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The Crystal Structure of {2-[(3-Aminopropyl)amino]ethanolato}-copper(II) Tetramer Sulfate Octahydrate, $[Cu_4(C_5H_{13}N_2O)_4](SO_4)_2.8H_2O$

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The title compound crystallizes in the orthorhombic space group *Pbcm* with unit cell dimensions $a = 10.525(10)$, $b = 21.130(8)$, $c = 21.028(10)$ Å and $Z = 8$ for $[Cu_2(C_5H_{13}N_2O)_2](SO_4).4H_2O$. The crystal structure has been determined by direct and Fourier methods from 4060 independent reflections collected with an automatic four-circle diffractometer and refined by block-diagonal least-squares methods to an R value of 0.073.

The complex has a tetranuclear structure with Cu···Cu distances 3.215 – 3.499 Å and a cubane-type Cu_4O_4 core. Four of the twelve Cu – O distances are long (2.571 – 2.584 Å) and eight short (1.949 – 1.970 Å). The amine is coordinated tridentately forming 6- and 5-membered rings. The cation $[Cu_4(C_5H_{13}N_2O)_4]^{4+}$ has C_2 symmetry. Each copper(II) ion has a distorted octahedral (4+2)-coordination with four atoms in equatorial positions at an average Cu – N distance of 2.019 Å and an average Cu – O distance of 1.961 Å, and two oxygen atoms in apical positions at an average distance of 2.623 Å. The sulfate ions form bridges between the cations in the direction of the *b*- and *c*-axes. Both asymmetric SO_4 ions are disordered.

The title compound belongs to a series of {2-[(3-aminopropyl)amino]ethanolato}copper(II)-1:1-complexes which are being studied at this Department by X-ray crystallography and magnetic measurements.[1-5] The crystal structures of $(CuLCl)_4.4H_2O$,[1] $(CuLNO_3)_4.2H_2O$,[2] and $(CuLBr)_4.3H_2O$,[3] $L = C_5H_{13}N_2O$, have been published earlier. In all these complexes a cubane-type Cu_4O_4 core was found and the coordination around the copper(II) ions varied from distorted square-pyramidal (4+1) to distorted octahedral (4+2). In the structures of $(CuLNO_3)_4.2H_2O$ and $(CuLBr)_4.3H_2O$ there were nitrate and bromide bridges between tetranuclear cations $[Cu_4L_4]^{4+}$, but there were no halogenide bridges in the structure of $(CuLCl)_4.4H_2O$. The structure of the present compound, $(CuL)_4(SO_4)_2.8H_2O$, was determined to obtain more information on tetranuclear Cu_4O_4 cores and on the copper(II) coordination sphere.

EXPERIMENTAL

Preparation and analyses of the compound. The complex was prepared by dissolving 0.025 mol $CuSO_4.5H_2O$ in 200 cm^3 of methanol and adding this solution to a stirred solution of 0.050 mol amine in 25 cm^3 of methanol. The blue precipitate that formed was separated and washed with methanol and then recrystallized from a boiling propanol – water mixture (5:1). After several days at room temperature blue platelike crystals were formed.

Copper, diamine and sulfate were analyzed by conventional methods, and water thermogravimetrically. The thermogram was recorded on a Perkin-Elmer TGS-1 thermobalance. The analyses showed the crystals to be hydroscopic, with the amount of water varying between 2 and 3.75 molecules per copper atom depending on the size of the crystals. After heating at 340 K, the smaller water content was found. Anal. calc. for the tetrameric formula $(CuL)_4(SO_4)_2.8H_2O$: Cu 24.00; *L* 44.25; SO_4 18.14; H_2O 13.61 %. Found: Cu 24.1; *L* 43.6; SO_4 19.1; H_2O 11.1 %.

