

# The Crystal Structure of {2-[(3-Aminopropyl)amino]ethanolato}-copper(II) Bromide Tetramer Trihydrate, [Cu<sub>4</sub>(C<sub>5</sub>H<sub>13</sub>N<sub>2</sub>O)<sub>4</sub>]Br<sub>4</sub>·3H<sub>2</sub>O

KARI NIEMINEN and AARNE PAJUNEN

Department of Inorganic Chemistry, University of Helsinki, SF-00100 Helsinki 10, Finland

The title compound crystallizes in the monoclinic space group  $P2_1/n$  with unit cell dimensions  $a=18.648(8)$ ,  $b=22.013(8)$ ,  $c=9.327(5)$  Å,  $\beta=90.08(4)^\circ$  and  $Z=4$ . The crystal structure has been determined by direct and Fourier methods from 3914 independent reflections collected with an automated four-circle diffractometer and refined by block-diagonal least-squares methods to an  $R$  value of 0.049. The complex has a tetranuclear structure with Cu··Cu distances 3.186–3.555 Å and a cubane-type Cu<sub>4</sub>O<sub>4</sub> core. Four of the twelve Cu–O distances are long (2.521–2.633 Å) and eight short (1.951–1.976 Å). Two of the longer distances are perpendicular to the other two. The amine is coordinated tridentately forming 6- and 5-membered rings. The cation [Cu<sub>4</sub>(C<sub>5</sub>H<sub>13</sub>N<sub>2</sub>O)<sub>4</sub>]<sup>4+</sup> has  $S_4$  pseudosymmetry. Each copper(II) ion has a distorted octahedral (4+2)-coordination with four atoms in equatorial positions at average distances Cu(i)–N(i1) 1.991 Å, Cu(i)–N(i2) 2.025 Å, Cu(i)–O(i) 1.955 Å, Cu(i)–O(j) 1.969 Å, and an oxygen atom and a bromide ion at average distances 2.583 and 3.240 Å in apical positions. One of the four bromide ions forms a bridge between the tetranuclear units in the direction of the  $c$ -axis.

In recent years several structures with a cubane-type Cu<sub>4</sub>O<sub>4</sub> core have been reported.<sup>1–9</sup> In all these structures an approximately tetrahedral array of copper(II) ions has been bridged by an also roughly tetrahedral array of the alkoxy-group oxygen atoms of different ligands. In each cube there are eight short and four long Cu–O distances. According to Mergehenn and Haase,<sup>8</sup> two types of cores can be distinguished: one having all four stretching directions parallel, and the other having two stretched

edges perpendicular to the other two. The coordination around copper(II) ions varies, being either distorted square pyramidal, distorted octahedral or distorted bipyramidal.

The compounds have also been studied magnetically and found to have nearly normal magnetic moments at room temperature.<sup>1,2,6,10–16</sup> Nishida and Kida<sup>15</sup> have distinguished four different types of magnetic behaviour for polynuclear alkoxy-bridged copper(II) complexes on the basis of  $\chi_M-T$  curves. Two types of these apply to tetranuclear Cu<sub>4</sub>O<sub>4</sub> cubane-type cores, one (*type-B*) obeying the Curie-Weiss law with positive Weiss constant, and the other (*type-C(a)*) obeying the Curie-Weiss law with negative Weiss constant.

The present determination of the crystal structure of the one-to-one complex formed by 2-[(3-aminopropyl)amino]ethanol and copper(II) bromide continues a series of investigations in this laboratory on structures having the above-described cubane-type Cu<sub>4</sub>O<sub>4</sub> core, and was performed to obtain more information on the coordination around the copper(II) ions and the effects of different anions on the geometry of the core.

## EXPERIMENTAL

The preparation of the blue plate-like crystals has been reported earlier.<sup>16</sup> The approximate dimensions of the crystal used for data collection were 0.4 × 0.3 × 0.1 mm<sup>3</sup>. Both the crystal data and the intensity data were measured on an automated Syntex P2<sub>1</sub> four-circle diffractometer using graphite-monochromated MoK $\alpha$  radiation ( $\lambda=0.7107$  Å).

The space group is monoclinic  $P2_1/n$  (No. 14), and not orthorhombic as reported earlier.<sup>16</sup>

The cell dimensions were obtained by least-squares refinement of setting angles for 14 well-centered reflections and the intensity data were collected by the  $\theta/2\theta$ -scanning method (scan range  $1.0^\circ$ , scan speed  $2.00-14.50^\circ \text{ min}^{-1}$  and  $5.0^\circ \leq$

$2\theta \leq 45.0^\circ$ ). Of the 6128 reflections recorded, 3914 had  $I > 2.0 \sigma(I)$  and were regarded as observed. Data were corrected for Lorentz and polarization effects and also for absorption from  $\phi$ -scan data. The standard reflections measured periodically during the data collection varied irregularly by about  $\pm 6\%$ .

