Z. Kristallogr. NCS 221 (2006) 527-528 / DOI 10.1524/ncrs.2006.0184

Crystal structure of tetrakis(μ-betaine-*O,O'*)dibromo-dicopper(II) dibromide dihydrate, $[Cu_2\{(CH_3)_3NCH_2COO\}_4Br_2]Br_2 \cdot 2H_2O$, *with a propeller-shaped dinuclear copper complex*

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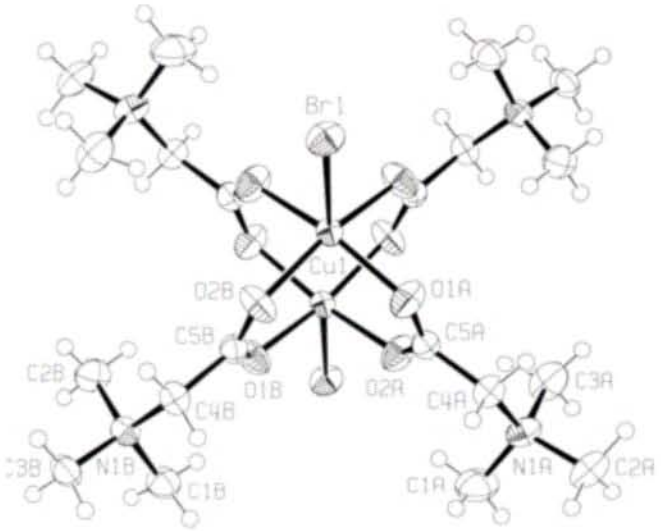
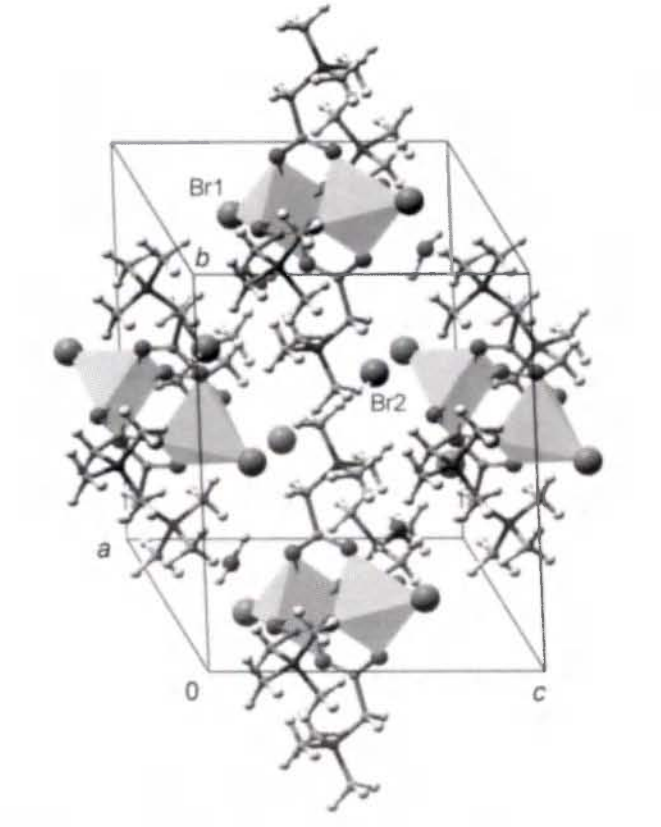
Received October 17, 2006, accepted and available on-line December 18, 2006; CCDC no. 1267/1913





Abstract

$C_{20}H_{48}Br_4Cu_2N_4O_{10}$, monoclinic, $P12_1/c1$ (no. 14), a = 11.3039(7) Å, b = 14.7663(9) Å, c = 11.3239(7) Å, β = 108.194(5)°, V = 1795.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.032, $wR_{ref}(F^2)$ = 0.085, T = 293 K.

