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Crystal structure of diaquabis(μ_3-hydroxo)bis(μ_2-hydroxo)-tetrakis(1,10-phenanthroline-*N*,*N*′)tetracopper(II) tetraperchlorate tetrakis(*N*,*N*-dimethylformamide) solvate dihydrate, $[Cu_4(C_{12}H_8N_2)_4(OH)_4(H_2O)_2][ClO_4]_4 \cdot 4(CH_3)_2NCHO \cdot 2H_2O$

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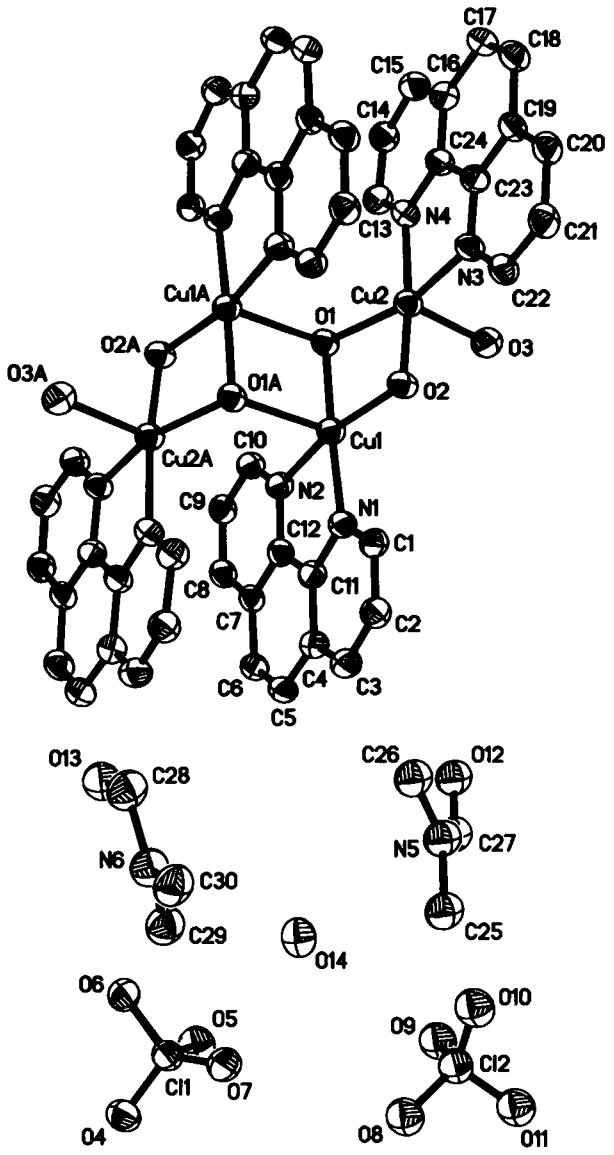

Abstract

$C_{60}H_{72}Cl_4Cu_4N_{12}O_{28}$, triclinic, $P\bar{1}$ (no. 2), a = 10.177(1) Å, b = 14.189(2) Å, c = 15.142(2) Å, α = 114.16(1)°, β = 92.98(1)°, γ = 109.77(1)°, V = 1830.7 Å^3, Z = 1, $R_{gt}(F)$ = 0.049, $wR_{ref}(F^2)$ = 0.155, T = 298 K.

Source of material

Reagents and solvents used were of commercially available quality. 1,10-phenanthroline monohydrate (198 mg, 1 mmol), and $Cu(ClO_4)_2 \cdot 6H_2O$ (371 mg, 1 mmol) were stirred in DMF (DMF = *N*,*N*-dimethylformamide) at room temperature for half an hour. To this solution was added sodium hydroxide (60 mg, 1.5 mmol). The mixture was stirred for 1 h, and then filtered. Blue block-shaped crystals suitable for X-ray structure determination were formed by slow evaporation of the solvent from the filtrate after several weeks.