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and thermal parameters<sup>a</sup> ( $\times 10^3$ ). Estimated standard deviations are given in parentheses.

Atom	X/a	Y/b	Z/c	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Br(1)	-2450(1)	2825(1)	-1554(1)	31(1)	43(1)	40(1)	1(1)	-1(1)	4(1)
Br(2)	113(1)	2640(1)	3448(1)	43(1)	42(1)	26(1)	1(1)	0(1)	2(1)
Br(3)	2544(1)	1939(1)	-1391(1)	35(1)	40(1)	45(1)	5(1)	-1(1)	-1(1)
Br(4)	2267(1)	-161(1)	-2735(2)	72(1)	46(1)	50(1)	2(1)	-6(1)	-1(1)
Cu(1)	-899(1)	2206(1)	-2267(1)	27(1)	21(1)	24(1)	-6(1)	-3(1)	3(1)
Cu(2)	-169(1)	3009(1)	195(1)	18(1)	19(1)	32(1)	-1(1)	2(1)	-2(1)
Cu(3)	539(1)	2888(1)	-3215(1)	18(1)	17(1)	31(1)	1(1)	3(1)	4(1)
Cu(4)	825(1)	1880(1)	-830(1)	29(1)	19(1)	26(1)	1(1)	-3(1)	2(1)
O(1)	-514(4)	2189(3)	-315(7)	25(4)	20(4)	24(4)	-2(3)	-2(3)	5(3)
O(2)	763(4)	2763(3)	-566(7)	17(4)	18(4)	28(4)	-4(3)	1(3)	2(3)
O(3)	-438(4)	3000(3)	-2518(8)	19(4)	20(4)	32(4)	-1(3)	-5(3)	-0(3)
O(4)	452(4)	2014(3)	-2767(7)	35(4)	17(4)	20(4)	7(3)	-6(3)	2(3)
N(11)	-1239(5)	2166(5)	-4318(9)	41(6)	40(6)	19(4)	-11(5)	-0(4)	-2(4)
N(12)	-1489(4)	1495(4)	-1599(9)	22(5)	7(4)	30(5)	-4(4)	-9(4)	0(4)
N(21)	-1111(5)	3312(5)	850(11)	23(5)	40(6)	40(6)	11(5)	-7(4)	-7(5)
N(22)	370(5)	3736(4)	964(9)	21(5)	28(5)	29(5)	-10(4)	8(4)	-6(4)
N(31)	1554(5)	2817(4)	-3806(11)	34(6)	18(5)	49(6)	9(4)	3(5)	-5(5)
N(32)	404(5)	3727(4)	-4067(9)	32(5)	19(5)	28(5)	4(4)	5(4)	-1(4)
N(41)	1101(6)	1717(5)	1196(11)	38(6)	34(6)	38(6)	8(5)	-6(5)	5(5)
N(42)	996(5)	1011(4)	-1513(10)	30(5)	12(4)	37(5)	-10(4)	3(4)	6(4)
C(11)	-1440(7)	1569(6)	-4927(12)	41(8)	49(8)	27(6)	-9(6)	-10(6)	-6(6)
C(12)	-1956(7)	1215(6)	-4015(13)	45(8)	42(8)	35(6)	-8(6)	-24(6)	-6(6)
C(13)	-1666(7)	968(6)	-2591(13)	44(8)	39(7)	35(6)	-1(6)	2(6)	-13(6)
C(14)	-1181(6)	1282(5)	-206(12)	24(6)	33(7)	31(6)	-1(5)	-8(5)	0(5)
C(15)	-953(6)	1830(6)	608(12)	23(6)	37(7)	36(6)	-5(5)	6(5)	3(5)
C(21)	-1259(6)	3957(6)	931(14)	26(7)	35(7)	50(8)	16(6)	1(6)	-6(6)
C(22)	-692(8)	4308(6)	1781(17)	43(8)	35(8)	73(10)	13(7)	7(7)	-14(7)
C(23)	43(7)	4354(6)	1055(14)	32(7)	33(7)	47(7)	15(6)	1(6)	-16(6)
C(24)	1075(6)	3759(5)	234(12)	35(7)	20(6)	36(6)	-9(5)	6(5)	-13(5)
C(25)	1332(6)	3116(5)	94(12)	13(5)	33(6)	38(6)	-6(5)	-8(5)	-8(5)
C(31)	1984(6)	3391(6)	-3849(14)	17(6)	30(7)	55(8)	-7(5)	9(6)	-2(6)
C(32)	1652(7)	3854(6)	-4874(14)	37(7)	33(7)	51(8)	-10(6)	16(6)	21(6)
C(33)	1002(6)	4163(6)	-4271(15)	27(7)	27(7)	67(9)	-11(6)	6(6)	7(6)
C(34)	-252(6)	3993(5)	-3434(15)	29(7)	24(6)	59(8)	13(6)	2(6)	-1(6)
C(35)	-791(6)	3509(5)	-3208(12)	26(6)	18(6)	38(6)	10(5)	6(5)	2(5)
C(41)	921(7)	1114(6)	1817(12)	40(7)	28(7)	33(6)	3(6)	-6(6)	8(5)
C(42)	1178(7)	600(6)	959(15)	40(7)	42(8)	57(9)	14(7)	5(7)	31(7)
C(43)	817(8)	500(6)	-478(14)	59(9)	29(7)	48(8)	10(7)	-3(7)	17(6)
C(44)	623(7)	946(5)	-2888(14)	37(7)	13(5)	48(7)	1(5)	-6(6)	-5(5)
C(45)	693(6)	1531(5)	-3688(11)	33(7)	33(7)	19(5)	14(5)	-8(5)	-11(5)
O(5)	2160(7)	581(6)	-5838(13)	94(9)	81(9)	69(7)	-13(7)	-19(7)	17(7)
O(6)	3170(5)	572(5)	-220(11)	56(6)	55(6)	56(6)	-7(5)	-16(5)	0(5)
O(7)	3326(7)	11(6)	2536(13)	85(9)	67(8)	80(8)	-12(7)	0(7)	-20(6)