Physical measurements. The approximate dimensions of the crystal used for data collection were $0.4 \times 0.4 \times 0.05$ mm. Both the crystal data and intensity data were measured on an automatic

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Syntex $P2_1$ four-circle diffractometer using graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å). The cell dimensions were obtained by least-squares refinement of the setting angles for 20 well-centered reflections. Preliminary rotation and equi-inclination Weissenberg photographs taken with a Nonius Weissenberg goniometer (Cu$K\alpha$ radiation, $\lambda =$ 1.5418 Å) showed the crystal to belong to the orthorhombic system. The systematic absences $0kl$ for $k = 2n+1$ and $h0l$ for $l = 2n+1$ indicated the centrosymmetric space group *Pbcm* (No. 57) or the non-centrosymmetric $Pbc2_1$.

The intensity data were collected by ω-scan technique at room temperature using scan range 1.0°, scan speed 2.55 – 19.53° min^{-1} depending upon the peak intensity, and 2θ values between 3.0 and 52.0°. Of the 5205 reflections recorded, 4060 had $I > 3\sigma(I)$ and were regarded as observed. The intensity of a standard reflection recorded after every 59 data reflections varied about ± 4 %, during the data collection. Data were corrected for Lorentz and polarizationation effects and also for absorption from ϕ-scan data.

The densities of crystals were measured by the flotation technique in chloroform and carbon tetrachloride. The great difference between measured and calculated density values is due to the uncertain number of water molecules present. During the flotation measurements the crystals continously increased in weight and it can been assumed that $CHCl_3$ or CCl_4 attached to the structure.

CRYSTAL DATA

$[Cu_2(C_5H_{13}N_2O)_2](SO_4).4H_2O$, FW = 529.54
Crystal system: Orthorhombic
Space group: *Pbcm* (No. 57) or $Pbc2_1$ (No. 29)
$a = 10.525(10)$, $b = 21.130(8)$, $c = 21.028(10)$, Å,
$V = 4677(5)$ Å^3, $Z = 8$, $F(000) = 2192$, μ(Mo$K\alpha$) = 20.2 cm^{-1}
$D_m = 1.58(1)$ g cm^{-3}, $D_x = 1.50$ g cm^{-3}.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by direct methods and Fourier syntheses. Since the sulfate ions and water molecules were very disordered, when solution was attempted in the centrosymmetric space group, the non-centrosymmetric one was also tried. In the former case a set of two independent copper atoms was located in an F_o statistical map and in the latter case a set of four independent copper atoms. After least-squares refinement the R values were 0.328 for the centrosymmetric structure and 0.306 for the non-centrosymmetric structure ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). In the calculations of F_c, atomic scattering factors computed from numerical Hartree-Fock wave functions were used for all non-hydrogen atoms.[6] The anomalous dispersion coefficients for copper and sulfur atoms were also included in the calculations.[7] The Fourier maps were very similar for the two sets of atoms, both showing disordered sulfate ions. In an attempt to avoid this disorder, refinement was performed in both space groups with tetrahedral rigid bodies. The R values proved poor, however, and there were large extra maxima in the difference Fourier maps.

Although the refinement of the structure in the space group $Pbc2_1$ gave essentially the same parameters as in *Pbcm*, the bond distances for the tetranuclear cation were more even in the latter and the structure was finally solved in the centrosymmetric space group without rigid bodies. The block-diagonal method was used in the refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 1/(25.0 + |F_o| + 0.004|F_o|^2)$. With isotropic thermal parameters for the oxygen atoms of water molecules and anisotropic thermal parameters for all other non-hydrogen atoms, the final R value was 0.073. The population parameters for the oxygen atoms of water molecules were found using the fixed isotropic thermal parameter $U = 0.1$ Å^2 and fixed coordinates. After refinement the population parameters were fixed with the value 1.0 given to those atoms that had large refined population parameters and values of 0.5 or 0.25 given to atoms with small refined population parameters. After final refinement the average shift/error value for coordinates and temperature factors was 0.058 (maxima value 0.538) and there were no peaks above 0.85 e Å^{-3} in the difference Fourier map. Because of the disordered structure no attempt was made to locate hydrogen atoms. The computations were performed on a UNIVAC 1108 computer with the X-Ray 76 program system.[8] The figures were drawn by ORTEP program.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The atomic coordinates and thermal parameters with their standard deviations are given in Table 1. A list of observed and calculated structure factors can be obtained from the author.

