Crystal structure of hexakis(μ_2-chloro)-μ_4-oxo-tetrakis((3,5-dimethylpyrazole)copper(II)) ethanol tetrasolvate, $Cu_4OCl_6(C_5H_8N_2)_4 \cdot 4C_2H_5OH$

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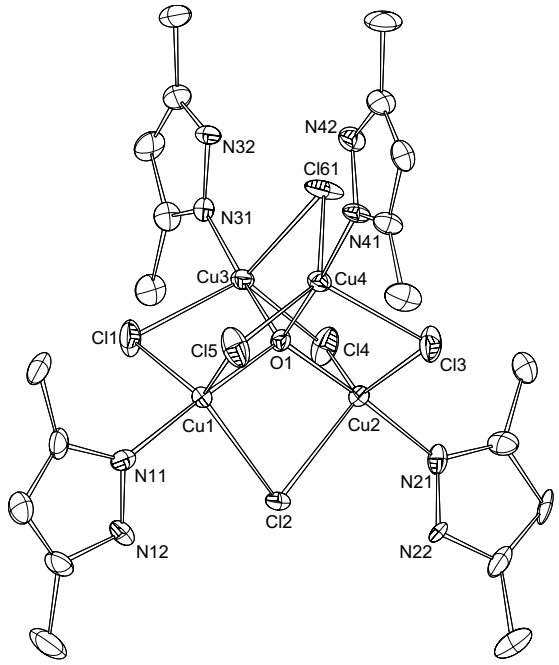

Abstract

$C_{28}H_{56}Cl_6Cu_4N_8O_5$, triclinic, $P\bar{1}$ (no. 2), a = 8.863(1) Å, b = 13.939(8) Å, c = 17.06(1) Å, α = 81.67(5)°, β = 85.68(3)°, γ = 84.91(3)°, V = 2073.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.080, $wR_{ref}(F^2)$ = 0.194, T = 293 K.

Source of material

3,5-dimethylpyrazole-1-carboxamide (0.14 g, 1 mmol) were dissolved in ethanol (5 ml) and added to the hot solution of $CuCl_2 \cdot 2H_2O$ (0.17 g, 1 mmol) in ethanol (7 ml). Green crystals were obtained after one week.

Experimental details

Chlorine atom Cl6 was modeled using two positions (Cl61, Cl62). During isotropic refinement their population parameters were refined to 0.60 and 0.42, respectively. In the subsequent anisotropic refinement partial occupancies of two Cl6 positions were held at 0.60 and 0.40. Following location of all the atoms of the complex molecule, residual electron density was observed, suggesting the presence of solvent molecules. However, attempts to find a satisfactory structural model failed. There are two solvent-accessible voids per unit cell. The solvent-accessible region was estimated with PLATON [1] to a volume of 538 Å^3 and corresponds to 101 electrons per unit cell, which is close to the required values for two ethanol molecules. The SQUEEZE function [1] was used to find unassigned electron density peaks in these two regions and to produce a corrected data set for which the residual electron density is eliminated from the voids. This new data set was used in subsequent refinements.

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Discussion

Complexes of the type $Cu_4OX_6L_4$ (where X is Cl or Br, and L is Cl, Br or ligands containing N, O or P donors), have been widely studied due to their interesting magnetic properties [2,3].