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

Table 2. Fractional atomic coordinates ( $\times 10^3$ ) for hydrogen atoms.

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
H(101)	-122(7)	232(7)	-504(15)	H(304)	243(7)	324(7)	-428(15)
H(102)	-163(8)	228(6)	-371(15)	H(305)	162(7)	366(6)	-587(14)
H(103)	-100(7)	139(6)	-497(14)	H(306)	212(7)	410(6)	-507(15)
H(104)	-172(7)	168(7)	-572(15)	H(307)	77(7)	437(6)	-521(14)
H(105)	-240(7)	152(7)	-377(14)	H(308)	112(8)	436(6)	-345(15)
H(106)	-211(7)	85(6)	-469(15)	H(309)	20(7)	361(6)	-484(15)
H(107)	-209(7)	69(6)	-222(15)	H(310)	-44(8)	431(6)	-388(15)
H(108)	-137(7)	85(6)	-307(15)	H(311)	-3(8)	417(6)	-256(15)
H(109)	-193(7)	176(7)	-169(14)	H(312)	-119(7)	366(6)	-257(15)
H(110)	-148(7)	104(6)	30(15)	H(313)	-93(7)	330(7)	-422(15)
H(111)	-87(7)	101(6)	-40(14)	H(401)	82(8)	206(6)	166(15)
H(112)	-72(7)	173(7)	178(15)	H(402)	142(7)	166(6)	144(14)
H(113)	-145(8)	205(6)	101(15)	H(403)	39(7)	99(7)	186(15)
H(201)	-69(7)	352(6)	135(15)	H(404)	126(7)	103(6)	295(15)
H(202)	-135(7)	315(6)	44(15)	H(405)	170(7)	69(6)	79(14)
H(203)	-140(8)	413(7)	-8(15)	H(406)	99(7)	34(6)	156(15)
H(204)	-176(7)	399(7)	116(15)	H(407)	104(8)	21(6)	-101(15)
H(205)	-69(8)	402(7)	284(15)	H(408)	24(7)	51(6)	-40(14)
H(206)	-115(7)	451(6)	193(15)	H(409)	136(7)	118(6)	-129(14)
H(207)	1(7)	454(6)	-5(15)	H(410)	21(7)	80(7)	-278(15)
H(208)	38(7)	453(7)	167(14)	H(411)	79(7)	49(7)	-336(14)
H(209)	52(7)	363(7)	188(14)	H(412)	33(7)	147(6)	-452(14)
H(210)	148(7)	403(6)	96(15)	H(413)	130(7)	150(6)	-401(14)
H(211)	105(7)	386(6)	-68(15)	H(51)	234(7)	107(7)	-598(15)
H(212)	146(8)	306(6)	111(15)	H(52)	222(7)	49(6)	-486(15)
H(213)	169(7)	315(6)	-31(15)	H(61)	285(7)	46(6)	-73(14)
H(301)	179(7)	256(6)	-319(14)	H(62)	300(7)	86(7)	51(15)
H(302)	139(8)	300(6)	-324(15)	H(71)	330(7)	21(6)	181(15)
H(303)	200(7)	357(6)	-289(15)	H(72)	293(7)	32(6)	298(15)