Table 1. Fractional atomic coordinates ($\times 10^4$), thermal parameters[a] ($\times 10^3$) and population parameters. Estimated standard deviations are given in parentheses.

Atom	X/a	Y/b	Z/c	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	PP
Cu(1)	3615(1)	2192(1)	4228(1)	25(1)	41(1)	43(1)	−2(1)	−4(1)	−3(1)	1.0
Cu(2)	5578(1)	3262(1)	4694(1)	25(1)	48(1)	36(1)	−5(1)	2(1)	−1(1)	1.0
O(1)	3776(6)	3049(3)	4571(3)	26(3)	42(4)	37(4)	9(3)	−5(3)	2(3)	1.0
O(2)	5419(6)	2927(3)	5554(3)	26(3)	34(4)	37(3)	−5(3)	−3(3)	−2(3)	1.0
N(11)	3345(9)	1288(5)	3955(5)	43(6)	41(5)	59(6)	−12(5)	−9(5)	−8(5)	1.0
N(12)	1932(8)	2501(5)	3873(4)	28(4)	52(5)	36(5)	−3(4)	−6(4)	0(5)	1.0
N(21)	5854(9)	3544(6)	3793(5)	33(5)	81(7)	41(5)	−10(5)	11(4)	9(5)	1.0
N(22)	7255(8)	3611(4)	5009(4)	32(5)	36(5)	47(5)	5(4)	8(4)	2(4)	1.0
C(11)	2040(13)	1032(7)	3953(8)	42(7)	75(10)	89(11)	−9(7)	−15(8)	−11(9)	1.0
C(12)	1116(12)	1440(7)	3564(7)	47(8)	69(9)	66(9)	−6(7)	−12(7)	−6(7)	1.0
C(13)	802(10)	2066(7)	3849(6)	24(6)	74(9)	61(8)	−14(6)	−13(6)	−1(7)	1.0
C(14)	1648(10)	3104(6)	4182(6)	30(6)	60(7)	57(7)	7(5)	3(6)	1(6)	1.0
C(15)	2901(10)	3474(6)	4259(6)	32(6)	56(7)	50(7)	3(5)	−2(6)	1(6)	1.0
C(21)	7192(14)	3540(8)	3534(7)	58(9)	87(10)	62(9)	−16(8)	20(7)	4(8)	1.0
C(22)	8073(12)	3938(7)	3949(7)	45(7)	68(9)	66(8)	−11(7)	14(7)	−1(7)	1.0
C(23)	8413(10)	3616(6)	4585(7)	27(6)	63(8)	71(9)	−1(6)	20(6)	10(7)	1.0
C(24)	7539(10)	3298(6)	5638(6)	27(5)	53(7)	53(7)	−0(5)	−8(5)	11(6)	1.0
C(25)	6295(10)	3240(6)	5978(5)	26(5)	62(7)	43(6)	−5(6)	−7(5)	−11(6)	1.0
S(11)	3933(9)	2804(5)	2500	56(5)	64(6)	30(4)	−8(5)	0	0	0.5
S(12)	4260(22)	2347(7)	2500	276(25)	89(9)	27(5)	−36(12)	0	0	0.5
S(2)	4684(7)	4980(3)	4778(4)	63(5)	31(3)	101(7)	4(3)	7(4)	−4(4)	0.5
O(11)	4343(12)	2527(6)	3079(5)	106(9)	116(9)	57(6)	−12(8)	−4(6)	10(6)	1.0
O(12)	2546(19)	2738(16)	2500	14(10)	173(29)	16(9)	5(14)	0	0	0.5
O(13)	4182(53)	3554(28)	2500	237(59)	254(59)	50(18)	−182(52)	0	0	0.5
O(14)	6007(50)	2507(32)	2500	90(36)	199(58)	151(46)	−68(41)	0	0	0.5
O(15)	4044(45)	1607(17)	2500	127(37)	57(21)	60(21)	−5(23)	0	0	0.5
O(21)	4858(13)	4431(5)	5069(7)	113(9)	57(6)	125(10)	4(6)	27(8)	−1(7)	1.0
O(22)	3289(22)	5071(9)	4844(16)	73(14)	40(11)	213(32)	6(10)	−11(19)	−24(15)	0.5
O(23)	4927(33)	4881(10)	3963(23)	146(25)	40(12)	397(58)	−22(15)	129(34)	−79(23)	0.5
$O_w(1)$	45(33)	3227(14)	2500	187(11)						1.0
$O_w(2)$	−1911(33)	2264(15)	2500	204(13)						1.0
$O_w(3)$	−1729(51)	1067(24)	2500	155(18)						0.5
$O_w(4)$	−1117(38)	6(17)	1567(19)	162(14)						0.5
$O_w(5)$	619(45)	−330(22)	2500	135(16)						0.5
$O_w(6)$	3042(49)	115(22)	2500	141(16)						0.5
$O_w(7)$	4520(42)	1145(21)	2500	127(14)						0.5
$O_w(8)$	−925(26)	−66(14)	405	262(13)						1.0
$O_w(9)$	3536(100)	4863(44)	1905(47)	218(41)						0.25
$O_w(10)$	3168(132)	6112(63)	2500	209(54)						0.25
$O_w(11)$	4199(126)	5812(62)	2500	197(52)						0.25

