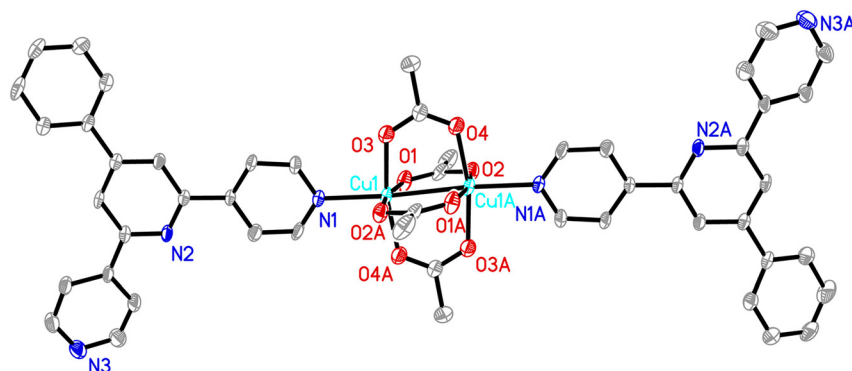


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The crystal structure of tetrakis(μ_2 -acetato- $\kappa^2O:O'$)-bis[(4'-phenyl-4,2':6',4''-terpyridine- κ^1N)]dicopper(II), $C_{25}H_{21}CuN_3O_4$



<https://doi.org/10.1515/ncrs-2024-0270>

Received June 26, 2024; accepted August 21, 2024;

published online September 4, 2024

Abstract

$C_{25}H_{21}CuN_3O_4$, triclinic, $P\bar{1}$ (no. 2), $a = 7.935(4)$ Å, $b = 10.849(6)$ Å, $c = 13.782(7)$ Å, $\alpha = 77.946(9)^\circ$, $\beta = 78.917(9)^\circ$, $\gamma = 82.223(10)^\circ$, $V = 1133.0(10)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0703$, $wR_{ref}(F^2) = 0.1781$, $T = 293$ K.

CCDC no.: 2361455

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

The reagents were purchased from standard commercial sources and used without further purification. A mixture of

Table 1: Data collection and handling.

Crystal:	Green block
Size:	$0.23 \times 0.21 \times 0.18$ mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.00 mm^{-1}
Diffractionmeter, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	25.0° , 99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	5,790, 3,968, 0.130
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2,513
$N(\text{param})_{\text{refined}}$:	300
Programs:	Bruker ¹ , SHELX ^{2,3} , Olex2 ⁴

$CuCl_2 \cdot 2H_2O$ (0.017 g, 0.10 mmol), 4264-phtpy (0.031 g, 0.10 mmol) was dispersed in mixed CH_3COOH (2 mL) and C_2H_5OH (8 mL) solutions and ammonia (25 %) were added until a pale blue solution were obtained. The resultant solution was allowed slowly to evaporate under room temperature for two weeks to give green crystals which were isolated by filtration and washed by deionized water and dried in air.

