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Crystal structure of tetrakis(μ-betaine-*O*,*O*′)dibromo-dicopper(II) tetrabromocuprate(II) monohydrate, $[Cu_2\{(CH_3)_3NCH_2COO\}_4Br_2][CuBr_4]\cdot H_2O$, *with a propeller-shaped dinuclear copper complex*

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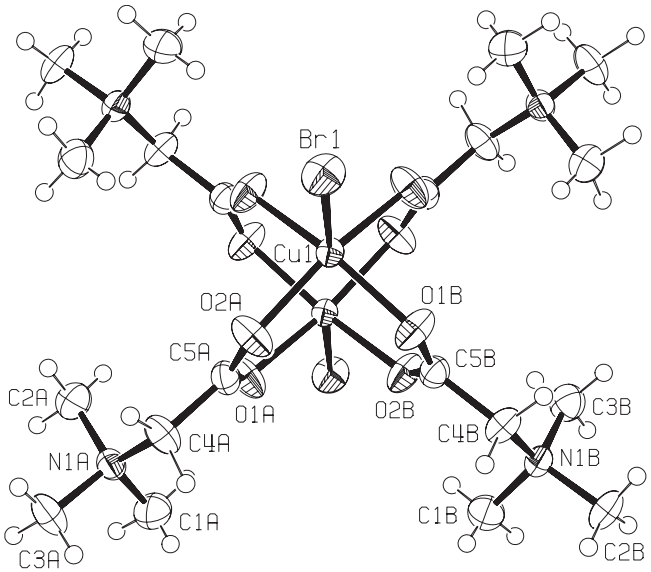

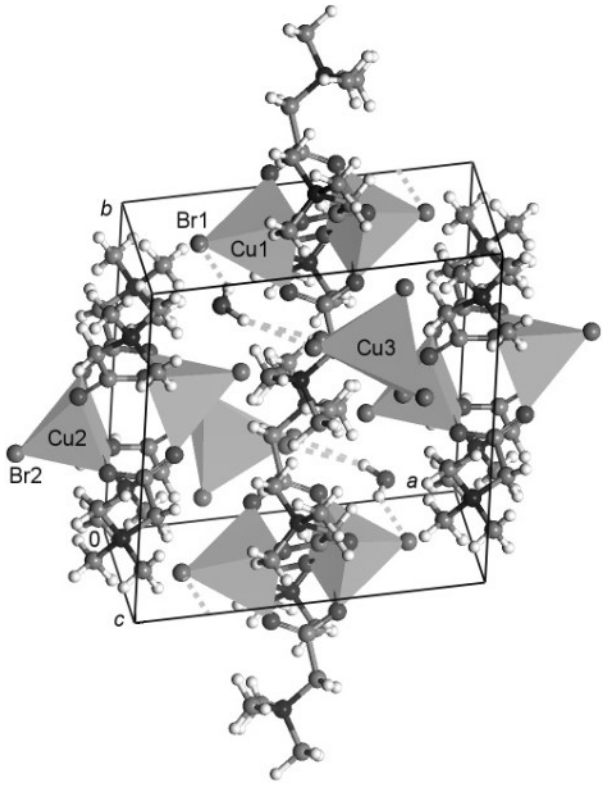

Abstract

$C_{20}H_{46}Br_6Cu_3N_4O_9$, triclinic, $P\bar{1}$ (no. 2), a = 11.6813(7) Å, b = 13.285(1) Å, c = 14.719(1) Å, α = 64.610(9)°, β = 75.233(6)°, γ = 74.823(7)°, V = 1964.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.030, $wR_{ref}(F^2)$ = 0.082, T = 293 K.

Source of material

Equal amounts of betaine monohydrate ($C_5H_{11}NO_2 \cdot H_2O$) and copper dibromide ($CuBr_2$) were dissolved in pure water under stirring at about 320 K. By slow evaporation of the solvent at 293 K intense violet, black appearing crystals emerged. All starting materials were commercial products.

Experimental details

The isotropic displacement parameters of H1W1 and H2W1, belonging to the water molecule, were fixed at a constant value.