## CRYSTAL DATA

[Cu<sub>4</sub>(C<sub>5</sub>H<sub>13</sub>N<sub>2</sub>O)<sub>4</sub>]Br<sub>4</sub>·3H<sub>2</sub>O, FW = 1096.52Crystal system: Monoclinic (*b* unique)Space group: *P*2<sub>1</sub>/*n* (No. 14)*a* = 18.648(8), *b* = 22.013(8), *c* = 9.327(5) Å, $\beta = 90.08(4)^\circ$ , *V* = 3828(3) Å<sup>3</sup>, *Z* = 4,*F*(000) = 2168,  $\mu(\text{MoK}\alpha) = 67.5 \text{ cm}^{-1}$ ,*D<sub>m</sub>* = 1.91 g cm<sup>-3</sup>, *D<sub>x</sub>* = 1.90 g cm<sup>-3</sup>

## STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by direct methods and Fourier syntheses. The four bromide and four copper(II) ions were located from the eight largest maxima of an *F<sub>o</sub>* statistical map. The other non-hydrogen atoms were located from successive Fourier syntheses and the hydrogen atoms from a difference Fourier map.

In the calculations of *F<sub>c</sub>*, atomic scattering factors computed from numerical Hartree-Fock wave functions were used for all nonhydrogen atoms<sup>17</sup> and for hydrogen atoms those reported by Stewart *et al.*<sup>18</sup> The anomalous dispersion coefficients for copper and bromine atoms were also included in the calculations.<sup>19</sup>

Atomic coordinates were refined by block-diagonal least-squares techniques to an *R* values of 0.049 ( $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ) with the weighting scheme  $w = 1 / (40.0 + |F_o| + 0.0035|F_o|^2)$  in minimizing the function  $\Sigma w(|F_o| - |F_c|)^2$ . Anisotropic thermal parameters were used for all non-hydrogen atoms and a fixed isotropic thermal parameter ( $U = 0.06 \text{ \AA}^2$ ) for all hydrogen atoms. The computations were performed on a UNIVAC 1108 computer with the X-Ray 76 program system.<sup>20</sup> The figures were drawn by the ORTEP program.

## DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The atomic coordinates and thermal parameters with their standard deviations for non-hydrogen atoms are given in Table 1 and the coordinates of hydrogen atoms in Table 2. A list of observed and calculated structure factors can be obtained from

Table 3. Interatomic distances (Å) between the copper(II) ions.

Cu(1)··Cu(2)	3.200(2)
Cu(1)··Cu(3)	3.199(2)
Cu(1)··Cu(4)	3.555(2)
Cu(2)··Cu(3)	3.455(2)
Cu(2)··Cu(4)	3.244(2)
Cu(3)··Cu(4)	3.186(2)

the authors. The distances between the copper(II) ions are shown in Table 3, and the intramolecular distances and angles in the complex  $[[\text{Cu}_4(\text{C}_5\text{H}_{13}\text{N}_2\text{O})_4]\text{Br}_3]^+$  are shown in Table 4. A stereoscopic drawing of the complex is seen in Fig. 1 (hydrogen atoms are omitted for clarity).

The structure consists of tetranuclear cations  $[\text{Cu}_4(\text{C}_5\text{H}_{13}\text{N}_2\text{O})_4]^{4+}$  having the same cubanetype  $\text{Cu}_4\text{O}_4$  core as found in the structures of {2-[(3-aminopropyl)amino]ethanolato}copper(II) chloride tetramer tetrahydrate,  $(\text{CuLCl})_4 \cdot 4\text{H}_2\text{O}$ ,<sup>5</sup> and {2-[(3-aminopropyl)amino]ethanolato}copper(II) nitrate tetramer dihydrate,  $(\text{CuLNO}_3)_4 \cdot 2\text{H}_2\text{O}$ .<sup>9</sup> However, the difference between the longest and shortest  $\text{Cu}\cdots\text{Cu}$  distances, 0.369 Å, is greater in the present compound than in  $(\text{CuLCl})_4 \cdot 4\text{H}_2\text{O}$ , 0.235 Å, and  $(\text{CuLNO}_3)_4 \cdot 2\text{H}_2\text{O}$ , 0.219 Å. The eight short  $\text{Cu}-\text{O}$  distances in the  $\text{Cu}_4\text{O}_4$  core are identical to those

