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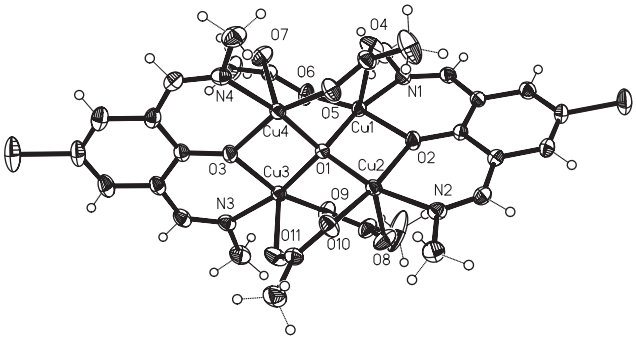
Crystal structure of tetrakis(μ$_2$-acetato-κ^2*O*:*O*′)-bis[μ$_3$-4-chloro-2,6-bis((methylimino)methyl) phenolato-κ^2*N*,*O*:*O*,*N*′]-(μ$_4$-oxido)tetracopper(II), $C_{28}H_{32}Cl_2Cu_4N_4O_{11}$



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Abstract

$C_{28}H_{32}Cl_2Cu_4N_4O_{11}$, triclinic, $P\bar{1}$ (no. 2), $a = 9.115(3)$ Å, $b = 12.769(4)$ Å, $c = 14.870(5)$ Å, $\alpha = 93.796(5)°$, $\beta = 93.548(5)°$, $\gamma = 91.917(5)°$, $V = 1722.2(10)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0303$, $\omega R_{ref}(F^2) = 0.082$, $T = 298$ K.

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The asymmetric unit of the 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:	Dark blue block
Size:	0.32 × 0.22 × 0.15 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	26.5 cm^{-1}
Diffractometer, scan mode:	Bruker XSCANS, *ω*-scans
$2\theta_{max}$, completeness:	50°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	18214, 6058, 0.042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5150
$N(param)_{refined}$:	459
Programs:	SHELX [6, 7]

Source of material

5-chloro-2-hydroxybenzene-1,3-dialdehyde (L) was synthesized based on the reported synthetic protocol [1, 2]. Activated MnO_2 (40 g) was added to 200 mL of $CHCl_3$ in a three-neck flask equipped with an overhead stirrer and a water-cooled condenser. The mixture was heated to reflux for about 15 min, and then the 4-chloro-2,6-bis(hydroxymethyl)phenol (5.64 g 0.03 mol) was added, refluxed for 24 h, cooled to room temperature and filtered, washed with $CHCl_3$ until the filtrate turned to be colorless. The filtrate was concentrated, yielding a yellow solid, which was purified by column chromatography on silica (eluted with petroleum ether : ethyl acetate = 1:2, Rf = 0.48). Anal. Calcd(%) for $C_8H_5O_3Cl$: C, 52.06; H, 2.73; Found(%): C, 52.01; H, 2.74. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 2.24 (s, 1H, CH_2OH), 7.36, 7.47 (m, 2H, 2Ar—H), 9.82, 10.16 (s, 2H, CHO), 11.12 (s, 1H, Ar—OH). The title tetranuclear copper complex was prepared from 5-chloro-2-hydroxybenzene-1,3-dialdehyde and methanamine, which were refluxed in ethanol for 3 h and the aqueous copper(II) acetate solution was added. This solution was refluxed for another 2 h. Several days later, dark blue crystals were obtained at room temperature.

Experimental details

All non-H atoms were refined anisotropically using absorption corrected data [6, 7]. Hydrogen atoms were placed geometrically and refined using a riding model approximation, with C—H = 0.96 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