Discussion

The structure is built up from $[Cu_2(BET)_4Br_2]^{2+}$ cations (BET = betaine, $C_5H_{11}NO_2$), $[CuBr_4]^{2-}$ anions and water molecules, which are linked by Coulomb interactions and hydrogen bonds. With respect to bond lengths and angles the environments of the two inequivalent $[Cu_2(BET)_4Br_2]^{2+}$ copper complexes located at inversion centers are similar to those of related binuclear complexes observed in other betaine compounds [1-3]. The polyhedron around each copper ion can be described by a square pyramid. Four oxygen atoms define the basal plane with Cu—O distances ranging from 1.961 Å to 1.981 Å. The apical positions are occupied by bromine ions with Cu—Br distances of about 2.60 Å. The Cu—Cu distances between adjacent pyramids in the dimers are 2.78 Å and 2.82 Å, respectively. The Cu—Cu dimer is bridged by the carboxylate groups of four betaine molecules giving rise to the propeller-like shape of the binuclear copper complex (figure, top). Charge compensation is achieved by a highly distorted tetrabromo cuprate tetrahedron. For one of its bromide ligands harmonic anisotropic displacement parameters were not adequate to model the observed electron density distribution. Introduction of a split position (Br61 and Br62) resulted in a significant reduction of the wR_{ref} value and more reliable temperature factors of the corresponding atoms. The $[CuBr_4]^{2-}$ complex is linked by hydrogen bonds via the water molecule to the apical bromide ion of a binuclear copper complex (figure, bottom). These hydrogen bonds are characterized by donor-acceptor distances between 3.322 Å and 3.437 Å.

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Table 1. Data collection and handling.

Crystal:	violet, prismatic, size 0.20 × 0.20 × 0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	77.54 cm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Xcalibur3 & Sapphire3 CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	27926, 7214
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5939
$N(param)_{refined}$:	571
Programs:	SHELXS-97 [3], SHELXL-97 [4]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1W1)	2*i*	0.762(7)	0.068(6)	0.198(4)	0.150
H(2W1)	2*i*	0.727(6)	0.132(6)	0.070(5)	0.150
H(11A)	2*i*	0.411(4)	0.328(3)	0.245(3)	0.05(1)
H(10A)	2*i*	0.378(4)	0.365(3)	0.333(3)	0.04(1)
H(9A)	2*i*	0.428(4)	0.539(4)	0.240(3)	0.05(1)
H(8A)	2*i*	0.446(4)	0.507(3)	0.152(3)	0.04(1)
H(7A)	2*i*	0.554(4)	0.560(3)	0.165(3)	0.05(1)
H(6A)	2*i*	0.521(4)	0.417(4)	0.387(4)	0.06(1)
H(5A)	2*i*	0.651(5)	0.448(4)	0.303(4)	0.07(1)
H(4A)	2*i*	0.617(4)	0.331(4)	0.375(3)	0.04(1)
H(3A)	2*i*	0.598(4)	0.352(4)	0.147(3)	0.05(1)
H(2A)	2*i*	0.672(4)	0.275(4)	0.228(3)	0.05(1)
H(1A)	2*i*	0.680(4)	0.403(4)	0.156(4)	0.06(1)
H(11B)	2*i*	0.630(4)	0.053(3)	0.729(3)	0.05(1)
H(10B)	2*i*	0.641(4)	0.168(3)	0.641(3)	0.04(1)
H(9B)	2*i*	0.360(4)	0.299(4)	0.705(4)	0.06(1)
H(8B)	2*i*	0.385(4)	0.252(4)	0.635(4)	0.05(1)
H(7B)	2*i*	0.465(4)	0.323(3)	0.621(3)	0.04(1)
H(6B)	2*i*	0.587(4)	0.148(4)	0.838(4)	0.07(1)
H(5B)	2*i*	0.468(5)	0.253(4)	0.823(4)	0.08(2)
H(4B)	2*i*	0.587(4)	0.256(3)	0.748(3)	0.05(1)
H(3B)	2*i*	0.445(4)	0.033(4)	0.849(4)	0.06(2)
H(2B)	2*i*	0.363(4)	0.074(4)	0.779(4)	0.06(1)
H(1B)	2*i*	0.344(4)	0.133(3)	0.851(3)	0.04(1)
H(11C)	2*i*	–0.120(3)	0.728(3)	0.211(3)	0.04(1)
H(10C)	2*i*	–0.104(4)	0.817(4)	0.242(3)	0.05(1)
H(9C)	2*i*	–0.068(4)	0.921(4)	0.069(3)	0.06(1)
H(8C)	2*i*	–0.065(4)	0.819(4)	0.051(3)	0.05(1)
H(7C)	2*i*	0.037(4)	0.887(4)	0.000(4)	0.06(1)
H(6C)	2*i*	0.054(6)	0.911(6)	0.171(5)	0.12(2)
H(5C)	2*i*	0.170(5)	0.867(5)	0.103(5)	0.09(2)
H(4C)	2*i*	0.152(4)	0.792(4)	0.223(3)	0.05(1)
H(3C)	2*i*	0.035(6)	0.641(5)	0.115(5)	0.11(2)
H(2C)	2*i*	0.160(4)	0.634(3)	0.181(3)	0.05(1)
H(1C)	2*i*	0.173(6)	0.698(5)	0.072(5)	0.12(2)
H(11D)	2*i*	–0.152(3)	0.796(3)	0.573(3)	0.05(1)
H(10D)	2*i*	–0.169(3)	0.702(3)	0.694(3)	0.04(1)
H(9D)	2*i*	0.013(5)	0.883(5)	0.499(4)	0.09(2)
H(8D)	2*i*	0.106(4)	0.770(4)	0.532(3)	0.05(1)
H(7D)	2*i*	0.108(5)	0.857(4)	0.579(4)	0.07(2)
H(6D)	2*i*	–0.133(6)	0.839(5)	0.740(5)	0.10(2)
H(5D)	2*i*	–0.135(6)	0.912(5)	0.641(5)	0.09(2)
H(4D)	2*i*	–0.039(6)	0.898(5)	0.691(5)	0.10(2)
H(3D)	2*i*	0.007(6)	0.654(6)	0.767(5)	0.09(2)
H(2D)	2*i*	0.106(6)	0.707(5)	0.727(5)	0.11(2)
H(1D)	2*i*	0.100(5)	0.620(5)	0.678(5)	0.10(2)

