Crystal structure of diaquatetrakis[μ-2,2′-(methylene-bis(sulfanediyl))bis(pyridine 1-oxide)dicopper(II) dibromide diperchlorate, $[Cu_2(H_2O)_2(C_{11}H_{11}N_2O_2S_2)_4]Br_2(ClO_4)_2$

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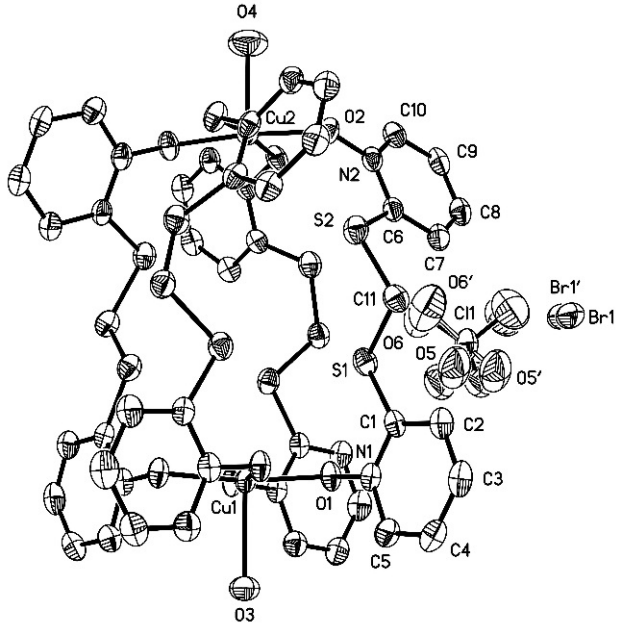

Abstract

$C_{44}H_{48}Br_2Cl_2Cu_2N_8O_{18}S_8$, tetragonal, *P*4/*n* (no. 85), *a* = 13.824(1) Å, *c* = 16.217(2) Å, *V* = 3099.1 Å^3, *Z* = 2, $R_{gt}(F)$ = 0.059, $wR_{ref}(F^2)$ = 0.189, *T* = 298 K.

Source of material

2,2′-(Methylene-bis(sulfanediyl))bis(pyridine 1-oxide) (mspo) and copper salts thereof were prepared, comprising the following steps: oxidizing a 2-acetylaminopyridine with hydrogen peroxide in an inert solvent to give a 2-acetamido-pyridine 1-oxide, cleaving the acetyl group with mineral acid to give a 2-aminopyridine 1-oxide, diazotizing the 2-aminopyridine 1-oxide and treating the diazonium salt with hydrochloric acid to give a 2-chloropridine 1-oxide, treating the 2-chloropridine 1-oxide with a sulfhydryl-donor to give a 2-mercaptopyridine 1-oxide, treating the latter with a CH_2Br_2 to give a 2,2′-(methylenebis(sulfanediyl))bis(pyridine 1-oxide). A solution of $CuBr_2$ (223 mg, 1 mmol) in water (5 mL) was dropped slowly into a solution of mspo (532 mg, 2 mmol) in EtOH (20 mL) and the pH was adjusted to 7-8 with $HClO_4$. The mixed solution was stirred for 2 h at 80 °C and was then cooled to room temperature to give brown-yellow microcrystals, which were collected by filtration, washed successively with H_2O and EtOH, and dried in vacuo. Brown-yellow square crystals suitable for X-ray analysis were obtained by recrystallization of the precipitate from *N*,*N*-dimethylformamide and alcohol (1:1).

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Elemental analysis — found: C, 33.54 %; H, 2.96 %; N, 7.34 %; calculated for $C_{44}H_{48}Br_2Cl_2Cu_2N_8O_{18}S_8$: C, 33.30 %; H, 2.79 %; N, 7.06 %; m.p.: 146-148°. IR data are available in the CIF file.

Experimental details

The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added according to theoretical models.
In the crystal structure, O5 and O5′, O6 and O6′, Br1 and Br1′ are disordered with occupancies of 0.86:0.14, 0.86:0.14, and 0.36:0.14, respectively. It is very difficult to locate the hydrogen atoms of coordinated water molecules, so their information is not provided.