[a] The anisotropic thermal parameters are of the form $\exp -2\pi^2[(h^2a^{*2}U_{11}+\cdots+2hka^*b^*U_{12}+\cdots)]$.

Two asymmetric dimeric units form a tetranuclear cation $[Cu_4(C_5H_{13}N_2O)_4]^{4+}$ (Fig. 1). The cation has C_2 symmetry (S_4 pseudosymmetry) and a cubane-type Cu_4O_4 core. In the core there are four long Cu−O distances (2.571−2.584 Å) and eight short Cu−O distances (1.949−1.970 Å). These distances are in agreement with those of $(CuLNO_3)_4.2H_2O$ and $(CuLBr)_4.3H_2O$. Two of the longer distances are perpendicular to the other two, as they were in the other copper(II) compounds of the present amine. The Cu···Cu distances in the core vary between 3.215 and 3.499 Å. The deviations of atoms from the least-squares limiting planes of the cube and the acute angles between the planes are shown in Table 2. These values, too, are similar to those of the nitrate and bromide salts of this cation.

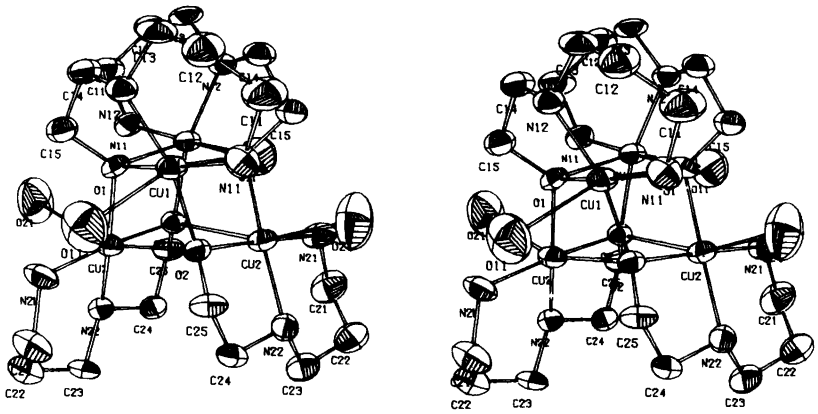

Fig. 1. Stereo view of the complex $[Cu_4(C_5H_{13}N_2O)_4]^{4+}$. The oxygen atoms O11 and O21 of the SO_4 groups are included in the drawing.

