The Crystal Structure of a Tetrameric Copper(II) Complex of 2-[(3-Aminopropyl)amino]ethanol: [Cu$_4$(C$_5$H$_{13}$N$_2$O)$_4$](NO$_3$)$_4$.2H$_2$O

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The crystal structure of tetrakis-μ_3-{2-[(3-aminopropyl)amino]ethanolato}-tetracopper(II) tetranitrate dihydrate, [Cu$_4$(C$_5$H$_{13}$N$_2$O)$_4$]-(NO$_3$)$_4$.2H$_2$O, has been determined by three-dimensional X-ray methods. The compound crystallizes in the monoclinic space group $C2/c$ with unit cell dimensions $a = 27.312(15)$, $b = 20.936(13)$, $c = 17.519(9)$ Å, $\beta = 128.82(3)°$, and $Z = 8$. The intensity data were collected with a four-circle automated diffractometer. The positions of copper(II) ions and the oxygen atoms of 2-[(3-aminopropyl)-amino]ethanols were determined by direct methods and the other non-hydrogen atoms by Fourier syntheses. The structure was refined by block-diagonal least-squares methods to an R value of 0.070 ($R_w = 0.101$) on the basis of 3400 independent reflections. The complex has a tetranuclear cubane-type structure. The four copper(II) ions, with interatomic distances 3.224 − 3.433 Å, are connected by oxygen bridges. The Cu − O distances vary between 1.937 and 2.633 Å. The cation [Cu$_4$(C$_5$H$_{13}$N$_2$O)$_4$]$^{4+}$ has S_4 pseudosymmetry. These tetranuclear units are joined by NO$_3$ groups and between these chains there are bridges formed by water molecules and nitrate ions. Each copper(II) ion has a distorted octahedral (4+2)-coordination. The equatorial interatomic distances (mean values): Cu(i) − N(i1) 1.99 Å, Cu(i) − N(i2) 2.02 Å, Cu(i) − O(i) 1.95 Å and Cu(i) − O(j) 1.98 Å are coordination bond values and the axial Cu − O distances 2.59 and 2.70 Å correspond to semicoordination bonds.

The reactions of 2-[(3-aminopropyl)amino]ethanol (HL) with copper(II) salts in methanol solution yield crystalline one-to-one complexes according to analysis.[1,2] On the basis of the crystal structure of CuLCl.H$_2$O (L = 2-[(3-aminopropyl)amino]ethanolato⁻) and ESR spectrometric studies, these complexes have evidently tetrameric structures.[3,4] The present investigation was undertaken in order to

study the possible tetrameric structure of the complex CuLNO$_3$.$\frac{1}{2}$H$_2$O.

EXPERIMENTAL

The preparation and crystal data. The preparation and crystal data of the compound have been published earlier.[1] Cell dimensions were obtained with a Syntex P2$_1$ automated four-circle diffractometer by a least-squares refinement of setting angles for 20 well-centered reflections. The radiation was MoKα-($\lambda = 0.7107$ Å) monochromatized by graphite. The cell dimensions were $a = 27.312(15)$ Å, $b = 20.936(13)$ Å, $c = 17.519(9)$ Å, $\beta = 128.82(3)°$, volume $V = 7805(7)$ Å^3, and there were eight formula units in each cell. Of the two possible space groups, Cc (No.9) and $C2/c$ (No. 15), the latter was found to describe the structure sufficiently well as far as the complexes are concerned.

Intensity data. The crystal selected for data collection was a plate with approximate dimensions $0.5 \times 0.4 \times 0.1$ mm. Intensities were collected by scanning in 2θ (scan speed varied between 2.93 and 29.30° min⁻¹, scan range was 1.0°, and 2θ varied between 5 and 50°). Of the 6059 reflections considered, 3400 had $F_o > 4.0\sigma(F_o)$, and these were regarded as observed. Data were corrected for Lorentz and polarization effects and also for absorption from ϕ-scan data [μ(MoKα) = 23.2 cm⁻¹]. The standard reflection measured periodically during the data collection varied about ± 8 %, but showed no systematic increase or decrease.