Table 4. Intramolecular distances (Å) and angles (°) in  $[\text{Cu}_4(\text{C}_5\text{H}_{13}\text{N}_2\text{O})_4]\text{Br}_3^+$ .

	i=1	i=2	i=3	i=4	
Cu(i)–Br(1)	3.266(2) <sup>l=1</sup>	3.185(2) <sup>l=2</sup>	<sup>a</sup> 3.256(2) <sup>l=2</sup>	3.251(2) <sup>l=3</sup>	
Cu(i)–O(i)	1.956(7)	1.954(7)	1.951(7)	1.957(7)	
Cu(i)–O(j)	1.962(7) <sup>j=3</sup>	1.975(7) <sup>j=1</sup>	1.976(7) <sup>j=4</sup>	1.962(7) <sup>j=2</sup>	
Cu(i)–O(k)	2.597(7) <sup>k=4</sup>	2.579(7) <sup>k=3</sup>	2.521(7) <sup>k=2</sup>	2.633(7) <sup>k=1</sup>	
Cu(i)–N(i1)	2.017(9)	1.977(10)	1.979(10)	1.991(10)	
Cu(i)–N(i2)	2.013(8)	2.020(9)	2.025(9)	2.043(9)	
N(i1)–C(i1)	1.48(2)	1.45(2)	1.50(2)	1.49(2)	
C(i1)–C(i2)	1.50(2)	1.53(2)	1.53(2)	1.47(2)	
C(i2)–C(i3)	1.53(2)	1.53(2)	1.50(2)	1.52(2)	
C(i3)–N(i2)	1.52(2)	1.49(2)	1.48(2)	1.52(2)	
N(i2)–C(i4)	1.49(1)	1.48(1)	1.48(2)	1.46(2)	
C(i4)–C(i5)	1.49(2)	1.50(2)	1.48(2)	1.49(2)	
C(i5)–O(i)	1.43(1)	1.45(1)	1.45(1)	1.44(1)	
	Range			Range	
O(i)–Cu(i)–Br(1)	96.5(2)–101.2(2)			Cu(i)–O(i)–Cu(j)	108.2(3)–111.9(3)
O(j)–Cu(i)–Br(1)	91.1(2)–92.8(2)			Cu(i)–O(i)–Cu(k)	98.5(3)–101.7(3)
O(k)–Cu(i)–Br(1)	162.7(2)–164.7(2)			Cu(j)–O(i)–Cu(k)	87.7(3)–89.9(3)
O(i)–Cu(i)–O(j)	86.9(3)–88.6(3)			Cu(i)–N(i1)–C(i1)	117.0(7)–121.0(8)
O(i)–Cu(i)–O(k)	78.1(3)–80.8(3)			N(i1)–C(i1)–C(i2)	111.3(10)–113.9(10)
O(j)–Cu(i)–O(k)	70.5(3)–72.5(3)			C(i1)–C(i2)–C(i3)	113.2(11)–116.8(11)
O(i)–Cu(i)–N(i1)	174.0(4)–175.6(4)			C(i2)–C(i3)–N(i2)	109.4(10)–111.2(10)
O(j)–Cu(i)–N(i1)	93.5(3)–95.3(4)			C(i3)–N(i2)–Cu(i)	117.4(7)–123.3(7)
O(k)–Cu(i)–N(i1)	96.1(3)–97.7(3)			Cu(i)–N(i2)–C(i4)	106.9(6)–107.8(7)
O(i)–Cu(i)–N(i2)	84.1(3)–84.7(3)			C(i3)–N(i2)–C(i4)	111.0(9)–114.6(9)
O(j)–Cu(i)–N(i2)	163.9(3)–167.5(3)			N(i2)–C(i4)–C(i5)	107.0(9)–109.6(9)
O(k)–Cu(i)–N(i2)	116.6(3)–120.3(3)			C(i4)–C(i5)–O(i)	107.7(9)–108.2(9)
N(i1)–Cu(i)–Br(1)	84.6(3)–87.3(3)			C(i5)–O(i)–Cu(i)	109.2(6)–111.9(6)
N(i2)–Cu(i)–Br(1)	75.4(3)–80.4(3)			C(i5)–O(i)–Cu(j)	122.7(6)–124.5(6)
N(i1)–Cu(i)–N(i2)	93.7(4)–95.1(4)			C(i5)–O(i)–Cu(k)	118.5(6)–122.1(6)

<sup>a</sup> Equivalent position  $x, y, z - 1$  of Br(2).