The copper(II) ions lie 0.08 – 0.10 Å outside and the oxygen atoms 0.07 – 0.11 Å inside the limiting planes.

The two independent copper(II) ions have distorted octahedral (4 + 2)-coordination. A ligand is coordinated to each copper(II) ion tridentately to form a six-membered chelate ring involving the nitrogen atoms of the ligand and five-membered chelate ring involving the oxygen atom of the ethanol group and the nitrogen atom attached to the ethanol group. The fourth equatorial position is occupied by the oxygen atom of the second ligand. The equatorial atoms deviate from least-squares planes by about ±0.15 Å and the copper(II) ions by 0.05 – 0.06 Å (Table 3). The dihedral angle between planes [Cu(1),N(11),N(12)] and [Cu(1),-O(1),O(2)^{I}] is 13.1° and that between planes [Cu(2),N(21),N(22)] and [Cu(2),O(2),O(1)] is 12.8°. These values indicate some tetrahedral distortion. In the planes the average interatomic distances are: Cu(i) – N(i1) 2.010, Cu(i) – N(i2) 2.027, Cu(i) –

Table 2. Deviations (Å) of atoms from least-squares planes for Cu_4O_4, and the acute angles (°) between the planes.

Plane 1:	Cu(1) −0.08	Cu(1)^{I} −0.09	O(1) 0.08	O(1)^{I} 0.09
Plane 2:	Cu(1) −0.08	Cu(2)^{I} −0.10	O(1)^{I} 0.07	O(2)^{I} 0.11
Plane 3:	Cu(2) 0.08	Cu(2)^{I} 0.08	O(2) −0.08	O(2)^{I} −0.08
Plane 4:	Cu(2) 0.10	Cu(1)^{I} 0.08	O(1) −0.07	O(2) −0.10
Plane 5:	Cu(1) −0.10	Cu(2) −0.08	O(1) 0.11	O(2)^{I} 0.08
Plane 6:	Cu(1)^{I} 0.10	Cu(2)^{I} 0.08	O(2) −0.08	O(1)^{I} −0.11

Acute angles (°) between the planes

Plane	2	3	4	5	6
1	80.4	0.0	80.2	80.2	80.1
2		80.4	19.3	88.0	88.7
3			80.3	80.2	80.1
4				88.5	88.2
5					19.7

[I] Equivalent position x, $1/2 - y$, $1 - z$.

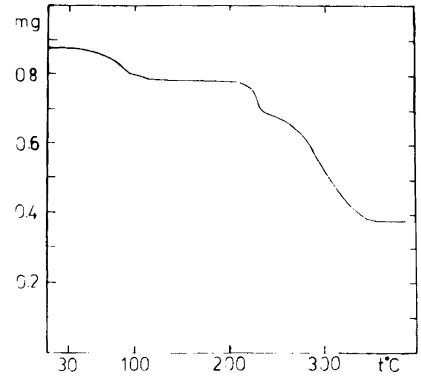

Fig. 2. Thermogram of $[Cu_4(C_5H_{13}N_2O)_4](SO_4)_2.8H_2O$.

Table 3. Least-squares planes through N(i1), N(i2), O(i), O(j) and the distances (Å) of some atoms from these planes.

N(11)	N(12)	O(1)	O(2)[I]	Cu(1)	O(1)[I]	O(11)
0.14	−0.15	0.17	−0.15	0.05	2.39	−2.57
N(21)	N(22)	O(2)	O(1)	Cu(2)	O(2)[I]	O(21)
−0.13	0.14	−0.16	0.14	−0.06	−2.39	2.63

[I] Equivalent position x, $1/2-y$, $1-z$.

