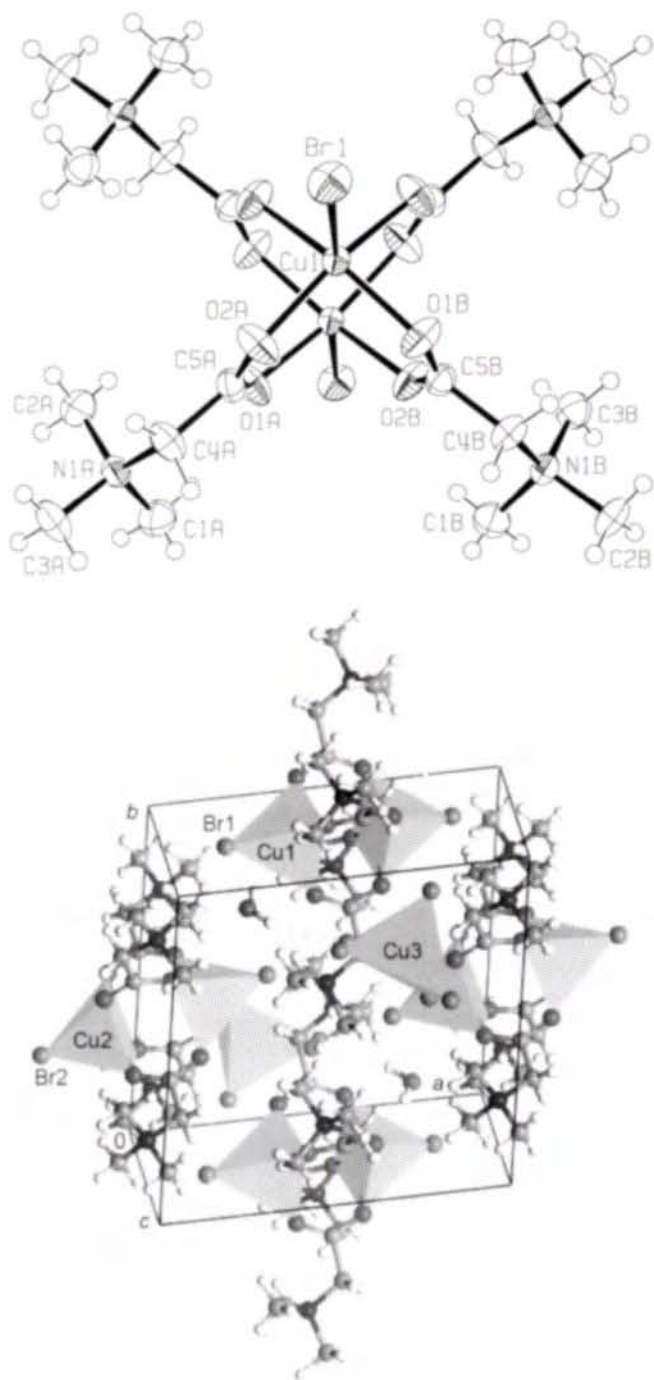


Crystal structure of tetrakis(μ -betaine- O,O')dibromo-dicopper(II) tetrabromocuprate(II) monohydrate, $[\text{Cu}_2\{(\text{CH}_3)_3\text{NCH}_2\text{COO}\}_4\text{Br}_2][\text{CuBr}_4]\cdot\text{H}_2\text{O}$, with a propeller-shaped dinuclear copper complex

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Abstract

$\text{C}_{20}\text{H}_{46}\text{Br}_6\text{Cu}_3\text{N}_4\text{O}_9$, triclinic, $P1$ (no. 2), $a = 11.6813(7)$ Å, $b = 13.285(1)$ Å, $c = 14.719(1)$ Å, $\alpha = 64.610(9)^\circ$, $\beta = 75.233(6)^\circ$, $\gamma = 74.823(7)^\circ$, $V = 1964.7$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.030$, $wR_{\text{ref}}(F^2) = 0.082$, $T = 293$ K.

Source of material

Equal amounts of betaine monohydrate ($\text{C}_5\text{H}_{11}\text{NO}_2 \cdot \text{H}_2\text{O}$) 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 $[\text{Cu}_2(\text{BET})_4\text{Br}_2]^{2+}$ cations (BET = betaine, $\text{C}_5\text{H}_{11}\text{NO}_2$), $[\text{CuBr}_4]^{2-}$ 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 $[\text{Cu}_2(\text{BET})_4\text{Br}_2]^{2+}$ 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 $[\text{CuBr}_4]^{2-}$ 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 Xcalibur 3 & Sapphire3 CCD, φ/ω
2θ _{max} :	52°
N(hkl) _{measured} , N(hkl) _{unique} :	27926, 7214
Criterion for I _{obs} , N(hkl) _{gt} :	I _{obs} > 2 σ(I _{obs}), 5939
N(param) _{refined} :	571
Programs:	SHELXS-97 [3], SHELXL-97 [4]