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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	0.17865(4)	0.16340(3)	0.17904(2)	0.03167(11)
Cu2	0.04228(4)	0.37157(3)	0.21006(2)	0.03278(11)
Cu3	0.32437(4)	0.33007(3)	0.33809(2)	0.03211(11)
Cu4	0.05064(4)	0.20351(3)	0.36612(2)	0.03212(11)
N1	0.2110(3)	0.07711(19)	0.06735(17)	0.0346(6)
N2	−0.0959(3)	0.44842(19)	0.13084(18)	0.0377(6)
N3	0.5023(3)	0.3642(2)	0.41950(19)	0.0389(6)
N4	−0.0294(3)	0.14914(19)	0.47461(18)	0.0383(6)
O1	0.1496(2)	0.26897(14)	0.27338(13)	0.0298(4)
O2	0.0616(2)	0.26196(16)	0.11067(14)	0.0405(5)
O3	0.2299(2)	0.25972(16)	0.43714(14)	0.0385(5)
O4[a]	−0.0709(8)	0.0832(6)	0.1904(6)	0.0517(16)
O4A[b]	−0.106(4)	0.061(3)	0.210(3)	0.060(8)
O5	−0.1373(2)	0.19967(19)	0.29786(15)	0.0456(6)
O6	0.3286(2)	0.09604(18)	0.24873(15)	0.0457(6)
O7	0.1813(3)	0.04530(18)	0.35316(17)	0.0501(6)
O8	0.2534(3)	0.44908(19)	0.15814(19)	0.0595(7)
O9	0.4222(2)	0.35453(19)	0.22832(15)	0.0474(6)
O10	0.0046(2)	0.46058(18)	0.31550(15)	0.0470(6)
O11	0.2320(2)	0.48644(17)	0.38083(17)	0.0507(6)
C1	0.0072(3)	0.2536(2)	0.02655(19)	0.0318(7)
C2	0.0425(3)	0.1683(2)	−0.0332(2)	0.0334(7)
C3	−0.0187(3)	0.1607(2)	−0.1223(2)	0.0387(7)
H3	0.0034	0.1045	−0.1616	0.046*
C4	−0.1108(4)	0.2357(3)	−0.1521(2)	0.0400(7)
C5	−0.1446(3)	0.3203(2)	−0.0963(2)	0.0400(8)
H5	−0.2061	0.3708	−0.1182	0.048*
C6	−0.0868(3)	0.3310(2)	−0.0067(2)	0.0346(7)
C7	0.1436(3)	0.0876(2)	−0.0097(2)	0.0356(7)
H7	0.1616	0.0377	−0.0558	0.043*
C8	−0.1300(3)	0.4224(2)	0.0474(2)	0.0385(7)
H8	−0.1904	0.4680	0.0175	0.046*
C9	0.3158(4)	−0.0081(3)	0.0717(2)	0.0484(9)
H9A	0.3103	−0.0490	0.0149	0.073*
H9B	0.2915	−0.0524	0.1188	0.073*
H9C	0.4137	0.0214	0.0842	0.073*
C10	−0.1616(4)	0.5439(3)	0.1694(2)	0.0522(9)
H10A	−0.2095	0.5799	0.1218	0.078*
H10B	−0.0859	0.5892	0.2003	0.078*
H10C	−0.2324	0.5248	0.2112	0.078*
C11	0.2744(3)	0.2482(2)	0.5214(2)	0.0359(7)
C12	0.4105(3)	0.2950(3)	0.5572(2)	0.0398(8)
C13	0.4519(4)	0.2876(3)	0.6493(2)	0.0508(9)
H13	0.5391	0.3207	0.6738	0.061*
C14	0.3657(4)	0.2325(3)	0.7030(2)	0.0548(10)
C15	0.2354(4)	0.1834(3)	0.6689(2)	0.0503(9)
H15	0.1791	0.1449	0.7062	0.060*
C16	0.1871(4)	0.1912(2)	0.5782(2)	0.0398(8)
C17	0.5129(4)	0.3502(3)	0.5045(2)	0.0438(8)
H17	0.5973	0.3793	0.5362	0.053*
C18	0.0422(4)	0.1446(2)	0.5510(2)	0.0402(7)
H18	−0.0035	0.1073	0.5938	0.048*
C19	0.6279(4)	0.4184(3)	0.3822(3)	0.0587(10)
H19A	0.6937	0.4483	0.4308	0.088*
H19B	0.5927	0.4732	0.3463	0.088*
H19C	0.6790	0.3690	0.3453	0.088*
C20	−0.1806(4)	0.1037(3)	0.4664(3)	0.0570(10)
H20A	−0.1990	0.0676	0.5193	0.085*
H20B	−0.1924	0.0551	0.4141	0.085*
H20C	−0.2489	0.1588	0.4602	0.085*
C21	−0.1642(4)	0.1396(3)	0.2273(2)	0.0424(8)
C22	−0.3143(4)	0.1494(4)	0.1807(3)	0.0822(15)
H22A	−0.3044	0.1585	0.1178	0.123*
H22B	−0.3608	0.2090	0.2076	0.123*
H22C	−0.3732	0.0869	0.1871	0.123*
C23	0.3031(4)	0.0529(2)	0.3214(2)	0.0382(7)
C24	0.4362(4)	0.0100(3)	0.3690(3)	0.0650(11)
H24A	0.4692	0.0570	0.4198	0.098*
H24B	0.5133	0.0032	0.3281	0.098*
H24C	0.4111	−0.0576	0.3896	0.098*
C25	0.3697(4)	0.4027(3)	0.1618(3)	0.0514(9)
C26	0.4589(6)	0.3950(6)	0.0800(3)	0.124(3)
H26A	0.3978	0.3667	0.0287	0.187*
H26B	0.5393	0.3498	0.0907	0.187*
H26C	0.4966	0.4636	0.0686	0.187*
C27	0.1009(4)	0.5077(2)	0.3712(2)	0.0412(8)
C28	0.0445(4)	0.5981(3)	0.4281(3)	0.0572(10)
H28A	0.0844	0.5962	0.4892	0.086*
H28B	−0.0609	0.5923	0.4267	0.086*
H28C	0.0741	0.6632	0.4046	0.086*
Cl1	−0.18527(12)	0.22345(8)	−0.26353(6)	0.0626(3)
Cl2	0.41963(14)	0.22397(12)	0.81739(7)	0.0904(4)

[a]Occupancy: 0.8; [b]Occupancy: 0.2.

Discussion

The asymmetric unit of the title structure contains one tetranuclear Cu(II) complex (*cf*. the figure). The central O1 oxygen atom is contacted with the four Cu atoms. The distance of atom O1 with each atom Cu are between 1.916(2)–1.9231(19) Å. The Cu—O—Cu angles range from 102.41(9) (Cu1-O1-Cu2) to 116.43(10)° (Cu2-O1-Cu4). The Cu-Cu distances within the complex are between 2.99 Å and 3.26 Å. For each Cu, it is in the same surrounding that consists of five atoms: O1, phenolic O atom, Schiff base N atom, two acetato O atoms. The distance of atom Cu and surrounding O atoms ranges from 1.917(2) to 2.545(3) Å, and the length of Cu-N are between 1.975(3)–1.998(3) Å. Each of the oxygen atoms of the acetato ligands coordinates to two Cu atoms (*cf*. the figure). Compared with the title complex, there were some similar complexes reported before [3–5].

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