Table 4. Intramolecular distances (Å) and angles (°) in $[Cu_4(C_5H_{13}N_2O)_4]^{4+}$. Estimated standard deviations are given in parentheses.

Cu(1)−O(11)	2.630(11)	O(11)−Cu(1)−O(1)	93.7(3)	Cu(1)−O(1)−Cu(2)	110.1(3)
Cu(1)−O(1)	1.957(7)	O(11)−Cu(1)−O(2)[I]	88.1(3)	Cu(1)−O(1)−Cu(1)[I]	99.9(3)
Cu(1)−O(2)[I]	1.970(7)	O(11)−Cu(1)−O(1)[I]	158.7(3)	Cu(2)−O(1)−Cu(1)[I]	88.8(2)
Cu(1)−O(1)[I]	2.584(7)	O(11)−Cu(1)−N(11)	92.0(4)	Cu(1)−N(11)−C(11)	118.7(8)
Cu(1)−N(11)	2.015(10)	O(11)−Cu(1)−N(12)	80.2(4)	N(11)−C(11)−C(12)	112.7(12)
Cu(1)−N(12)	2.030(9)	O(1)−Cu(1)−O(2)[I]	87.1(3)	C(11)−C(12)−C(13)	115.1(12)
N(11)−C(11)	1.48(2)	O(1)−Cu(1)−O(1)[I]	79.4(3)	C(12)−C(13)−N(12)	112.4(9)
C(11)−C(12)	1.54(2)	O(1)[I]−Cu(1)−O(2)[I]	71.5(2)	C(13)−N(12)−Cu(1)	120.3(7)
C(12)−C(13)	1.49(2)	O(1)−Cu(1)−N(11)	174.1(4)	Cu(1)−N(12)−C(14)	107.2(7)
C(13)−N(12)	1.50(1)	O(2)[I]−Cu(1)−N(11)	94.6(3)	C(13)−N(12)−C(14)	112.7(9)
N(12)−C(14)	1.46(2)	O(1)[I]−Cu(1)−N(11)	95.8(3)	N(12)−C(14)−C(15)	108.3(9)
C(14)−C(15)	1.54(2)	O(1)−Cu(1)−N(12)	85.0(3)	C(14)−C(15)−O(1)	106.2(9)
C(15)−O(1)	1.44(1)	O(2)[I]−Cu(1)−N(12)	165.5(3)	C(15)−O(1)−Cu(1)	110.6(6)
		O(1)[I]−Cu(1)−N(12)	118.7(3)	C(15)−O(1)−Cu(2)	122.2(6)
		N(11)−Cu(1)−N(12)	94.4(4)	C(15)−O(1)−Cu(1)[I]	121.7(6)
Cu(2)−O(21)	2.703(11)	O(21)−Cu(2)−O(2)	92.1(3)	Cu(2)−O(2)−Cu(1)[I]	110.2(3)
Cu(2)−O(2)	1.949(7)	O(21)−Cu(2)−O(1)	88.7(4)	Cu(2)−O(2)−Cu(2)[I]	99.3(3)
Cu(2)−O(1)	1.967(7)	O(21)−Cu(2)−O(2)[I]	159.1(3)	Cu(2)[I]−O(2)−Cu(1)[I]	89.1(2)
Cu(2)−O(2)[I]	2.571(7)	O(21)−Cu(2)−N(21)	92.5(4)	Cu(2)−N(21)−C(21)	118.2(8)
Cu(2)−N(21)	2.007(10)	O(21)−Cu(2)−N(22)	79.4(4)	N(21)−C(21)−C(22)	111.0(11)
Cu(2)−N(22)	2.024(9)	O(1)−Cu(2)−O(2)	87.5(3)	C(21)−C(22)−C(23)	113.2(12)
N(21)−C(21)	1.51(2)	O(2)−Cu(2)−O(2)[I]	80.1(3)	C(22)−C(23)−N(22)	109.2(9)
C(21)−C(22)	1.53(2)	O(1)−Cu(2)−O(2)[I]	71.8(3)	C(23)−N(22)−Cu(2)	120.9(7)
C(22)−C(23)	1.54(2)	O(2)−Cu(2)−N(21)	174.9(4)	Cu(2)−N(22)−C(24)	107.4(6)
C(23)−N(22)	1.51(1)	O(1)−Cu(2)−N(21)	94.7(3)	C(23)−N(22)−C(24)	111.2(8)
N(22)−C(24)	1.51(2)	O(2)[I]−Cu(2)−N(21)	96.3(4)	N(22)−C(24)−C(25)	106.4(9)
C(24)−C(25)	1.50(2)	O(2)−Cu(2)−N(22)	84.5(3)	C(24)−C(25)−O(2)	107.5(9)
C(25)−O(2)	1.44(1)	O(1)−Cu(2)−N(22)	165.3(3)	C(25)−O(2)−Cu(2)	110.6(6)
		O(2)[I]−Cu(2)−N(22)	118.6(3)	C(25)−O(2)−Cu(1)[I]	122.0(6)
		N(21)−Cu(2)−N(22)	94.3(4)	C(25)−O(2)−Cu(2)[I]	122.1(6)

