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Crystal structure of hexa- μ_2 -chlorido- μ_4 -oxido-tetrakis(1-vinyl-1*H*-imidazole- κN)tetracopper(II), $C_{20}H_{24}Cu_4Cl_6N_8O$

Table 1: Data collection and handling.

Crystal:	Purple block
Size:	0.20 × 0.18 × 0.16 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	3.03 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
$\theta_{\max}$, completeness:	24.7°, >98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	18666, 5539, 0.040
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4535
$N(\text{param})_{\text{refined}}$:	352
Programs:	Bruker programs [1], SHELX [2, 3], OLEX2 [4], DIAMOND [5]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.19811(8)	−0.05200(7)	0.78909(5)	0.0383(3)
Cu2	0.26451(8)	0.13036(7)	0.71042(5)	0.0369(3)
Cu3	0.28627(9)	−0.06414(7)	0.63591(5)	0.0416(3)
Cu4	0.05199(8)	0.01722(8)	0.66515(5)	0.0412(3)
Cl1	0.30780(19)	0.07812(15)	0.83000(10)	0.0471(7)
Cl2	0.0953(2)	0.18816(16)	0.66677(13)	0.0601(8)
Cl3	0.12232(18)	−0.04840(16)	0.55970(10)	0.0478(7)
Cl4	0.27783(19)	−0.18410(15)	0.72576(10)	0.0467(7)
Cl5	−0.00334(17)	−0.03948(17)	0.77673(11)	0.0534(8)
Cl6	0.41425(18)	0.06458(17)	0.63958(12)	0.0536(7)
N1	0.1928(6)	−0.1146(5)	0.8795(3)	0.044(2)
N2	0.1415(7)	−0.2094(5)	0.9631(4)	0.059(3)
N3	0.3289(5)	0.2560(4)	0.7187(3)	0.041(2)
N4	0.3465(5)	0.4094(4)	0.7129(4)	0.044(2)
N5	0.3696(6)	−0.1370(5)	0.5675(3)	0.049(2)
N6	0.4359(7)	−0.1876(5)	0.4675(4)	0.070(3)
N7	−0.0989(5)	0.0327(5)	0.6293(3)	0.052(2)
N8	−0.2477(6)	0.0204(6)	0.5629(4)	0.082(3)
O1	0.1999(4)	0.0081(3)	0.6999(2)	0.0308(15)
C1	0.2669(8)	−0.1086(6)	0.9341(4)	0.064(3)
H1	0.3286	−0.0702	0.9354	0.076*
C2	0.2347(8)	−0.1678(7)	0.9855(5)	0.073(4)
H2	0.2699	−0.1777	1.0279	0.088*
C3	0.0945(15)	−0.3207(10)	1.0491(6)	0.154(7)
H3A	0.1580	−0.3063	1.0739	0.184*
H3B	0.0463	−0.3660	1.0658	0.184*
C4	0.0752(12)	−0.2816(8)	0.9964(5)	0.101(5)
H4	0.0107	−0.2987	0.9736	0.121*
C5	0.1195(8)	−0.1743(6)	0.8999(4)	0.057(3)

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Abstract

$C_{20}H_{24}Cu_4Cl_6N_8O$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 12.159(7)$ Å, $b = 14.299(8)$ Å, $c = 19.186(11)$ Å, $V = 3336(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0382$, $wR_{\text{ref}}(F^2) = 0.0615$, $T = 296(2)$ 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

1-Vinylidazole (0.5 mmol), copper(II) chloride (1 mmol), methanol anhydrous (1.5 mL) and deionized water (0.3 mL)

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H5	0.0583	−0.1910	0.8736	0.068*
C6	0.4367(7)	0.2791(6)	0.7271(4)	0.051(3)
H6	0.4936	0.2366	0.7340	0.061*
C7	0.4488(8)	0.3728(6)	0.7240(4)	0.054(3)
H7	0.5141	0.4061	0.7284	0.065*
C8	0.3806(9)	0.5708(7)	0.6880(6)	0.091(5)
H8A	0.4559	0.5592	0.6878	0.109*
H8B	0.3545	0.6309	0.6796	0.109*
C9	0.3138(8)	0.5047(6)	0.6995(5)	0.066(3)
H9	0.2391	0.5185	0.6993	0.079*
C10	0.2770(7)	0.3352(5)	0.7106(4)	0.045(3)
H10	0.2015	0.3402	0.7039	0.055*
C11	0.4525(9)	−0.1961(7)	0.5802(5)	0.070(4)
H11	0.4789	−0.2116	0.6242	0.084*
C12	0.4929(8)	−0.2307(7)	0.5181(5)	0.074(4)
H12	0.5484	−0.2749	0.5124	0.088*
C13	0.5214(11)	−0.2343(9)	0.3603(6)	0.125(5)
H13A	0.5768	−0.2654	0.3844	0.150*
H13B	0.5214	−0.2339	0.3119	0.150*
C14	0.4483(10)	−0.1939(9)	0.3925(5)	0.099(5)
H14	0.3950	−0.1639	0.3658	0.119*
C15	0.3623(8)	−0.1309(7)	0.4989(5)	0.067(4)
H15	0.3130	−0.0925	0.4754	0.081*
C16	−0.1798(8)	0.0900(7)	0.6551(5)	0.067(4)
H16	−0.1737	0.1280	0.6942	0.081*
C17	−0.2691(8)	0.0821(9)	0.6146(5)	0.087(4)
H17	−0.3351	0.1139	0.6209	0.105*
C18	−0.3974(12)	0.0267(11)	0.4826(8)	0.170(5)
H18A	−0.4262	0.0754	0.5090	0.204*
H18B	−0.4345	0.0060	0.4431	0.204*
C19	−0.3115(10)	−0.0099(10)	0.4996(7)	0.121(4)
H19	−0.2840	−0.0585	0.4726	0.145*
C20	−0.1423(8)	−0.0080(7)	0.5740(5)	0.071(4)
H20	−0.1055	−0.0509	0.5461	0.085*

were placed in the heat-resistant glass tube. The mixtures were carefully stirred, and then frozen the tube, finally evacuated and sealed with a gas burner. The tube was placed in the oven at 60° C under the hydro-thermal reaction conditions for 4 days to get good quality white block crystal appeared in the tube wall.

Experimental details

The methyl groups and the NH₃ groups were idealized and refined using rigid groups allowed to rotate about the P–C bond (AFIX 137 option of the SHELXL program [2]).

Discussion

The first laboratory synthesis of a copper cluster complex with the Cu₄OCl₆ structural motif was achieved by Bertrand *et al.* in 1966 [6]. From that time, many copper clusters of this

type were reported [7–12], and their structural properties and catalytic performance were investigated [13–17]. Systematic investigation of μ₄-oxido cluster formation was reported, helping to understand the formation and stability of the μ₄-oxido motif in general [18]. In this study, we chose 1-vinylimidazole and cuprous chloride to synthesis the copper cluster unit of the type “Cu₄OCl₆”.

The complex has no crystallographic symmetry and contains a tetrahedron of four Cu II atoms coordinating a central μ₄-O atom, with the six edges of the tetrahedron bridged by Cl atoms. The copper(II) cations are fourfold coordinated by one O atom, three chloro ligands and one N atom of the ligand. The chloride ligands as the bridges link four copper atoms. The copper(II) and nitrogen distances range from 1.954(6) Å to 1.971(7) Å, respectively. The oxygen atom is associated with four copper atoms with bond lengths from 1.914(5) Å to 1.927(5) Å, which are all within a reasonable range.

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