Li-Qin Shi*

Crystal structure of tetrakis(μ -naphthalene-1-carboxylato- $\kappa^2 O, O'$)bis(methanol)copper(II), $C_{46}H_{36}Cu_2O_{10}$

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.47 × 0.24 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.14 mm ⁻¹
Diffractometer, scan mode:	Rigaku R-Axis RAPID, ω
$\theta_{\max}$, completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14878, 3469, 0.054
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2299
$N(\text{param})_{\text{refined}}$:	262
Programs:	Rigaku [1], SHELX [2, 3]

Source of material

The reaction of 0.172 g (1.0 mmol) $CuCl_2 \cdot 2H_2O$ with 0.344 g (2.0 mmol) 1-naphthoic acid (HNAP) in 20 mL methanol for 15 min afforded green solid, which was then filtered. The green filtrate was allowed to stand at room temperature by slow evaporation within two days; green block crystals suitable for X-ray diffraction were obtained (yield: 63.5% based on $CuCl_2 \cdot 2H_2O$ input).

Experimental details

The structure was solved by direct methods with the SHELXS program. All H-atoms from C atoms were positioned with idealized geometry ($U_{\text{iso}}(H) = 1.2 U_{\text{eq}}(C)$ and $U_{\text{iso}}(H) = 1.5 U_{\text{eq}}(C)$ for aromatic and methyl H atoms, respectively) using a riding model with C–H = 0.93 or 0.96 Å. H atom attached to the O atom was refined using a riding model, with the O–H distance fixed with $U_{\text{iso}}(H)$ values set at $1.5 U_{\text{eq}}(O)$.

Comment

Construction of supramolecular systems and crystal engineering have been one of the most active fields in chemistry and materials science, due to their fascinating structures and potential applications in ion exchange [4], catalysis [5, 6], gas storage and separation [7, 8], fluorescent sensing

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Abstract

$C_{46}H_{36}Cu_2O_{10}$, monoclinic, $C2/c$ (no. 15), $a = 32.663(7)$ Å, $b = 7.4214(15)$ Å, $c = 21.785(4)$ Å, $\beta = 131.68(3)^\circ$, $V = 3944.0(19)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0478$, $wR_{\text{ref}}(F^2) = 0.1583$, $T = 295$ K.

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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.

*Corresponding author: Li-Qin Shi, Ningbo Polytechnic, Ningbo 315800, P.R.China, E-mail: nzyslq@163.com. <https://orcid.org/0000-0002-8955-0134>