Structure determination and refinement. The structure was solved by direct methods and Fourier techniques. In the calculations of F_c, atomic scattering factors computed from numerical Hartree-Fock wave functions were used for all atoms.[5] The effects of anomalous dispersion of copper were included in the calculations and the values of $\Delta f' = 0.30$ and $\Delta f'' = 1.35$ were taken from International Tables for X-Ray Crystallography.[6]

Table 1. Fractional atomic coordinates ($\times$ 10^4) and thermal parameters [a] ($\times$ 10^3). 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}
Cu(1)	214(1)	−2273(2)	105(1)	28(1)	31(1)	35(1)	8(1)	21(1)	10(1)
Cu(2)	1134(1)	−3045(1)	359(1)	32(1)	33(1)	29(1)	8(1)	19(1)	4(1)
Cu(3)	1767(1)	−1854(1)	1849(1)	31(1)	25(1)	39(1)	1(1)	25(1)	4(1)
Cu(4)	1156(1)	−3060(1)	2121(1)	33(1)	26(1)	30(1)	0(1)	21(1)	4(1)
O(1)	897(4)	−2215(4)	21(6)	31(5)	31(5)	37(5)	10(4)	24(4)	15(4)
O(2)	1879(4)	−2766(4)	1712(6)	28(5)	27(5)	36(5)	2(4)	22(4)	−5(4)
O(3)	1131(4)	−2113(4)	1960(6)	34(5)	21(4)	34(5)	6(3)	24(4)	0(4)
O(4)	541(4)	−3123(4)	700(6)	32(4)	22(4)	43(5)	−8(4)	27(4)	6(4)
N(11)	−452(5)	−2281(5)	257(10)	45(7)	27(6)	82(9)	12(5)	55(7)	12(6)
N(12)	−153(5)	−1512(5)	−813(8)	37(6)	22(6)	49(7)	19(5)	27(6)	29(5)
N(21)	755(5)	−3397(6)	−1009(8)	44(7)	58(8)	27(6)	10(6)	20(6)	−1(5)
N(22)	1964(5)	−3764(5)	848(8)	41(6)	25(6)	42(6)	6(5)	29(6)	8(5)
N(31)	2367(5)	−1562(5)	1643(9)	29(6)	40(7)	60(8)	1(5)	34(6)	6(6)
N(32)	1708(5)	−995(5)	2301(8)	38(6)	17(5)	44(6)	−7(4)	24(6)	−4(5)
N(41)	1840(5)	−3045(6)	3581(7)	44(7)	43(7)	25(6)	6(5)	20(5)	10(5)
N(42)	928(5)	−3981(5)	2129(7)	31(6)	24(6)	31(6)	8(4)	20(5)	8(4)
C(11)	−695(7)	−1635(7)	300(12)	49(9)	48(9)	66(10)	11(7)	41(9)	21(8)
C(12)	−979(7)	−1249(8)	−643(12)	56(10)	61(11)	69(11)	30(8)	48(9)	32(9)
C(13)	−452(8)	−983(7)	−665(11)	61(10)	40(9)	47(9)	13(7)	31(8)	14(7)
C(14)	338(6)	−1273(8)	−862(11)	35(8)	58(10)	59(9)	22(7)	33(8)	26(8)
C(15)	709(6)	−1833(7)	−793(10)	39(8)	42(8)	46(8)	18(6)	35(7)	28(7)
C(21)	676(9)	−4112(8)	−1043(13)	89(14)	47(10)	62(11)	19(9)	36(11)	−9(9)
C(22)	1300(9)	−4465(8)	−624(13)	93(14)	42(10)	53(10)	5(9)	32(10)	−17(8)
C(23)	1742(7)	−4436(7)	489(12)	44(9)	42(9)	71(12)	6(7)	34(9)	−14(8)