Discussion

The crystal structure of the title compound consists of tetranuclear $[Cu_4(phen)_4(OH)_4(H_2O)_2]^{4+}$ complex cations, $[ClO_4]^-$ anions, DMF molecules and hydrogen bonded H_2O molecules. The centrosymmetric complex cation is formed by condensation of four CuN_2O_3 square pyramids of two types, namely with $Cu1N_2O_3$ and $Cu2N_2O_3$. The Cu1 atoms are penta-coordinated by one bidentate chelating phenanthroline ligand and three bridging hydroxide groups to form a distorted square pyramid with two phen N atoms, one μ_2-hydroxide O atom and one μ_3-bridging hydroxide O atom at the basal positions and another μ_3-bridging hydroxide O atom at the apical position (d(Cu—N) = 2.006(4) Å, 2.026(4) Å; d(Cu—OH) = 1.937(3) Å, 1.907 Å; d(Cu—O^i(OH)) = 2.340(3) Å, symmetry code i: $-x$,1$-y$,$-z$). The Cu1 atom is shifted by 0.135 Å from the basal plane toward the apical hydroxide O atom. Differently to $Cu1N_2O_3$, in similar $Cu2N_2O_3$ the apical position is occupied by a water molecule. The corresponding distances are d(Cu—N) = 2.014(4) Å, 2.010(4) Å; d(Cu—OH) = 1.940(3) Å, 1.918(3) Å; d(Cu—O(H_2O)) = 2.252(4) Å. The Cu2 atom lies 0.275 Å out of the least-squares basal plane, towards water O.

The central Cu_4O_4 fragment has the composition of a heterocubane, but exhibits a zigzag band of three condensed Cu_2O_2 squares ('opened' cubane): $[Cu_4(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2]^{4+}$, as have been reported [1,2]. The Cu···Cu distance is 2.916 Å. Two bidentate phen ligands are almost parallel with a small dihedral angle of 3.3°. Their interplanar spacing of about 3.38 Å (inter) and 3.44 Å (intra) suggests substantial intra- and intermolecular π-π stacking interactions [3]. Through the latter stacking interactions, the complexes cations are assembled into 2D layers. The $[ClO_4]^-$ anions, DMF and lattice H_2O molecules are inserted between the 2D layers. Hydrogen bonding plays an important role in formation of the whole 3D network.

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Table 1. Data collection and handling.

Crystal:	blue block, size 0.25 × 0.35 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.83 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9122, 6305
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4323
$N(param)_{refined}$:	491
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.3224	0.6892	0.2534	0.059
H(2)	2*i*	0.4827	0.6776	0.3545	0.065
H(3)	2*i*	0.5785	0.5472	0.2942	0.068
H(5)	2*i*	0.5913	0.3817	0.1391	0.064
H(6)	2*i*	0.5107	0.2636	−0.0220	0.065
H(8)	2*i*	0.3433	0.1940	−0.1921	0.064
H(9)	2*i*	0.1676	0.2148	−0.2734	0.066
H(10)	2*i*	0.0861	0.3544	−0.1910	0.062
H(13)	2*i*	−0.0845	0.5873	−0.2288	0.067
H(14)	2*i*	−0.2279	0.6223	−0.3257	0.071
H(15)	2*i*	−0.3149	0.7561	−0.2529	0.075
H(17)	2*i*	−0.3149	0.9219	−0.0933	0.074
H(18)	2*i*	−0.2310	1.0296	0.0719	0.074
H(20)	2*i*	−0.0664	1.0807	0.2312	0.071
H(21)	2*i*	0.1040	1.0485	0.3073	0.075
H(22)	2*i*	0.1635	0.8985	0.2176	0.067
H(25A)	2*i*	0.8308	0.3996	0.5359	0.114
H(25B)	2*i*	0.8372	0.2865	0.4610	0.114
H(25C)	2*i*	0.6962	0.2866	0.4979	0.114
H(26A)	2*i*	0.5477	0.3410	0.4475	0.114
H(26B)	2*i*	0.5344	0.3372	0.3424	0.114
H(26C)	2*i*	0.6248	0.4506	0.4367	0.114
H(27)	2*i*	0.8494	0.2856	0.2979	0.092
H(28)	2*i*	0.0923	0.8115	0.4598	0.097
H(29A)	2*i*	0.3535	0.9687	0.3734	0.119
H(29B)	2*i*	0.4532	1.0581	0.4778	0.119
H(29C)	2*i*	0.3250	1.0765	0.4357	0.119
H(30A)	2*i*	0.1422	1.0306	0.5735	0.115
H(30B)	2*i*	0.3074	1.1007	0.6154	0.115
H(30C)	2*i*	0.2331	0.9904	0.6258	0.115
H(1A)	2*i*	−0.0309	0.4915	−0.1263	0.057
H(2A)	2*i*	0.2102	0.7501	0.1679	0.059
H(3A)	2*i*	0.3343	0.8124	−0.0116	0.074
H(3B)	2*i*	0.2642	0.7315	−0.1081	0.074
H(14A)	2*i*	0.9987	0.4400	0.6647	0.078
H(14B)	2*i*	0.8957	0.4066	0.7144	0.078