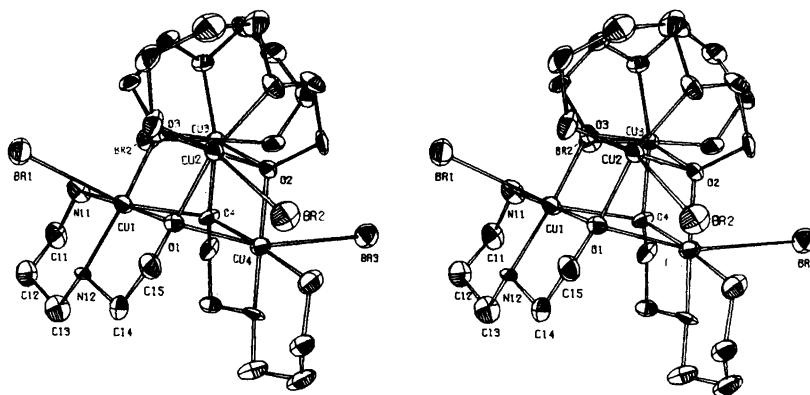


Fig. 1. Stereo view of the complex  $[\text{Cu}_4(\text{C}_5\text{H}_{13}\text{N}_2\text{O})_4]\text{Br}_3^+$ .

of  $(\text{CuLCl})_4 \cdot 4\text{H}_2\text{O}$  and  $(\text{CuLNO}_3)_4 \cdot 2\text{H}_2\text{O}$ . The four long Cu–O distances are also identical within standard deviation to those of  $(\text{CuLNO}_3)_4 \cdot 2\text{H}_2\text{O}$ , but are considerably longer than those of  $(\text{CuLCl})_4 \cdot 4\text{H}_2\text{O}$ , 2.448 Å. In the  $\text{Cu}_4\text{O}_4$  core, as also in the  $\text{Cu}_4\text{O}_4$  cores of  $(\text{CuLCl})_4 \cdot 4\text{H}_2\text{O}$  and  $(\text{CuLNO}_3)_4 \cdot 2\text{H}_2\text{O}$ , two stretched distances are perpendicular to the other two. The deviations of atoms from the limiting planes of the cube and the angles between the planes are shown in Table 5. The cation  $[\text{Cu}_4(\text{C}_5\text{H}_{13}\text{N}_2\text{O})_4]^{4+}$  has  $S_4$  pseudosymmetry in the direction of the *b*-axis.

The average Cu··Br distance 3.240 Å is smaller than the Cu··Cl distance 3.335 Å in  $(\text{CuLCl})_4 \cdot 4\text{H}_2\text{O}$ . Since the sum of the ionic radii of  $\text{Cu}^{2+}$  and  $\text{Br}^-$  ions is 3.23 Å,<sup>21</sup> it can be assumed that there is a semicoordination bond between copper(II) and

bromide ions. On the opposite side of each copper(II) ion lies an oxygen atom O(k) at average distance 2.583 Å, corresponding to a semicoordination bond.<sup>21</sup> The two nitrogen atoms and the oxygen atoms O(i) of amine (i) and O(j) of amine (j) lie almost in a plane (Table 6) nearly perpendicular to the line Br··O(k). The angle between the normal of the plane and the line is about 16°. In the plane the average bond distances are Cu(i)–N(i1) 1.991 Å, Cu(i)–N(i2) 2.025 Å, Cu(i)–O(i) 1.955 Å, and Cu(i)–O(j) 1.969 Å. Thus the coordination around the copper(II) ion is distorted octahedral (4+2). The dihedral angles between planes [Cu(i),N(i1),N(i2)] and [Cu(i),O(i),O(j)] are 12.3, 11.4, 14.7 and 10.6° for *i*=1, 2, 3 and 4, respectively, indicating some tetrahedral distortion. The octahedral copper(II) coordination is also found in

Table 5. Deviations (Å) of atoms from least-squares planes for  $\text{Cu}_4\text{O}_4$ , and the angles (°) between the planes.