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

Atom	x	y	z	U_{iso}^*/U_{eq}
Cu1	0.00310 (3)	0.83972 (8)	0.48061 (4)	0.0417 (2)
O1	0.03638 (19)	0.7646 (5)	0.5920 (3)	0.0592 (11)
O2	0.03265 (18)	1.0437 (5)	0.6249 (2)	0.0611 (12)
O3	0.07396 (16)	0.9280 (5)	0.5230 (3)	0.0566 (11)
O4	0.06879 (17)	1.2057 (5)	0.5548 (3)	0.0646 (13)
O5	0.01618 (17)	0.5841 (5)	0.4482 (3)	0.0563 (11)
H5B	−0.008630	0.506780	0.431370	0.084*
C1	0.0639 (3)	0.9459 (9)	0.7684 (4)	0.0638 (18)
H1A	0.046669	1.05534	0.743762	0.077*
C2	0.0836 (3)	0.9086 (10)	0.8470 (5)	0.079 (2)
H2A	0.079015	0.992446	0.873748	0.095*
C3	0.1093 (3)	0.7505 (10)	0.8840 (4)	0.0657 (18)
H3A	0.122609	0.727272	0.936533	0.079*
C4	0.1162 (2)	0.6210 (8)	0.8446 (4)	0.0509 (15)
C5	0.1428 (3)	0.4556 (9)	0.8837 (4)	0.0626 (18)
H5A	0.155936	0.433214	0.936163	0.075*
C6	0.1494 (3)	0.3303 (10)	0.8464 (4)	0.0688 (19)
H6A	0.165805	0.220615	0.872186	0.083*
C7	0.1317 (3)	0.3647 (9)	0.7688 (4)	0.0680 (19)
H7A	0.137125	0.278491	0.743771	0.082*
C8	0.1067 (2)	0.5231 (8)	0.7297 (4)	0.0561 (16)
H8A	0.095783	0.543825	0.678498	0.067*
C9	0.0969 (2)	0.6574 (8)	0.7646 (3)	0.0460 (13)
C10	0.0693 (2)	0.8251 (7)	0.7270 (3)	0.0426 (13)
C11	0.0446 (2)	0.8798 (8)	0.6416 (4)	0.0443 (13)
C12	0.1682 (3)	0.9853 (9)	0.5590 (4)	0.0593 (17)
H12A	0.149284	0.876727	0.537478	0.071*
C13	0.2175 (3)	1.0052 (11)	0.5757 (5)	0.080 (2)
H13A	0.230352	0.911808	0.563903	0.096*
C14	0.2462 (3)	1.1599 (11)	0.6088 (5)	0.074 (2)
H14A	0.278707	1.172371	0.619237	0.089*
C15	0.2280 (2)	1.3028 (9)	0.6278 (4)	0.0577 (17)
C16	0.2593 (3)	1.4604 (11)	0.6656 (5)	0.076 (2)
H16A	0.292466	1.470001	0.677709	0.092*
C17	0.2425 (3)	1.5994 (11)	0.6849 (5)	0.082 (2)
H17A	0.264090	1.701892	0.710673	0.098*
C18	0.1924 (3)	1.5861 (10)	0.6654 (5)	0.075 (2)
H18A	0.180502	1.681383	0.677885	0.090*
C19	0.1604 (3)	1.4356 (9)	0.6284 (4)	0.0602 (17)
H19A	0.127000	1.431288	0.615511	0.072*
C20	0.1771 (2)	1.2866 (8)	0.6092 (3)	0.0489 (15)
C21	0.1473 (2)	1.1197 (8)	0.5732 (3)	0.0441 (13)
C22	0.0932 (2)	1.0845 (8)	0.5493 (3)	0.0446 (13)
C23	0.0381 (3)	0.5763 (10)	0.4102 (5)	0.079 (2)
H23A	0.041028	0.452762	0.400421	0.118*
H23B	0.014436	0.639929	0.358870	0.118*
H23C	0.073797	0.630818	0.445444	0.118*

[9, 10], optical and magnetic properties [11, 12], and so on. In the past decades, considerable effort has been devoted to design the supramolecular assemblies by carefully selecting building blocks and organic ligands [13]. Aromatic carboxylate ligands, due to their versatile coordination

modes and potential luminescence nature, have been extensively employed as linkers to construct functional materials. Up to now, many complexes which were assembled by 1-naphthoates (NAP) have been reported [14–16].

Crystallographic analysis of the title complex shows that it crystallizes in the monoclinic space group $C2/c$, containing a dinuclear paddle-wheel complex $[Cu_2(NAP)_4(MeOH)_2]$, which is composed of two Cu^{II} ions, four NAP ligands and two methanol molecules. Each Cu ion is coordinated by four O atoms from four different NAP ligands, while the O atom from methanol occupies the apical position, forming a slightly distorted square pyramid with $d(Cu1-O1) = 1.969(4) \text{ \AA}$, $d(Cu1-O2^{#1}) = 1.956(4) \text{ \AA}$, $d(Cu1-O3) = 1.949(4) \text{ \AA}$, $d(Cu1-O4^{#1}) = 1.953(4) \text{ \AA}$, $d(Cu1-O5) = 2.163(4) \text{ \AA}$ ($\#1 = -x, -y + 2, -z + 1$), which are in good agreement with those reported for similar complexes [17]. The $Cu \cdots Cu$ distance is $2.578(1) \text{ \AA}$, which is observed within the normal range for dinuclear paddle-wheel units in the structures of Cu^{II} carboxylate complexes [18, 19]. The dinuclear Cu^{II} units are further connected to form one-dimensional chains by hydrogen bonds [$d(O5 \cdots O1^{#2}) = 2.900(4) \text{ \AA}$, $O5-H5B \cdots O1^{#2} = 150(2)^\circ$, $\#2 = -x, -y + 2, -z + 1$].

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