[I] Equivalent position x, $1/2-y$, $1-z$.

O(i) 1.954 and Cu(i)−O(j) 1.967 Å for i,j = 1,2 and i ≠ j, all of which are typical to coordination bonds. In the axial positions of the octahedron lie the oxygen atom of the third amine and the oxygen atom of a sulfate ion. The average axial Cu−O distances of 2.578 Å for the amine oxygen atom and 2.667 Å for the sulfate oxygen atom indicate weak interactions. The angle between the axial line and the normal to the equatorial plane is about 14.5°.

The six-membered ring of the ligand amine is in chair conformation. The bond lengths and angles

Table 5. Bond lengths (Å) and angles (°) in SO_4^{2-} ions. Estimated standard deviations are given in parentheses.

$SO_4(11)$		$SO_4(12)$		$SO_4(2)$	
S(11)–O(11)	1.42(1)	S(12)–O(11)	1.28(1)	S(2)–O(21)	1,32(1)
S(11)–O(12)	1.47(2)	S(12)–O(14)	1.87(6)	S(2)–O(22)	1.49(2)
S(11)–O(13)	1.61(6)	S(12)–O(15)	1.57(4)	S(2)–O(23)	1.74(5)
S(11)–O(11)^{II}	1.42(1)	S(12)–O(11)^{II}	1.28(1)	S(2)–O(21)^{III}	1.37(1)
O(11)–S(11)–O(11)^{II}	118(1)	O(11)–S(12)–O(11)^{II}	144(2)	O(21)–S(2)–O(21)^{III}	129(1)
O(11)–S(11)–O(12)	105(1)	O(11)–S(12)–O(14)	83(1)	O(21)–S(2)–O(22)	102(1)
O(11)–S(11)–O(13)	111(1)	O(11)–S(12)–O(15)	108(1)	O(21)–S(2)–O(23)	109(1)
O(12)–S(11)–O(11)^{II}	105(1)	O(14)–S(12)–O(11)^{II}	83(1)	O(22)–S(2)–O(21)^{III}	102(1)
O(12)–S(11)–O(13)	105(3)	O(14)–S(12)–O(15)	109(3)	O(22)–S(2)–O(23)	105(2)
O(13)–S(11)–O(11)^{II}	111(1)	O(15)–S(12)–O(11)^{II}	108(1)	O(23)–S(2)–O(21)^{III}	107(1)

Equivalent positions: II, $x,y,1/2-z$; III, $1-x,1-y,1-z$.