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*i*	0.16873(6)	0.55212(5)	0.02774(4)	0.0496(4)	0.0424(3)	0.0442(4)	0.0220(3)	0.0066(3)	0.0126(3)
Cu(2)	2*i*	0.06735(6)	0.70859(5)	−0.00172(4)	0.0529(4)	0.0432(3)	0.0455(4)	0.0236(3)	0.0084(3)	0.0147(3)
C(1)	2*i*	0.3582(5)	0.6337(4)	0.2266(3)	0.050(3)	0.044(3)	0.043(3)	0.017(2)	0.004(2)	0.012(2)
C(2)	2*i*	0.4554(6)	0.6274(4)	0.2872(4)	0.058(3)	0.051(3)	0.047(3)	0.019(3)	0.007(3)	0.019(2)
C(3)	2*i*	0.5127(6)	0.5504(4)	0.2518(4)	0.055(3)	0.054(3)	0.054(3)	0.020(3)	0.004(3)	0.021(3)
C(4)	2*i*	0.4722(5)	0.4743(4)	0.1496(4)	0.050(3)	0.051(3)	0.055(3)	0.020(2)	0.009(2)	0.023(3)
C(5)	2*i*	0.5225(5)	0.3887(4)	0.1021(4)	0.055(3)	0.048(3)	0.060(3)	0.027(3)	0.009(3)	0.022(3)
C(6)	2*i*	0.4741(6)	0.3183(4)	0.0064(4)	0.053(3)	0.048(3)	0.066(4)	0.026(3)	0.014(3)	0.025(3)
C(7)	2*i*	0.3675(5)	0.3232(4)	−0.0550(4)	0.050(3)	0.038(2)	0.054(3)	0.019(2)	0.014(2)	0.017(2)
C(8)	2*i*	0.3103(6)	0.2497(4)	−0.1584(4)	0.059(3)	0.044(3)	0.056(3)	0.024(2)	0.016(3)	0.019(2)
C(9)	2*i*	0.2068(6)	0.2628(4)	−0.2062(4)	0.061(4)	0.043(3)	0.052(3)	0.021(3)	0.012(3)	0.013(2)
C(10)	2*i*	0.1577(5)	0.3477(4)	−0.1562(4)	0.053(3)	0.045(3)	0.050(3)	0.024(2)	0.009(2)	0.011(2)
C(11)	2*i*	0.3679(5)	0.4828(4)	0.0931(4)	0.047(3)	0.047(3)	0.048(3)	0.019(2)	0.012(2)	0.019(2)
C(12)	2*i*	0.3154(5)	0.4062(4)	−0.0112(4)	0.050(3)	0.042(3)	0.050(3)	0.018(2)	0.013(2)	0.019(2)
C(13)	2*i*	−0.1129(6)	0.6466(4)	−0.1988(4)	0.060(3)	0.055(3)	0.045(3)	0.021(3)	0.005(3)	0.018(3)
C(14)	2*i*	−0.2023(6)	0.6658(4)	−0.2571(4)	0.064(4)	0.054(3)	0.052(3)	0.020(3)	0.006(3)	0.020(3)
C(15)	2*i*	−0.2510(6)	0.7465(5)	−0.2145(4)	0.061(4)	0.062(3)	0.064(4)	0.025(3)	0.002(3)	0.028(3)
C(16)	2*i*	−0.2069(6)	0.8154(4)	−0.1141(4)	0.053(3)	0.055(3)	0.063(4)	0.020(3)	0.011(3)	0.029(3)