Plane 1:	Cu(1)	Cu(2)	O(1)	O(3)	Plane 4:	Cu(1)	Cu(4)	O(1)	O(4)
	–0.11	–0.09	0.11	0.08		–0.06	–0.06	0.07	0.07
Plane 2:	Cu(2)	Cu(3)	O(2)	O(3)	Plane 5:	Cu(1)	Cu(3)	O(3)	O(4)
	0.08	0.08	–0.08	–0.08		–0.07	–0.09	0.10	0.07
Plane 3:	Cu(3)	Cu(4)	O(2)	O(4)	Plane 6:	Cu(2)	Cu(4)	O(1)	O(2)
	0.10	0.12	–0.09	–0.13		0.11	0.08	–0.08	–0.12
Angles (°) between the planes									
Plane	2	3	4	5	6				
1	80.6	20.4	80.5	87.6	88.7				
2		79.0	0.3	80.5	80.8				
3			79.1	89.4	87.7				
4				80.7	80.6				
5					18.7				

Table 6. 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(3)	Cu(1)	O(4)	Br(1)
0.13	-0.14	0.15	-0.14	0.06	2.42	-3.16
N(21)	N(22)	O(2)	O(1)	Cu(2)	O(3)	Br(2)
0.11	-0.13	0.13	-0.13	0.05	2.40	-3.09
N(31)	N(32)	O(3)	O(4)	Cu(3)	O(2)	Br(2) <sup>a</sup>
0.14	-0.16	0.17	-0.16	0.08	2.36	-3.13
N(41)	N(42)	O(4)	O(2)	Cu(4)	O(1)	Br(3)
-0.12	0.13	-0.14	0.13	-0.03	-2.41	3.18

<sup>a</sup> Equivalent position  $x, y, z - 1$ .

Table 7. Bond lengths (Å) and angles (°) in water molecules. Interatomic distances and angles between the bromide ions, the hydrogen atoms of water molecules and the oxygen atoms of water molecules.

O(5)–H(51)	1.14(14)	H(51)–O(5)–H(52)	106(11)
O(5)–H(52)	0.94(14)	H(61)–O(6)–H(62)	111(13)
O(6)–H(61)	0.80(14)	H(71)–O(7)–H(72)	86(12)
O(6)–H(62)	0.99(14)	<sup>a</sup> Br(1)··H(51)–O(5)	170(10)
O(7)–H(71)	0.81(14)	Cu(1)·· <sup>a</sup> Br(1)··H(51)	126(3)
O(7)–H(72)	1.09(14)	Br(4)··H(52)–O(5)	156(12)
<sup>a</sup> Br(1)··H(51)	2.52(14)	H(52)··Br(4)··H(61)	107(4)
Br(4)··H(52)	2.45(14)	Br(4)··H(61)–O(6)	156(13)
Br(4)··H(61)	2.56(14)	Br(3)··H(62)–O(6)	112(13)
Br(3)··H(62)	3.08(14)	O(6)··H(71)–O(7)	169(14)
O(6)··H(71)	2.07(14)	<sup>b</sup> O(5)··H(72)–O(7)	158(11)
<sup>b</sup> O(5)··H(72)	1.90(14)	H(71)··O(6)–H(61)	121(11)
		H(71)··O(6)–H(62)	70(9)
		H(72)·· <sup>b</sup> O(5)– <sup>b</sup> H(51)	90(8)
		H(72)·· <sup>b</sup> O(5)– <sup>b</sup> H(52)	114(9)

<sup>a</sup> Equivalent position  $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ . <sup>b</sup> Equivalent position  $x, y, z + 1$ .

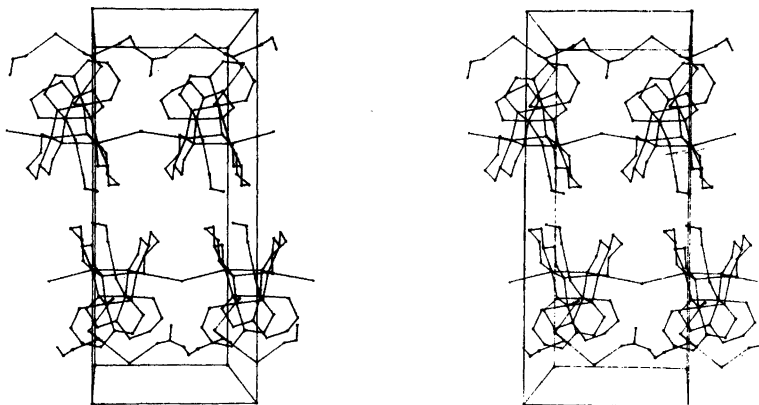


Fig. 2. Stereo view of the packing along the  $a$ -axis. (The front part of the unit cell is omitted for clarity.)