C(24)	2394(6)	−3752(6)	1940(11)	32(7)	33(8)	63(10)	17(6)	33(7)	13(7)
C(25)	2496(6)	−3050(6)	2246(9)	31(7)	39(8)	36(7)	17(6)	22(6)	11(6)
C(31)	2279(7)	−891(7)	1245(12)	56(9)	35(8)	71(11)	4(7)	49(9)	16(7)
C(32)	2281(7)	−363(6)	1874(11)	56(9)	18(7)	60(10)	−17(6)	35(8)	−2(6)
C(33)	1710(6)	−393(6)	1836(10)	41(8)	26(7)	42(8)	3(6)	20(7)	0(6)
C(34)	1129(8)	−1028(7)	2250(12)	78(11)	37(8)	75(11)	−20(8)	65(10)	−20(8)
C(35)	1094(6)	−1672(7)	2538(10)	38(8)	44(8)	44(8)	−5(6)	29(7)	2(7)
C(41)	2229(7)	−3628(7)	4051(10)	50(9)	52(9)	26(7)	11(7)	14(7)	22(7)
C(42)	1824(8)	−4223(8)	3863(11)	79(12)	47(9)	45(9)	−8(8)	42(9)	1(7)
C(43)	1404(7)	−4470(7)	2790(11)	56(9)	36(8)	60(9)	26(7)	43(8)	23(7)
C(44)	520(6)	−4225(6)	1090(10)	32(7)	29(7)	36(7)	−2(6)	17(6)	−6(6)
C(45)	104(7)	−3654(7)	417(10)	48(8)	35(8)	35(8)	7(7)	22(7)	10(6)
O(111)	−474(5)	−2875(6)	−1723(11)	32(6)	76(9)	108(11)	−4(6)	32(7)	−17(8)
N(111)	−977(6)	−3118(7)	−2084(10)	43(7)	66(9)	57(8)	−5(7)	27(7)	−10(7)
O(112)	−1251(6)	−2991(7)	−1769(10)	65(8)	108(11)	80(9)	−5(8)	47(8)	−26(8)
O(113)	−1144(12)	−3545(14)	−2629(20)	238(26)	289(32)	261(29)	−189(25)	220(26)	−213(27)
O(211)	2151(10)	−2521(11)	141(19)	182(19)	164(19)	215(23)	−89(16)	172(20)	−45(16)
N(211) [b]	2444(52)	−2548(58)	−129(80)	85(12)					
O(212) [b]	2393(18)	−1848(17)	−156(33)	146(30)	133(29)	240(43)	22(24)	175(34)	61(28)
O(311)	2647(6)	−1983(7)	3778(9)	57(8)	99(11)	58(8)	−26(7)	18(7)	−5(7)
N(311)	3136(6)	−1722(7)	4377(10)	51(8)	82(10)	63(9)	14(7)	44(7)	−5(7)
O(312)	3127(9)	−1125(7)	4177(11)	158(16)	73(10)	84(10)	−24(11)	59(11)	−1(9)
O(313)	3593(7)	−1903(9)	5159(10)	74(9)	171(17)	57(8)	76(10)	23(7)	22(9)
O(411)	294(6)	−2862(5)	2296(9)	76(8)	52(7)	104(10)	4(6)	80(8)	9(6)
N(411)	0(−)	−3166(8)	2500(−)	38(4)					
O(412)	0(−)	−3763(7)	2500(−)	51(4)					
O(511)	1024(8)	−415(11)	−1565(18)	87(12)	134(17)	211(24)	−27(12)	58(14)	53(16)
N(511)	1528(10)	−96(11)	−940(15)	114(15)	133(18)	86(13)	25(13)	62(12)	39(12)
O(512)	1952(10)	−213(14)	−896(17)	118(15)	309(33)	152(19)	27(18)	103(15)	30(19)
O(513)	1524(12)	359(12)	−451(17)	200(22)	131(19)	134(18)	2(17)	90(17)	7(15)
O(6)	1289(9)	−1463(11)	−2116(12)	112(13)	181(20)	81(11)	−1(13)	63(11)	−9(12)
O(7)	0(−)	471(26)	−2500(−)	270(21)					
O(8) [b]	3823(20)	−599(23)	3906(33)	167(16)					