C(17)	2*i*	−0.2507(6)	0.9079(4)	−0.0594(4)	0.062(4)	0.053(3)	0.076(4)	0.030(3)	0.015(3)	0.030(3)
C(18)	2*i*	−0.1995(6)	0.9728(4)	0.0387(4)	0.067(4)	0.049(3)	0.074(4)	0.031(3)	0.023(3)	0.025(3)
C(19)	2*i*	−0.0983(6)	0.9566(4)	0.0929(4)	0.056(3)	0.042(3)	0.066(4)	0.024(2)	0.016(3)	0.024(3)
C(20)	2*i*	−0.0385(6)	1.0227(4)	0.1945(4)	0.061(4)	0.044(3)	0.068(4)	0.023(3)	0.020(3)	0.018(3)
C(21)	2*i*	0.0610(6)	1.0024(4)	0.2403(4)	0.068(4)	0.045(3)	0.059(3)	0.023(3)	0.017(3)	0.010(3)
C(22)	2*i*	0.0971(6)	0.9129(4)	0.1861(4)	0.064(4)	0.042(3)	0.054(3)	0.026(3)	0.010(3)	0.011(2)
C(23)	2*i*	−0.0563(5)	0.8699(4)	0.0446(4)	0.050(3)	0.044(3)	0.059(3)	0.024(2)	0.016(3)	0.017(3)
C(24)	2*i*	−0.1125(5)	0.7959(4)	−0.0617(4)	0.051(3)	0.050(3)	0.060(3)	0.024(3)	0.015(3)	0.029(3)
C(25)	2*i*	0.7772(7)	0.3278(5)	0.4801(4)	0.083(5)	0.071(4)	0.061(4)	0.032(3)	0.006(3)	0.017(3)
C(26)	2*i*	0.5969(7)	0.3706(5)	0.4063(4)	0.083(5)	0.071(4)	0.061(4)	0.031(3)	0.006(3)	0.017(3)
C(27)	2*i*	0.7822(7)	0.3178(5)	0.3072(5)	0.083(5)	0.070(4)	0.061(4)	0.031(3)	0.006(4)	0.017(3)
C(28)	2*i*	0.1709(8)	0.8434(5)	0.4376(5)	0.093(5)	0.065(4)	0.076(4)	0.037(4)	0.021(4)	0.020(3)
C(29)	2*i*	0.3568(7)	1.0214(5)	0.4392(5)	0.088(5)	0.069(4)	0.076(4)	0.033(4)	0.014(4)	0.027(3)
C(30)	2*i*	0.2334(7)	1.0262(5)	0.5840(4)	0.094(5)	0.064(4)	0.067(4)	0.038(3)	0.016(3)	0.019(3)
Cl(1)	2*i*	0.5086(2)	0.9943(1)	0.2030(1)	0.0555(8)	0.0545(8)	0.0584(8)	0.0240(7)	0.0070(6)	0.0143(6)
Cl(2)	2*i*	0.8133(2)	0.7060(1)	0.4931(1)	0.072(1)	0.0599(8)	0.0555(9)	0.0302(8)	0.0065(7)	0.0155(7)
N(1)	2*i*	0.3133(4)	0.5627(3)	0.1304(3)	0.048(3)	0.043(2)	0.049(2)	0.020(2)	0.008(2)	0.017(2)
N(2)	2*i*	0.2111(4)	0.4185(3)	−0.0604(3)	0.048(3)	0.045(2)	0.044(2)	0.021(2)	0.009(2)	0.014(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(3)	2*i*	0.0385(4)	0.8469(3)	0.0894(3)	0.055(3)	0.045(2)	0.048(2)	0.025(2)	0.010(2)	0.017(2)