In the tetranuclear copper(II) complex $Cu_4OCl_6L_4$ where L = 3,5-dimethylpyrazole, four copper atoms (separated by 3.070(2) Å – 3.198(3) Å) encapsulate central oxygen atom in a distorted tetrahedral arrangement, with the Cu—O bond lengths of 1.903(6) Å – 1.914(6) Å, and the Cu–O–Cu angles of 107.3(3)° – 114.3(3)°. Between each pair of copper atoms, there is a bridging chlorine atom with Cu—Cl1 distances of 2.340(4) Å – 2.509(3) Å. Closer inspection of the Cu—Cl distances reveals grouping of values around every copper atom in two ′short′ and one ′long′ distances. Average values are 2.375 Å and 2.459 Å for eight short and six long Cu—Cl distances, respectively. Copper coordination sphere is completed by the 3,5-dimethylpyrazole ligand with Cu—N distances of 1.952(7) Å – 1.957(9) Å. Coordination polyhedron can be described as a slightly distorted trigonal bipyramid where three chlorine atoms lie in the equatorial positions while the central oxygen and the ′pyridine′ nitrogen from pyrazolyl ligand are placed at the axial sites. The structure in general is analogous to the structures of previously described tetranuclear complexes of copper $[Cu_4(O)(\mu\text{-}X)_6L_4]$, where L = ligand containing N, O or P donor and X is halogen [4-8]. Complete description of the intermolecular contacts leading to the association of molecules in the crystal is not possible due to the presence of the disordered solvent. Direct contact between the tetranuclear units is achieved by the N–H···Cl hydrogen bonds (N22–H22···Cl61^{i} with 2.65 Å/154°, N32–H32···Cl2^{ii} with 2.79 Å/165°, N42–H42···Cl2^{ii} with 2.71 Å/163°; symmetry codes: i = 1+x,y,z; ii = –1+x,y,z).

Table 1. Data collection and handling.

Crystal:	green prism, size 0.22 × 0.24 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	24.34 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius TurboCAD4, $\omega/2\theta$
$2\theta_{max}$:	59.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10110, 9537
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3092
$N(param)_{refined}$:	361
Programs:	SHELXS-97 [9], SHELXL-97 [10], ORTEP-3 [11], WinGX [12], ORTEP-II [13]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(6)	2*i*	–0.4039	0.3967	1.0487	0.056
H(11)	2*i*	0.4544	–0.1603	0.9507	0.069
H(14)	2*i*	0.4031	0.6513	0.5573	0.078
H(12)	2*i*	0.5148	0.3979	0.6655	0.064
H(14A)	2*i*	0.7370	0.4764	0.6186	0.153
H(14B)	2*i*	0.7163	0.5457	0.5386	0.153
H(14C)	2*i*	0.7125	0.5892	0.6185	0.153
H(15A)	2*i*	0.0509	0.5683	0.6569	0.107
H(15B)	2*i*	0.1011	0.6546	0.5936	0.107
H(15C)	2*i*	0.0643	0.5569	0.5665	0.107
H(22)	2*i*	0.5301	0.0925	0.8321	0.061
H(23)	2*i*	–0.2629	0.1074	0.4279	0.072
H(24A)	2*i*	0.7359	0.0172	0.9364	0.132
H(24B)	2*i*	0.7382	–0.0966	0.9500	0.132
H(24C)	2*i*	0.7755	–0.0416	0.8648	0.132
H(25A)	2*i*	0.1189	–0.0863	0.8388	0.095
H(25B)	2*i*	0.1670	–0.1628	0.9112	0.095
H(25C)	2*i*	0.0917	–0.0601	0.9254	0.095
H(32)	2*i*	–0.3605	0.1934	0.6334	0.055
H(34A)	2*i*	–0.5668	0.0832	0.5349	0.094
H(34B)	2*i*	–0.5875	0.1837	0.5671	0.094
H(34C)	2*i*	–0.5668	0.1802	0.4755	0.094
H(35A)	2*i*	0.1032	0.1038	0.5256	0.093
H(35B)	2*i*	0.0498	0.0850	0.4441	0.093
H(35C)	2*i*	0.0727	0.1912	0.4583	0.093
H(42)	2*i*	–0.4108	0.2940	0.8506	0.054
H(44A)	2*i*	–0.6664	0.2785	0.9602	0.120
H(44B)	2*i*	–0.6875	0.3766	0.9959	0.120
H(44C)	2*i*	–0.6747	0.3777	0.9036	0.120
H(45A)	2*i*	0.0003	0.3514	0.9691	0.101
H(45B)	2*i*	–0.0801	0.4389	1.0085	0.101
H(45C)	2*i*	–0.0762	0.3334	1.0553	0.101