2 Experimental details

The structure was solved by Direct Methods with the SHELXT-2018 program. All H-atoms from C atoms were positioned with idealized geometry and refined isotropically ($U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$) using a riding model with C–H = 0.93 and 0.97 Å.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
Cu1	0.45002 (8)	0.09534 (6)	0.93013 (4)	0.0384 (3)
O1	0.2215 (5)	0.0786 (4)	1.0157 (3)	0.0540 (10)
O2	0.3039 (5)	−0.0860 (4)	1.1312 (3)	0.0493 (10)
O3	0.4236 (5)	−0.0512 (4)	0.8677 (3)	0.0499 (10)
O4	0.5022 (5)	−0.2107 (3)	0.9866 (3)	0.0535 (11)
N1	0.3694 (6)	0.2412 (4)	0.8072 (3)	0.0381 (10)
N2	0.2679 (6)	0.6262 (4)	0.5403 (3)	0.0389 (11)
N3	0.2472 (8)	1.1038 (5)	0.4737 (4)	0.0680 (16)
C1	0.3481 (8)	0.2027 (5)	0.7250 (4)	0.0497 (15)
H1	0.357549	0.116000	0.726520	0.060*
C2	0.3127 (8)	0.2835 (5)	0.6372 (4)	0.0461 (14)
H2	0.296185	0.250617	0.582968	0.055*
C3	0.3024 (6)	0.4123 (5)	0.6312 (3)	0.0329 (12)
C4	0.3265 (8)	0.4530 (5)	0.7172 (4)	0.0521 (16)
H4	0.321522	0.539086	0.717601	0.063*
C5	0.3578 (8)	0.3645 (6)	0.8015 (4)	0.0505 (15)
H5	0.371470	0.394152	0.857843	0.061*
C6	0.2686 (6)	0.5034 (5)	0.5394 (4)	0.0339 (12)
C7	0.2382 (7)	0.4607 (5)	0.4544 (4)	0.0380 (12)
H7	0.240547	0.374407	0.455938	0.046*
C8	0.2051 (7)	0.5468 (5)	0.3694 (4)	0.0377 (12)
C9	0.2038 (7)	0.6746 (5)	0.3720 (4)	0.0404 (13)
H9	0.181602	0.735553	0.316335	0.048*
C10	0.2357 (7)	0.7122 (5)	0.4574 (4)	0.0391 (13)
C11	0.2407 (7)	0.8464 (5)	0.4618 (4)	0.0408 (13)
C12	0.2672 (8)	0.9415 (5)	0.3764 (4)	0.0502 (15)
H12	0.283200	0.920885	0.312887	0.060*
C13	0.2701 (9)	1.0646 (6)	0.3848 (5)	0.0593 (17)
H13	0.288911	1.124716	0.325915	0.071*
C14	0.2201 (11)	1.0120 (7)	0.5545 (5)	0.080 (2)
H14	0.201302	1.035577	0.617153	0.096*
C15	0.2173 (9)	0.8867 (6)	0.5536 (4)	0.066 (2)
H15	0.199966	0.828642	0.613784	0.079*
C16	0.1719 (7)	0.5038 (5)	0.2784 (4)	0.0408 (13)
C17	0.1118 (8)	0.3870 (6)	0.2870 (4)	0.0501 (15)
H17	0.088916	0.335683	0.350117	0.060*
C18	0.0855 (9)	0.3456 (6)	0.2030 (5)	0.0619 (17)
H18	0.044887	0.267074	0.210389	0.074*
C19	0.1187 (11)	0.4194 (8)	0.1093 (5)	0.077 (2)
H19	0.102081	0.391109	0.052949	0.093*
C20	0.1767 (11)	0.5353 (8)	0.0994 (5)	0.090 (3)
H20	0.198061	0.585944	0.035821	0.108*
C21	0.2044 (10)	0.5792 (6)	0.1833 (5)	0.0680 (19)
H21	0.244292	0.658048	0.175426	0.082*
C22	0.1902 (7)	−0.0036 (6)	1.0939 (4)	0.0465 (15)
C23	0.0074 (7)	−0.0074 (7)	1.1497 (5)	0.071 (2)
H23A	−0.030376	−0.088841	1.153035	0.107*
H23B	−0.066469	0.057283	1.115021	0.107*
H23C	0.002678	0.006821	1.216679	0.107*
C24	0.4499 (7)	−0.1682 (5)	0.9078 (4)	0.0404 (13)
C25	0.4164 (9)	−0.2601 (6)	0.8440 (5)	0.0607 (17)
H25A	0.512991	−0.267281	0.790805	0.091*
H25B	0.314072	−0.228540	0.815508	0.091*
H25C	0.401309	−0.341880	0.885714	0.091*

3 Comment

In the past decades, there are a growing interest in the design of organic ligands and syntheses of metal-organic frameworks for their diverse structures and wide applications.^{5–8} Terpyridine possesses 48 isomers, among which the bis-chelating 2,2':6',2''-terpyridine is the best known and the adoption of 3,2':6',3''-terpyridine and 4,2':6',4''-terpyridine in construction of coordination complexes have become more widespread over the last twenty years.^{9–13} Just as the design and syntheses of organic ligands in some cases are time-consuming and laborious, usually with strict synthesis conditions, low yields, and high costs, an alternative strategy is to introduce metalloligands¹⁴ which are preassembled by common organic ligands and metal ions. The metalloligand still possess unsaturated coordination groups, which are important to direct the assembly of large molecular arrays and one-, two- and three-dimensional coordination polymers and networks.^{15,16} A Cu(II) metalloligand was obtained with 4'-phenyl-4,2':6',4''-terpyridine(phtpy) and its structure has been determined.

The asymmetric unit contains one Cu(II) ion, one phtpy ligand, and two acetate anions. As shown in the figure, each Cu(II) ion is five coordinated by one N atom from phtpy and four O atoms from four acetates, comprising a $Cu_2(CH_3CO_2)_4$ paddle-wheel core axially bound by two terminal phtpy ligands. In this complex, the Cu–O distances ranged from 1.971(4) to 2.010(4) Å, the Cu–N distance is 2.193(4) Å and the distance between two nearby Cu(II) ions is 2.6640(12) Å showing weak interaction. All these bond lengths are similar with other paddle-wheel Cu(II) complexes.^{17,18}

In the crystal, three C atoms, C1, C2 and C12 acted as hydrogen donors, contributing hydrogen atoms H1, H2 and H12 to O3, N3 and O2 to form non-classic hydrogen bonds, C1–H1...O3, with $d(C1...O3) = 3.092(7)$ Å, $\angle(C1-H1...O3) = 126^\circ$, C2–H2...N3_1545, with $d(C2...N3_{1545}) = 3.422(8)$ Å, $\angle(C2-H2...N3_{1545}) = 163^\circ$, C12–H12...O2_1564, with $d(C12...O2_{1564}) = 3.408(7)$ Å, $\angle(C12-H12...O2_{1564}) = 168^\circ$. In addition, there are three kinds of offset face to face π – π stacking interactions with center to center distances of 3.789(5) Å, 3.870(4) Å, 3.871(4) Å, between pyridine rings. The discrete complexes were further extended into 3D network mainly by the hydrogen bonding interaction and the π – π stacking interactions.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

Research funding: This work was supported by the 2023 Innovation and Entrepreneurship Training Program for Nanyue College of Hengyang Normal University students (No. NYD202319), and the Scientific Research Project of Hengyang Normal University (2023HSKFJJ013).

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