Discussion

The practical interest in heteroaromatic N-oxides is caused first of all by the fact that many of them show biological activity and extraction properties [1,2]. Among N-oxides, there are substances possessing carcinogenic, cancerostatic, mutagenic, insecticidal, herbicidal, fungicidal, anticonvulsant, analgesic and plant-growing properties. Both biological activity and extractional properties are connected with complexation of N-oxide. We have been interested in the study of metal complexes of 2-mercapto-pyridine 1-oxide (Hmpo) due to the fact that these complexes have been successfully used as bactericidal and antifungal agents [3-5].
The Cu(II) complex is a dinuclear cage compound. Each Cu(II) coordination sphere is formed by four mspo ligands and one

water molecule, of which the atoms occupy equatorial and axial positions. Each mspo ligand utilizes terminal oxygen atoms of N-oxide connecting two copper centres. The Cu(II) ion is located on a 2-fold rotation axis, and the coordination sphere can be described as square-pyramidal with an Addison's criterion of 0 (which is 1 for an ideal trigonal bipyramid and 0 for an ideal tetragonal pyramid [6]). In the square pyramid, the basal plane is composed of oxygen atoms O1, O1A, O1B and O1C. The Cu1 and O3 are 0.142(5) Å and 2.509(1) Å above the basal plane. The Cu atom lies nicely in the plane. The coordination bond distances d(Cu—O) = 1.955 Å (av.) for the mspo ligand are comparable with those described in the literature [7,8]. The longer distance d(Cu—O) = 2.269 Å (av.) for the water molecule ligand is in good agreement with d(Cu—O) = 2.262 Å and d(Cu—O) = 2.249 Å reported in the $\{[Cu(H_2O)(bpdo)_2](S_2O_6)(H_2O)\}_n$ and [Cu(bpno){$N(CN)_2$}$_2$ (H_2O)], respectively [7,8]. The bond distances $d(C_{py}—S)$ = 1.741 Å (av.) and d(N—O) = 1.353 Å (av.) agree well with those reported in the literature [3,9]. The angle ∠Cu–O–N = 120.4° (av.) shows that the bonding orbitals of the oxygen atom are of sp^2 character, almost the same as that in mpH_2 ligated complexes [10]. Between Cu1 and Cu2, the distance is 7.947 Å. The dihedral angle between the two pyridine ring planes I (C1, C2, C3, C4, C5 and N1) and II (C6, C7, C8, C9, C10 and N2) is 88.96 (0.19)°. Weak intermolecular hydrogen bonds are observed with d(O3···H3–Br1a^{i}) = 3.367 Å, d(O3···H3–Br1b^{i}) = 3.451 Å, d(O4···H4–Br1b^{ii}) = 3.195 Å, and d(O4···H4–Br1a^{ii}) = 3.251 Å (symmetry code i: –x+1,–y+1,–z+1; ii: –x+1,–y+1,–z).

Table 1. Data collection and handling.

Crystal:	brown-yellow prism, size 0.13 × 0.18 × 0.21 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	24.04 cm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15910, 2741
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1763
$N(param)_{refined}$:	227
Programs:	SHELXS-97, SHELXL-97 [11]

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

Atom	Site	x	y	z	U_{iso}
H(2A)	8g	0.6123	0.3935	0.3623	0.069
H(3A)	8g	0.6167	0.3233	0.4891	0.082
H(4A)	8g	0.6233	0.4177	0.6070	0.075
H(5A)	8g	0.6319	0.5846	0.5943	0.069
H(7A)	8g	0.4677	0.5555	0.1771	0.068
H(8A)	8g	0.3387	0.5998	0.0925	0.071
H(9A)	8g	0.3663	0.6569	–0.0391	0.070
H(10A)	8g	0.5245	0.6721	–0.0860	0.065
H(11A)	8g	0.6916	0.4611	0.2577	0.068
H(11B)	8g	0.5830	0.4692	0.2297	0.068