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*i*		0.1852(1)	0.35210(9)	0.69967(7)	0.0295(7)	0.0401(8)	0.0353(8)	–0.0069(6)	–0.0018(6)	0.0060(6)
Cu(2)	2*i*		0.1992(1)	0.13594(9)	0.79362(7)	0.0290(7)	0.0410(8)	0.0352(8)	0.0008(6)	–0.0035(6)	0.0047(6)
Cu(3)	2*i*		–0.0278(1)	0.20360(9)	0.66376(7)	0.0292(7)	0.0486(9)	0.0325(7)	–0.0082(6)	–0.0026(6)	–0.0050(6)
Cu(4)	2*i*		–0.0679(1)	0.28366(9)	0.82642(7)	0.0284(7)	0.0487(9)	0.0330(7)	–0.0047(6)	0.0028(6)	–0.0057(6)
Cl(1)	2*i*		0.0903(4)	0.3289(2)	0.5794(2)	0.104(3)	0.070(2)	0.041(2)	–0.036(2)	–0.026(2)	0.019(2)
Cl(2)	2*i*		0.4087(3)	0.2434(2)	0.7442(2)	0.022(1)	0.071(2)	0.081(2)	–0.006(1)	–0.003(1)	0.029(2)
Cl(3)	2*i*		0.0644(4)	0.1626(2)	0.9139(2)	0.083(2)	0.067(2)	0.038(2)	0.017(2)	0.013(2)	0.012(2)
Cl(4)	2*i*		0.1287(4)	0.0540(2)	0.6912(2)	0.107(3)	0.048(2)	0.054(2)	0.003(2)	–0.029(2)	–0.008(2)
Cl(5)	2*i*		0.0501(4)	0.4343(2)	0.7993(2)	0.105(3)	0.043(2)	0.065(2)	–0.009(2)	0.027(2)	–0.008(2)
Cl(61)	2*i*	0.60	–0.2304(5)	0.1832(4)	0.7684(3)	0.027(2)	0.120(5)	0.058(3)	–0.026(3)	0.012(2)	–0.044(3)
O(1)	2*i*		0.0757(7)	0.2444(4)	0.7463(4)	0.034(4)	0.025(4)	0.037(4)	–0.003(3)	–0.008(3)	0.002(3)
N(11)	2*i*		0.3076(9)	0.4584(6)	0.6523(5)	0.032(5)	0.047(6)	0.056(6)	–0.003(4)	–0.012(4)	0.004(5)
N(12)	2*i*		0.461(1)	0.4488(7)	0.6457(5)	0.044(6)	0.051(6)	0.062(6)	–0.020(5)	0.006(5)	0.009(5)
N(21)	2*i*		0.337(1)	0.0318(6)	0.8441(5)	0.062(6)	0.026(5)	0.043(6)	0.002(4)	–0.006(5)	0.007(4)
N(22)	2*i*		0.4840(9)	0.0424(7)	0.8531(5)	0.030(5)	0.064(7)	0.051(6)	–0.001(5)	–0.021(4)	0.030(5)
N(31)	2*i*		–0.1520(9)	0.1686(6)	0.5840(5)	0.038(5)	0.042(5)	0.035(5)	–0.005(4)	–0.005(4)	0.005(4)
N(32)	2*i*		–0.3086(9)	0.1748(6)	0.5929(5)	0.025(5)	0.065(7)	0.046(6)	–0.011(4)	–0.003(4)	0.000(5)
N(41)	2*i*		–0.2297(8)	0.3212(6)	0.9028(5)	0.022(4)	0.052(6)	0.037(5)	–0.004(4)	0.011(4)	–0.018(4)
N(42)	2*i*		–0.3790(9)	0.3148(6)	0.8910(5)	0.041(5)	0.053(6)	0.042(6)	–0.006(5)	0.006(4)	–0.010(5)
C(11)	2*i*		0.520(1)	0.529(1)	0.6047(7)	0.049(7)	0.08(1)	0.055(8)	–0.039(7)	–0.005(6)	–0.003(7)