N(4)	2*i*	−0.0678(4)	0.7118(3)	−0.1011(3)	0.056(3)	0.047(2)	0.053(3)	0.026(2)	0.014(2)	0.023(2)
N(5)	2*i*	0.7263(6)	0.3445(4)	0.3943(4)	0.082(4)	0.070(3)	0.061(3)	0.032(3)	0.006(3)	0.017(3)
N(6)	2*i*	0.2605(5)	0.9601(4)	0.4873(3)	0.081(4)	0.060(3)	0.056(3)	0.032(3)	0.010(3)	0.013(2)
O(1)	2*i*	0.0319(3)	0.5500(2)	−0.0676(2)	0.056(2)	0.039(2)	0.041(2)	0.021(2)	0.007(2)	0.011(2)
O(2)	2*i*	0.1707(4)	0.6986(2)	0.1015(2)	0.060(2)	0.043(2)	0.039(2)	0.028(2)	0.005(2)	0.008(2)
O(3)	2*i*	0.2585(4)	0.7832(3)	−0.0561(3)	0.060(2)	0.059(2)	0.055(2)	0.023(2)	0.011(2)	0.016(2)
O(4)	2*i*	0.6572(4)	1.0440(3)	0.2455(3)	0.061(3)	0.071(2)	0.071(3)	0.022(2)	0.003(2)	0.023(2)
O(5)	2*i*	0.4861(4)	0.9765(3)	0.1015(3)	0.077(3)	0.076(3)	0.056(2)	0.033(2)	0.006(2)	0.018(2)
O(6)	2*i*	0.4483(4)	0.8869(3)	0.2053(3)	0.071(3)	0.056(2)	0.071(2)	0.028(2)	0.006(2)	0.018(2)
O(7)	2*i*	0.4395(4)	1.0640(3)	0.2555(3)	0.072(3)	0.058(2)	0.072(3)	0.030(2)	0.015(2)	0.017(2)
O(8)	2*i*	0.9227(4)	0.7534(3)	0.5747(3)	0.082(3)	0.071(2)	0.061(2)	0.031(2)	0.005(2)	0.017(2)
O(9)	2*i*	0.8303(4)	0.6290(3)	0.4076(3)	0.082(3)	0.071(3)	0.061(2)	0.032(2)	0.006(2)	0.017(2)
O(10)	2*i*	0.6788(5)	0.6646(3)	0.5107(3)	0.084(3)	0.076(3)	0.061(3)	0.032(2)	0.006(2)	0.018(2)
O(11)	2*i*	0.8318(4)	0.7885(3)	0.4626(3)	0.085(3)	0.076(3)	0.062(2)	0.032(2)	0.006(2)	0.018(2)
O(12)	2*i*	0.7376(5)	0.3393(3)	0.2479(3)	0.083(3)	0.071(3)	0.061(3)	0.032(2)	0.006(2)	0.017(2)
O(13)	2*i*	0.2045(4)	0.7888(3)	0.3645(3)	0.082(3)	0.070(3)	0.061(3)	0.031(2)	0.006(2)	0.017(2)
O(14)	2*i*	0.9850(4)	0.4313(3)	0.7163(2)	0.077(3)	0.070(2)	0.049(2)	0.038(2)	0.013(2)	0.021(2)

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