(CuLNO<sub>3</sub>)<sub>4</sub>·2H<sub>2</sub>O, but the other compounds having the cubane-type Cu<sub>4</sub>O<sub>4</sub> core have either distorted square-pyramidal or distorted bipyramidal copper(II) coordination sphere.

As reported earlier, the amine coordinates tridentately forming six- and five-membered rings.<sup>5,9</sup> The bond distances correspond to single bond values and are in agreement with those reported for (CuLCl)<sub>4</sub>·4H<sub>2</sub>O and (CuLNO<sub>3</sub>)<sub>4</sub>·2H<sub>2</sub>O. All the bond angles are also normal for the amine. The angles around the oxygen atoms vary between 88 and 125° having the average value 109°, which can be assumed to correspond to sp<sup>3</sup>-hybridization. The distortion of the angles can be thought of as the effect of the Cu<sub>4</sub>O<sub>4</sub> core. The six-membered ring is in chair conformation.

There are three types of bromide ions in the structure: (a) Br(1) is semicoordinated to Cu(1) and Br(3) to Cu(4), and water molecules are joined to these ions by hydrogen bonds. (b) Br(2) is joined to two copper(II) ions by semicoordination bonds, forming a bridge between Cu(2) and Cu(3) (at *x, y, z* + 1) in the direction of the *c*-axis; (c) Br(4) is joined to the structure by water molecules. The bond lengths and angles for the water molecules forming hydrogen bonds with bromide ions and with each other are shown in Table 7. One of the three water molecules, H<sub>2</sub>O(5), is joined to bromide ion Br(1) (at  $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ) and to the free bromide ion Br(4). A second water molecule, H<sub>2</sub>O(6), is located between Br(4) and Br(3) ions, and the third water molecule, H<sub>2</sub>O(7), joins together water molecules H<sub>2</sub>O(6) and H<sub>2</sub>O(5) (at *x, y, z* + 1). A stereo view of the packing is shown in Fig. 2.

The magnetic data of this compound have been published earlier.<sup>16</sup> A detailed interpretation of the relation between the molecular geometries and magnetic properties will be given later.

## REFERENCES

- Bertland, J. and Kelley, J. *Inorg. Chim. Acta* 4 (1970) 203.
- Haase, W. *Chem. Ber.* 106 (1973) 3132.
- Dixon Estes, E. and Hodgson, D. *Inorg. Chem.* 14 (1975) 334.
- von Mergehenn, R., Haase, W. and Allmann, R. *Acta Crystallogr. B* 31 (1975) 1847.
- Pajunen, A. and Nieminen, K. *Finn. Chem. Lett.* (1975) 67.
- Matsumoto, N., Ueda, I., Nishida, Y. and Kida, S. *Bull. Chem. Soc. Jpn.* 49 (1976) 1308.
- von Mergehenn, R., Merz, L., Haase, W. and Allmann, R. *Acta Crystallogr. B* 32 (1976) 505.
- von Mergehenn, R. and Haase, W. *Acta Crystallogr. B* 33 (1977) 1877.
- Nieminen, K. *Acta Chem. Scand. A* 31 (1977) 693.
- Uhlig, E. and Steiger, K. *Z. Anorg. Allg. Chem.* 346 (1966) 21.
- Uhlig, E. and Steiger, K. *Z. Anorg. Allg. Chem.* 360 (1968) 39.
- Näsänen, R., Luukkonen, E., Kalmi, H. and Nieminen, K. *Suom. Kemistil. B* 44 (1971) 327.
- Merz, L., Haase, W. and Keller, G. *Ber. Bunsenges. Phys. Chem.* 80 (1976) 305.
- Merz, L. and Haase, W. *Z. Naturforsch. Teil A* 31 (1976) 177.
- Nishida, Y. and Kida, S. *J. Inorg. Nucl. Chem.* 38 (1976) 451.
- Nieminen, K. and Pajunen, S. *Suom. Kemistil. B* 45 (1972) 391.
- Cromer, D. and Mann, J. *Acta Crystallogr. A* 24 (1968) 321.
- Stewart, R., Davidson, E. and Simpson, W. *J. Phys. Chem.* 42 (1965) 3175.
- International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. 3, Table 3.3.2C.
- Stewart, J. M., Ed., *The X-Ray System, Version of 1976*, Technical Report TR-446, Computer Science Center, University of Maryland, College Park 1976.
- Pauling, L. *The Nature of the Chemical Bond*, 3rd. Ed., Cornell University Press, Ithaca 1960, pp. 160, 252, 260.

Received February 6, 1978.