C(12)	2*i*		0.399(2)	0.5893(9)	0.5857(8)	0.074(9)	0.046(8)	0.070(9)	–0.016(7)	–0.007(8)	0.012(7)
C(13)	2*i*		0.267(1)	0.5477(9)	0.6138(6)	0.073(9)	0.060(9)	0.031(6)	–0.022(7)	–0.019(6)	0.014(6)
C(14)	2*i*		0.686(1)	0.536(1)	0.5942(9)	0.07(1)	0.14(2)	0.10(1)	–0.06(1)	0.016(9)	0.00(1)
C(15)	2*i*		0.107(1)	0.5851(9)	0.6071(7)	0.074(9)	0.070(9)	0.063(9)	0.002(7)	–0.031(7)	0.022(7)
C(21)	2*i*		0.548(1)	–0.032(1)	0.8971(6)	0.061(8)	0.071(9)	0.037(7)	0.026(7)	–0.016(6)	0.003(7)
C(22)	2*i*		0.441(1)	–0.1000(8)	0.9194(7)	0.082(9)	0.034(7)	0.046(7)	0.020(7)	–0.016(7)	0.022(6)
C(23)	2*i*		0.310(1)	–0.0568(9)	0.8841(7)	0.036(6)	0.046(8)	0.072(9)	0.007(6)	0.002(6)	–0.015(7)
C(24)	2*i*		0.715(1)	–0.039(1)	0.9136(9)	0.063(9)	0.09(1)	0.11(1)	0.029(8)	–0.040(9)	–0.01(1)
C(25)	2*i*		0.159(1)	–0.0948(8)	0.8904(7)	0.069(9)	0.050(8)	0.066(9)	–0.018(7)	–0.002(7)	0.011(7)
C(31)	2*i*		–0.371(1)	0.1479(9)	0.5301(7)	0.046(7)	0.060(8)	0.051(8)	–0.011(6)	–0.012(6)	–0.007(6)
C(32)	2*i*		–0.256(1)	0.1269(9)	0.4773(7)	0.066(8)	0.075(9)	0.046(8)	–0.013(7)	–0.027(7)	–0.017(7)
C(33)	2*i*		–0.119(1)	0.1409(8)	0.5134(7)	0.055(8)	0.046(7)	0.046(7)	0.001(6)	0.004(6)	–0.012(6)
C(34)	2*i*		–0.538(1)	0.1488(9)	0.5266(7)	0.035(7)	0.08(1)	0.070(9)	–0.004(6)	–0.012(6)	–0.007(8)
C(35)	2*i*		0.041(1)	0.1292(9)	0.4827(6)	0.065(8)	0.10(1)	0.026(6)	0.001(7)	0.004(6)	–0.024(7)
C(41)	2*i*		–0.473(1)	0.3463(9)	0.9528(7)	0.040(7)	0.066(8)	0.040(7)	0.003(6)	0.011(6)	–0.015(6)
C(42)	2*i*		–0.376(1)	0.3720(8)	1.0015(6)	0.064(8)	0.047(7)	0.028(6)	–0.008(6)	0.013(6)	–0.011(5)
C(43)	2*i*		–0.227(1)	0.3563(8)	0.9712(7)	0.036(6)	0.050(7)	0.053(8)	–0.014(5)	0.000(6)	–0.017(6)
C(44)	2*i*		–0.640(1)	0.345(1)	0.9531(8)	0.024(6)	0.14(1)	0.07(1)	0.001(7)	0.009(6)	–0.015(9)
C(45)	2*i*		–0.083(1)	0.371(1)	1.0039(7)	0.059(8)	0.11(1)	0.048(8)	–0.027(8)	–0.003(6)	–0.039(8)
Cl(62)	2*i*	0.40	–0.2399(7)	0.3031(7)	0.7206(5)	0.022(3)	0.128(8)	0.061(5)	0.019(4)	–0.009(3)	–0.043(5)

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