalytic aerobic alcohol oxidations – observation of mixed-valence Cu^ICu^{II} assemblies. *Eur. J. Inorg. Chem.* **2015** (2015) 939–947.
11. Kobayashi, A.; Oizumi, S.; Shigeta, Y.; Yoshida, M.; Kato, M.: Proton-switchable vapochromic behaviour of a platinum(II)-carboxy-terpyridine complex. *Dalton Trans.* **45** (2016) 17485–17494.