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(9B)	2i	0.360(4)	0.299(4)	0.705(4)	0.06(1)
H(8B)	2i	0.385(4)	0.252(4)	0.635(4)	0.05(1)
H(7B)	2i	0.465(4)	0.323(3)	0.621(3)	0.04(1)
H(6B)	2i	0.587(4)	0.148(4)	0.838(4)	0.07(1)
H(5B)	2i	0.468(5)	0.253(4)	0.823(4)	0.08(2)
H(4B)	2i	0.587(4)	0.256(3)	0.748(3)	0.05(1)
H(3B)	2i	0.445(4)	0.033(4)	0.849(4)	0.06(2)
H(2B)	2i	0.363(4)	0.074(4)	0.779(4)	0.06(1)
H(1B)	2i	0.344(4)	0.133(3)	0.851(3)	0.04(1)
H(11C)	2i	-0.120(3)	0.728(3)	0.211(3)	0.04(1)
H(10C)	2i	-0.104(4)	0.817(4)	0.242(3)	0.05(1)
H(9C)	2i	-0.068(4)	0.921(4)	0.069(3)	0.06(1)
H(8C)	2i	-0.065(4)	0.819(4)	0.051(3)	0.05(1)
H(7C)	2i	0.037(4)	0.887(4)	0.000(4)	0.06(1)
H(6C)	2i	0.054(6)	0.911(6)	0.171(5)	0.12(2)
H(5C)	2i	0.170(5)	0.867(5)	0.103(5)	0.09(2)
H(4C)	2i	0.152(4)	0.792(4)	0.223(3)	0.05(1)
H(3C)	2i	0.035(6)	0.641(5)	0.115(5)	0.11(2)
H(2C)	2i	0.160(4)	0.634(3)	0.181(3)	0.05(1)
H(1C)	2i	0.173(6)	0.698(5)	0.072(5)	0.12(2)
H(11D)	2i	-0.152(3)	0.796(3)	0.573(3)	0.05(1)
H(10D)	2i	-0.169(3)	0.702(3)	0.694(3)	0.04(1)
H(9D)	2i	0.013(5)	0.883(5)	0.499(4)	0.09(2)
H(8D)	2i	0.106(4)	0.770(4)	0.532(3)	0.05(1)
H(7D)	2i	0.108(5)	0.857(4)	0.579(4)	0.07(2)
H(6D)	2i	-0.133(6)	0.839(5)	0.740(5)	0.10(2)
H(5D)	2i	-0.135(6)	0.912(5)	0.641(5)	0.09(2)
H(4D)	2i	-0.039(6)	0.898(5)	0.691(5)	0.10(2)
H(3D)	2i	0.007(6)	0.654(6)	0.767(5)	0.09(2)
H(2D)	2i	0.106(6)	0.707(5)	0.727(5)	0.11(2)
H(1D)	2i	0.100(5)	0.620(5)	0.678(5)	0.10(2)

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(1W1)	2i	0.762(7)	0.068(6)	0.198(4)	0.150
H(2W1)	2i	0.727(6)	0.132(6)	0.070(5)	0.150
H(11A)	2i	0.411(4)	0.328(3)	0.245(3)	0.05(1)
H(10A)	2i	0.378(4)	0.365(3)	0.333(3)	0.04(1)
H(9A)	2i	0.428(4)	0.539(4)	0.240(3)	0.05(1)
H(8A)	2i	0.446(4)	0.507(3)	0.152(3)	0.04(1)
H(7A)	2i	0.554(4)	0.560(3)	0.165(3)	0.05(1)
H(6A)	2i	0.521(4)	0.417(4)	0.387(4)	0.06(1)
H(5A)	2i	0.651(5)	0.448(4)	0.303(4)	0.07(1)
H(4A)	2i	0.617(4)	0.331(4)	0.375(3)	0.04(1)
H(3A)	2i	0.598(4)	0.352(4)	0.147(3)	0.05(1)
H(2A)	2i	0.672(4)	0.275(4)	0.228(3)	0.05(1)
H(1A)	2i	0.680(4)	0.403(4)	0.156(4)	0.06(1)
H(11B)	2i	0.630(4)	0.053(3)	0.729(3)	0.05(1)
H(10B)	2i	0.641(4)	0.168(3)	0.641(3)	0.04(1)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cu(1)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i	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)	2i	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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		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)	2i		-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)	2i		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)	2i		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)	2i		-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)	2i		-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)	2i		−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)	2i		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)	2i		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)	2i		−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)	2i		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)	2i		−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)	2i		−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)	2i		−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)	2i		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)	2i		−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)	2i		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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