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*		0.62121(3)	0.98986(3)	0.45733(3)	0.0250(2)	0.0254(2)	0.0270(2)	–0.0048(1)	–0.0038(1)	–0.0115(2)
Cu(2)	2*i*		0.87974(3)	0.48436(3)	0.52119(3)	0.0243(2)	0.0345(2)	0.0316(2)	–0.0075(2)	–0.0030(2)	–0.0146(2)
Cu(3)	2*i*		0.68855(4)	0.72188(4)	0.96978(3)	0.0561(3)	0.0383(2)	0.0338(2)	–0.0087(2)	–0.0122(2)	–0.0144(2)
Br(1)	2*i*		0.83638(3)	0.96725(3)	0.36108(3)	0.0298(2)	0.0593(2)	0.0499(2)	–0.0102(2)	0.0043(2)	–0.0285(2)
Br(2)	2*i*		0.67799(3)	0.42944(3)	0.54970(3)	0.0293(2)	0.0629(3)	0.0556(2)	–0.0203(2)	0.0002(2)	–0.0261(2)
Br(3)	2*i*		0.78608(4)	0.62211(3)	1.11761(3)	0.0531(2)	0.0446(2)	0.0417(2)	–0.0120(2)	–0.0171(2)	–0.0126(2)
Br(4)	2*i*		0.74521(4)	0.57744(4)	0.90524(3)	0.0828(3)	0.0517(3)	0.0490(2)	–0.0098(2)	–0.0110(2)	–0.0298(2)
Br(5)	2*i*		0.73225(4)	0.90602(3)	0.91655(3)	0.0760(3)	0.0375(2)	0.0466(2)	–0.0132(2)	–0.0156(2)	–0.0122(2)
Br(61)	2*i*	0.78(4)	0.4751(3)	0.7681(3)	0.9638(2)	0.0581(9)	0.0573(7)	0.060(2)	–0.0062(8)	–0.028(1)	–0.019(1)
Br(62)	2*i*	0.22	0.498(3)	0.781(2)	0.933(4)	0.080(6)	0.070(4)	0.13(1)	0.015(4)	–0.062(8)	–0.049(6)
O(1W1)	2*i*		0.7871(4)	0.0955(5)	0.1215(3)	0.075(3)	0.161(4)	0.076(3)	–0.024(3)	–0.003(2)	–0.017(3)
O(1A)	2*i*		0.5710(2)	0.1498(2)	0.3716(2)	0.031(1)	0.027(1)	0.056(2)	–0.002(1)	–0.004(1)	–0.003(1)
O(2A)	2*i*		0.3759(2)	0.1626(2)	0.4346(2)	0.034(1)	0.032(1)	0.050(2)	–0.007(1)	–0.007(1)	0.002(1)
N(1A)	2*i*		0.5358(2)	0.3912(2)	0.2590(2)	0.036(1)	0.026(1)	0.032(1)	–0.008(1)	–0.007(1)	–0.008(1)
C(5A)	2*i*		0.4653(3)	0.2017(3)	0.3768(2)	0.035(2)	0.027(2)	0.036(2)	–0.008(1)	–0.010(1)	–0.010(1)
C(4A)	2*i*		0.4359(3)	0.3242(3)	0.3054(3)	0.033(2)	0.028(2)	0.047(2)	–0.006(2)	–0.012(2)	–0.002(2)
C(3A)	2*i*		0.4799(4)	0.5102(3)	0.1994(4)	0.056(3)	0.026(2)	0.054(2)	–0.010(2)	–0.014(2)	–0.000(2)
C(2A)	2*i*		0.5912(4)	0.3928(4)	0.3390(3)	0.056(3)	0.048(3)	0.046(2)	–0.014(2)	–0.012(2)	–0.020(2)
C(1A)	2*i*		0.6317(5)	0.3493(4)	0.1879(3)	0.059(3)	0.054(3)	0.041(2)	–0.019(2)	0.004(2)	–0.021(2)
O(1B)	2*i*		0.6468(2)	0.0432(2)	0.5559(2)	0.040(1)	0.067(2)	0.050(2)	–0.008(1)	–0.005(1)	–0.042(1)
O(2B)	2*i*		0.4518(2)	0.0589(2)	0.6214(2)	0.037(1)	0.062(2)	0.051(2)	–0.012(1)	–0.005(1)	–0.039(1)