Source of material

Betaine monohydrate ($C_5H_{11}NO_2 \cdot H_2O$) and copper dibromide ($CuBr_2$) were dissolved in a non-stoichiometric ratio of 4:3 in pure water under stirring at about 320 K. By slow evaporation of the solvent at 293 K green 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 title structure is composed of binuclear copper complexes, $[Cu_2(BET)_4Br_2]^{2+}$ (BET = betaine, $(CH_3)_3NCH_2COO$), isolated Br^- anions and water molecules in the ratio of 1:2:2. Each copper ion is surrounded by four oxygen atoms in a square planar coordination with Cu—O distances ranging from 1.965 Å to 1.977 Å. In addition, a bromide ion coordinates to copper with d(Cu1—Br1) = 2.556 Å such that a square pyramid with Br in the apical position is formed. The pyramids are bridged pairwise by the carboxylate groups of four betaine molecules, leading to a close Cu—Cu contact of 2.768 Å (figure, top). The resulting propeller-shaped binuclear copper complex is situated on an inversion center. The water molecule links the copper-coordinated Br1 with the free Br2 via hydrogen bonds characterized by donor-acceptor distances of d(O1W1···Br1) = 3.487 Å and d(O1W1···Br2) = 3.309 Å.

The crystal structure of $[Cu_2(BET)_4Br_2]Br_2 \cdot 2H_2O$ (figure, bottom) is essentially isostructural to those of the corresponding chlorine compounds $[Cu_2(BET)_4Cl_2]Cl_2 \cdot 4H_2O$ [1] and $[Rh_2(BET)_4Cl_2]Cl_2 \cdot 4H_2O$ [2]. Variations in position and number of the solvent molecules are probably related to the different sizes of the anions with ionic radii of $r(Cl^-)$ = 1.81 Å and $r(Br^-)$ = 1.96 Å. The water molecules as well as the free halogenide anions required for charge compensation are located in channels along [001] which are formed by the betaine molecules. The smaller chloride ions allow for four H_2O molecules per formula unit. In [1] these water molecules are disordered, whereas in the rhodium compound [2] all water molecules are linked together and to the chloride ions via hydrogen bonds with a shortest O···Cl distance of 3.084 Å, which is considerably shorter than the corresponding O···Br value of 3.309 Å. Substitution of Cl^- by the larger Br^- reduces the space for solvent molecules. Consequently, the number of water molecules is halvened and they are fixed in position and orientation by hydrogen bonds to Br^- as described above.

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Table 1. Data collection and handling.

Crystal:	light green plate, size 0.08 × 0.14 × 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	56.83 cm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Xcalibur3 & Sapphire3 CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12155, 3499
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2900
$N(param)_{refined}$:	275
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)	4e	0.890(5)	−0.197(5)	0.933(6)	0.150
H(2W1)	4e	0.764(7)	−0.260(4)	0.826(6)	0.150
H(11A)	4e	0.832(3)	0.049(2)	0.826(3)	0.032(9)
H(10A)	4e	0.826(4)	−0.049(3)	0.814(4)	0.05(1)
H(9A)	4e	0.939(4)	0.136(3)	0.706(4)	0.07(1)
H(8A)	4e	0.872(4)	0.069(3)	0.582(4)	0.07(1)
H(7A)	4e	1.019(4)	0.084(3)	0.640(4)	0.06(1)
H(6A)	4e	1.044(4)	0.068(3)	0.894(4)	0.07(1)
H(5A)	4e	1.125(4)	0.012(2)	0.826(3)	0.05(1)
H(4A)	4e	1.055(3)	−0.051(3)	0.898(4)	0.05(1)
H(3A)	4e	1.039(5)	−0.091(3)	0.661(5)	0.09(2)
H(2A)	4e	0.885(4)	−0.086(2)	0.598(4)	0.05(1)
H(1A)	4e	0.941(4)	−0.131(3)	0.712(4)	0.05(1)
H(11B)	4e	0.639(3)	0.261(2)	0.420(3)	0.030(8)
H(10B)	4e	0.501(3)	0.281(2)	0.375(3)	0.025(8)
H(9B)	4e	0.632(4)	0.461(3)	0.566(4)	0.06(1)
H(8B)	4e	0.562(4)	0.437(3)	0.422(4)	0.05(1)
H(7B)	4e	0.699(3)	0.407(2)	0.486(3)	0.034(9)
H(6B)	4e	0.660(3)	0.237(3)	0.687(4)	0.05(1)
H(5B)	4e	0.689(3)	0.338(2)	0.716(3)	0.033(9)
H(4B)	4e	0.756(4)	0.293(2)	0.639(4)	0.05(1)
H(3B)	4e	0.434(3)	0.291(3)	0.597(3)	0.04(1)
H(2B)	4e	0.395(4)	0.358(3)	0.480(4)	0.06(1)
H(1B)	4e	0.478(4)	0.381(3)	0.636(4)	0.07(1)