(Table 4) are normal for this amine. The distortion of the sp^3-hybrid orbitals of the oxygen atoms coordinated to three copper(II) ions is similar to that reported earlier for other copper(II) salts of this amine.[2,3] The average angles around the oxygen atoms are 109°.

The tetranuclear cations are joined together by sulfate ions: by $SO_4(1)$ in the direction of the *c*-axis and by $SO_4(2)$ in the direction of the *b*-axis. The geometry of the disordered sulfate ions is irregular (Table 5). Where the oxygen atoms of the sulfate ions are semicoordinated to copper(II) ions,

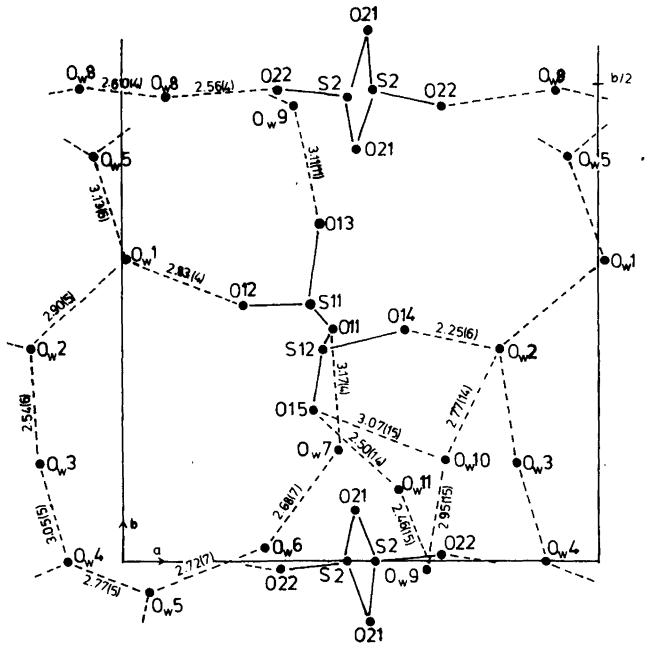

Fig. 3. Schematic projection of the structure showing the oxygen atoms of water molecules and sulfate ions in the *ab*-plane and the interatomic distances (Å) between the oxygen atoms. Standard deviations are in parentheses. The oxygen atom O23 and the lower $O_w8\cdots O22-S2-S2-O22\cdots O_w8$ chain (located near the *a* axis) are omitted for clarity.

the S–O distances are markedly shorter than the typical S–O bond length 1.51 Å.[9] One of the remaining S–O distances is long and one normal in each SO_4 group, resulting in average bond lengths of 1.48 Å for $SO_4(11)$, 1.50 Å for $SO_4(12)$ and 1.48 Å for $SO_4(2)$. The average bond angles are, respectively, 109, 106 and 109°. Similar disordered sulfate groups have also been found in other compounds.[10,11] Usually S–O bonds where the oxygen atom is coordinated to a copper(II) ion are long and the other bonds short reflecting the strength of the coordination bond relative to the hydrogen bond.[11,12] Because this is not the case in the present compound, the bond stretching and shortening seem to depend upon the environment in which the sulfate ion is located.

The water molecules are lattice water bound loosely to the structure, as indicated also in the thermogram of the compound (Fig. 2). Some interatomic distances between water and sulfate oxygen atoms below 3.20 Å are shown in Fig. 3. It can be assumed that several of the water molecules act as bridges joined to the structure by hydrogen bonds. Besides the bridges shown in Fig. 3 there is probably a bridge $O_w(8)\cdots O_w(4)\cdots O_w(4)'\cdots O_w(8)'$ in the direction of the *c*-axis. The split SO_4 groups and half oxygen atoms indicate that the bridges are being broken. The $O_w(10)\cdots O_w(11)$ distance of 1.26 Å indicates that these atoms cannot be present in both places simultaneously. One of these atoms exists only when the position $SO_4(12)$ is occupied.

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