N(1B)	2*i*		0.4821(2)	0.1713(2)	0.7373(2)	0.038(2)	0.032(2)	0.031(1)	–0.009(1)	–0.005(1)	–0.017(1)
C(5B)	2*i*		0.5567(3)	0.0683(3)	0.6146(2)	0.035(2)	0.029(2)	0.033(2)	–0.002(1)	–0.011(1)	–0.013(1)
C(4B)	2*i*		0.5859(3)	0.1148(3)	0.6824(3)	0.034(2)	0.046(2)	0.039(2)	–0.002(2)	–0.009(2)	–0.026(2)
C(3B)	2*i*		0.4125(4)	0.2719(4)	0.6641(4)	0.046(2)	0.040(2)	0.048(2)	–0.000(2)	–0.010(2)	–0.020(2)
C(2B)	2*i*		0.5350(4)	0.2115(4)	0.7966(3)	0.057(3)	0.053(3)	0.047(2)	–0.008(2)	–0.009(2)	–0.036(2)
C(1B)	2*i*		0.3996(5)	0.0921(4)	0.8132(3)	0.065(3)	0.053(3)	0.038(2)	–0.027(2)	0.006(2)	–0.017(2)
O(1C)	2*i*		–0.1273(2)	0.6128(2)	0.3895(2)	0.040(1)	0.057(2)	0.039(1)	–0.011(1)	–0.011(1)	–0.004(1)
O(2C)	2*i*		0.0637(2)	0.6357(2)	0.3536(2)	0.044(1)	0.051(2)	0.047(2)	–0.012(1)	–0.018(1)	–0.000(1)
N(1C)	2*i*		0.0349(3)	0.7791(3)	0.1476(2)	0.050(2)	0.036(2)	0.043(2)	–0.014(1)	–0.005(1)	–0.011(1)
C(5C)	2*i*		–0.0393(3)	0.6568(3)	0.3343(3)	0.040(2)	0.034(2)	0.036(2)	–0.006(2)	–0.010(2)	–0.015(2)
C(4C)	2*i*		–0.0682(3)	0.7484(3)	0.2332(3)	0.042(2)	0.038(2)	0.037(2)	–0.010(2)	–0.010(2)	–0.011(2)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(3C)	2*i*		–0.0214(6)	0.8567(5)	0.0535(4)	0.080(4)	0.055(3)	0.044(2)	–0.024(3)	–0.013(2)	0.001(2)
C(2C)	2*i*		0.1105(6)	0.8419(5)	0.1653(5)	0.072(3)	0.070(4)	0.081(4)	–0.040(3)	–0.017(3)	–0.018(3)
C(1C)	2*i*		0.1090(5)	0.6763(4)	0.1304(4)	0.071(3)	0.057(3)	0.059(3)	–0.002(2)	0.002(3)	–0.024(2)
O(1D)	2*i*		–0.1544(2)	0.5924(2)	0.5878(2)	0.039(1)	0.056(2)	0.061(2)	–0.015(1)	0.003(1)	–0.040(1)
O(2D)	2*i*		0.0368(2)	0.6149(2)	0.5528(2)	0.030(1)	0.063(2)	0.076(2)	–0.008(1)	0.004(1)	–0.050(2)
N(1D)	2*i*		–0.0183(3)	0.7723(3)	0.6452(2)	0.032(2)	0.053(2)	0.046(2)	–0.012(1)	–0.002(1)	–0.027(2)
C(5D)	2*i*		–0.0717(3)	0.6370(3)	0.5859(2)	0.032(2)	0.037(2)	0.031(2)	–0.004(1)	–0.003(1)	–0.015(1)
C(4D)	2*i*		–0.1141(3)	0.7286(3)	0.6278(3)	0.027(2)	0.041(2)	0.041(2)	–0.007(1)	–0.002(1)	–0.021(2)
C(3D)	2*i*		0.0647(5)	0.8265(5)	0.5489(4)	0.054(3)	0.057(3)	0.067(3)	–0.027(2)	0.009(2)	–0.031(3)
C(2D)	2*i*		–0.0840(6)	0.8612(7)	0.6867(7)	0.053(3)	0.103(5)	0.126(6)	–0.026(3)	0.012(4)	–0.090(5)
C(1D)	2*i*		0.0534(6)	0.6794(6)	0.7215(5)	0.061(3)	0.101(5)	0.066(4)	–0.017(3)	–0.030(3)	–0.027(3)

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