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)	2c		¾	¾	0.47301(8)	0.0346(5)	U_{11}	0.0484(8)	0	0	0
Cu(2)	2c		¾	¾	–0.01701(9)	0.0413(5)	U_{11}	0.0428(8)	0	0	0
Br(1)	8g	0.36(4)	0.428(2)	0.335(2)	0.2596(5)	0.088(5)	0.15(1)	0.050(2)	–0.058(7)	0.000(2)	0.001(3)
Br(1')	8g	0.14	0.395(4)	0.385(6)	0.252(1)	0.09(1)	0.15(3)	0.050(5)	–0.06(2)	0.000(6)	0.001(8)
N(1)	8g		0.6267(3)	0.5850(3)	0.4709(3)	0.036(2)	0.038(3)	0.065(4)	–0.003(2)	0.002(2)	0.004(2)
N(2)	8g		0.5850(4)	0.6243(3)	0.0174(3)	0.042(3)	0.040(3)	0.063(3)	–0.003(2)	0.005(3)	–0.012(2)
O(1)	8g		0.6268(3)	0.6826(3)	0.4643(3)	0.037(2)	0.034(2)	0.077(3)	0.001(2)	–0.003(2)	–0.002(2)
O(2)	8g		0.6770(3)	0.6285(3)	–0.0108(3)	0.041(2)	0.047(2)	0.075(3)	–0.003(2)	0.016(2)	–0.007(2)
O(3)	2c		¾	¾	0.6190(6)	0.077(4)	U_{11}	0.049(5)	0	0	0
O(4)	2c		¾	¾	–0.1508(7)	0.147(7)	U_{11}	0.058(7)	0	0	0
O(5)	8g	0.86(5)	0.320(2)	0.709(1)	0.2852(8)	0.15(1)	0.15(1)	0.16(1)	–0.05(1)	–0.043(9)	0.069(8)
O(6)	8g	0.86	0.291(1)	0.821(2)	0.190(1)	0.11(1)	0.21(2)	0.20(1)	–0.01(1)	–0.029(9)	0.09(1)
O(5')	8g	0.14	0.26(1)	0.667(8)	0.289(5)	0.15(8)	0.15(8)	0.16(6)	–0.05(6)	–0.04(5)	0.07(5)
O(6')	8g	0.14	0.332(9)	0.76(1)	0.190(7)	0.11(7)	0.2(1)	0.20(8)	–0.01(6)	–0.03(6)	0.09(7)
S(1)	8g		0.6231(1)	0.6016(1)	0.3122(1)	0.057(1)	0.0416(8)	0.066(1)	0.0003(7)	–0.0078(8)	–0.0029(8)
S(2)	8g		0.6806(1)	0.5571(1)	0.1406(1)	0.0416(9)	0.062(1)	0.071(1)	0.0018(7)	0.0010(8)	–0.0018(9)
Cl(1)	4f		¼	¾	0.2407(3)	0.056(2)	0.126(3)	0.112(3)	–0.032(2)	0	0
C(1)	8g		0.6223(4)	0.5320(4)	0.4023(4)	0.036(3)	0.038(3)	0.061(4)	–0.001(2)	–0.006(3)	–0.006(3)
C(2)	8g		0.6170(4)	0.4317(4)	0.4094(5)	0.051(4)	0.047(4)	0.076(5)	–0.004(3)	–0.002(3)	0.002(3)
C(3)	8g		0.6187(5)	0.3903(5)	0.4846(5)	0.053(4)	0.049(4)	0.102(6)	–0.008(3)	0.003(4)	0.008(4)
C(4)	8g		0.6233(4)	0.4465(5)	0.5552(5)	0.049(4)	0.061(4)	0.078(5)	0.001(3)	0.010(4)	0.020(4)
C(5)	8g		0.6280(4)	0.5454(5)	0.5477(4)	0.050(4)	0.055(4)	0.066(4)	–0.001(3)	0.006(3)	0.003(3)
C(6)	8g		0.5721(4)	0.5880(4)	0.0940(4)	0.043(3)	0.041(3)	0.057(4)	–0.006(2)	0.003(3)	–0.010(3)
C(7)	8g		0.4788(4)	0.5789(4)	0.1241(4)	0.049(4)	0.052(4)	0.068(4)	–0.007(3)	0.003(3)	–0.007(3)
C(8)	8g		0.4017(4)	0.6055(5)	0.0732(5)	0.042(3)	0.055(4)	0.080(5)	–0.004(3)	–0.002(3)	–0.011(4)
C(9)	8g		0.4179(5)	0.6400(5)	–0.0053(5)	0.045(4)	0.050(4)	0.079(5)	–0.002(3)	–0.012(3)	–0.016(3)
C(10)	8g		0.5119(4)	0.6492(4)	–0.0332(4)	0.053(4)	0.044(3)	0.066(4)	0.002(3)	–0.006(3)	–0.009(3)
C(11)	8g		0.6425(5)	0.5053(4)	0.2375(4)	0.054(4)	0.051(4)	0.065(4)	0.003(3)	–0.005(3)	–0.007(3)

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