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)	4e	0.44567(3)	0.02394(2)	0.58939(3)	0.0286(2)	0.0268(2)	0.0262(2)	−0.0027(1)	0.0111(1)	−0.0022(1)
Br(1)	4e	0.31587(3)	0.07848(2)	0.72430(3)	0.0370(2)	0.0520(2)	0.0351(2)	0.0048(1)	0.0185(1)	−0.0019(1)
Br(2)	4e	0.90118(3)	0.21869(3)	0.94946(4)	0.0482(2)	0.0482(2)	0.0596(3)	−0.0056(2)	0.0201(2)	−0.0056(2)
O(1W1)	4e	0.8033(4)	−0.2074(3)	0.8770(6)	0.080(3)	0.073(2)	0.214(6)	−0.003(2)	0.004(3)	0.019(3)
O(1A)	4e	0.6138(2)	0.0155(2)	0.7113(2)	0.031(1)	0.065(2)	0.033(1)	−0.000(1)	0.010(1)	−0.007(1)
O(2A)	4e	0.6985(2)	−0.0203(2)	0.5640(2)	0.034(1)	0.069(2)	0.030(1)	0.002(1)	0.007(1)	−0.009(1)
N(1A)	4e	0.9427(2)	−0.0007(2)	0.7329(3)	0.032(1)	0.047(2)	0.032(1)	0.008(1)	0.012(1)	0.007(1)
C(5A)	4e	0.7039(3)	−0.0029(2)	0.6727(3)	0.034(2)	0.029(2)	0.029(2)	−0.001(1)	0.009(1)	−0.000(1)
C(4A)	4e	0.8286(3)	−0.0027(3)	0.7738(3)	0.032(2)	0.040(2)	0.029(2)	0.000(1)	0.010(1)	0.002(2)
C(3A)	4e	0.9419(4)	0.0827(3)	0.6562(4)	0.042(2)	0.065(3)	0.050(2)	−0.004(2)	0.016(2)	0.022(2)
C(2A)	4e	1.0527(3)	0.0072(3)	0.8508(4)	0.031(2)	0.073(3)	0.041(2)	0.006(2)	0.006(2)	0.008(2)
C(1A)	4e	0.9587(5)	−0.0848(3)	0.6660(5)	0.058(3)	0.065(3)	0.060(3)	0.021(2)	0.021(2)	−0.008(2)
O(1B)	4e	0.4912(2)	0.1448(1)	0.5433(2)	0.063(2)	0.028(1)	0.053(1)	−0.006(1)	0.037(1)	−0.001(1)
O(2B)	4e	0.5708(2)	0.1075(1)	0.3936(2)	0.067(2)	0.026(1)	0.045(1)	−0.006(1)	0.031(1)	−0.004(1)
N(1B)	4e	0.5824(2)	0.3257(2)	0.5436(2)	0.036(1)	0.028(1)	0.027(1)	−0.000(1)	0.012(1)	−0.001(1)
C(5B)	4e	0.5403(3)	0.1622(2)	0.4629(3)	0.031(2)	0.030(2)	0.030(2)	−0.001(1)	0.006(1)	0.002(1)
C(4B)	4e	0.5680(3)	0.2601(2)	0.4390(3)	0.041(2)	0.030(2)	0.029(2)	−0.004(1)	0.012(2)	−0.001(1)
C(3B)	4e	0.6226(4)	0.4136(2)	0.5008(4)	0.045(2)	0.025(2)	0.049(2)	−0.003(1)	0.017(2)	0.000(2)
C(2B)	4e	0.6808(4)	0.2951(3)	0.6589(3)	0.046(2)	0.046(2)	0.031(2)	0.005(2)	0.006(2)	0.001(2)
C(1B)	4e	0.4616(3)	0.3412(3)	0.5703(4)	0.044(2)	0.040(2)	0.048(2)	0.002(2)	0.023(2)	−0.003(2)

Acknowledgment. The authors gratefully acknowledge the financial support of the DFG (Forschergruppe 412 "Spin- und Ladungskorrelationen in niedrigdimensionalen Festkörpern").

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