[a] The anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]$. [b] Population parameter 0.5.

The 322 reflections having $|E_o| \geq 1.50$ were used to calculate an F_o statistical map from which the positions of the copper atoms and the four oxygen atoms in the ethanolato groups were located. With these atoms, isotropic thermal parameters and unit weights, the R value after one cycle was 0.329 ($R = \sum ||F_o| - |F_c||/\sum |F_o|$).' The other non-hydrogen atoms were located from successive Fourier syntheses. One oxygen atom and the nitrogen atom of one NO_3^- ion and the oxygen atom of one water molecule are located on the *two*-fold axis. Near the special position (1/4, 1/4, 1/2) there is a disordered NO_3^- ion. The nitrogen atom and one oxygen atom of this NO_3^- ion are situated in two positions, with the population parameter 0.5. All the other atoms occupy general positions.

According to the analysis there are two water molecules in the asymmetric unit. Because there is one water molecule in a general position and a half molecule in a special position, there must be another half molecule in a special position or in a general position with the population parameter 0.5. In the difference-Fourier map the only noticeable maximum 1.12 e Å⁻³ is at the general position (0.3823, −0.0599, 0.3906), and the other half of the water molecule is located in that position.

Atomic coordinates were refined by block-diagonal least-squares techniques to an R value of 0.070 ($R_w = 0.101$, with the weighting scheme $w = 1/(35.0 + |F_o| + 0.031 |F_o|^2)$. Isotropic thermal parameters were used for the four atoms located in the special positions and for O(8), and unisotropic thermal parameters for all the other atoms. The computations were performed on a UNIVAC 1108 computer using the X-Ray 72 program system.[7] The figures were drawn by a Honeywell GE 635 computer using the Perspect graphic program.[8]
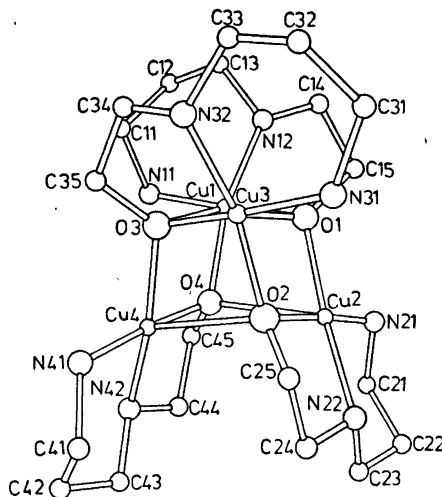

Fig. 1. Perspective view of the cation $[Cu_4(C_5H_{13}N_2O)_4]^{4+}$.

RESULTS 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 is obtainable from the author. The structure consists of tetrameric units formed by four copper(II) ions and four deprotonated 2-[(3-aminopropyl)amino]ethanols (Fig. 1). The array of copper(II) ions is roughly tetrahedral having interatomic distances Cu···Cu 3.224−3.443 Å (Table 2). Two of the

Table 2. Interatomic distances (Å), bond lengths (Å) and bond angles (°) for the tetranuclear unit Cu_4O_4. Estimated standard deviations are given in parentheses.

Cu(1)···Cu(2)	3.233(3)	O(1)−Cu(1)−O(3)	82.5(4)	Cu(1)−O(1)−Cu(2)	110.2(5)
Cu(1)···Cu(3)	3.443(2)	O(1)−Cu(1)−O(4)	87.7(4)	Cu(1)−O(1)−Cu(3)	95.9(5)
Cu(1)···Cu(4)	3.227(2)	O(3)−Cu(1)−O(4)	72.1(3)	Cu(2)−O(1)−Cu(3)	88.5(2)
Cu(2)···Cu(3)	3.249(2)	O(1)−Cu(2)−O(2)	87.6(4)	Cu(2)−O(2)−Cu(3)	112.4(4)
Cu(2)···Cu(4)	3.411(3)	O(1)−Cu(2)−O(4)	72.0(4)	Cu(2)−O(2)−Cu(4)	97.7(4)
Cu(3)···Cu(4)	3.224(3)	O(2)−Cu(2)−O(4)	81.3(4)	Cu(3)−O(2)−Cu(4)	89.7(5)
Cu(1)−O(1)	1.967(13)	O(1)−Cu(3)−O(2)	70.4(3)	Cu(1)−O(3)−Cu(3)	97.6(5)
Cu(1)−O(3)	2.596(7)	O(1)−Cu(3)−O(3)	81.9(4)	Cu(1)−O(3)−Cu(4)	88.2(3)
Cu(1)−O(4)	1.971(8)	O(2)−Cu(3)−O(3)	87.6(4)	Cu(3)−O(3)−Cu(4)	109.7(5)
Cu(2)−O(1)	1.977(9)	O(2)−Cu(4)−O(3)	71.7(4)	Cu(1)−O(4)−Cu(2)	89.3(4)
Cu(2)−O(2)	1.937(8)	O(2)−Cu(4)−O(4)	81.8(4)	Cu(1)−O(4)−Cu(4)	110.9(4)
Cu(2)−O(4)	2.587(13)	O(3)−Cu(4)−O(4)	87.8(3)	Cu(2)−O(4)−Cu(4)	96.6(4)
Cu(3)−O(1)	2.633(8)				
Cu(3)−O(2)	1.972(9)				
Cu(3)−O(3)	1.944(13)				
Cu(4)−O(2)	2.561(13)				
Cu(4)−O(3)	2.000(8)				
Cu(4)−O(4)	1.947(8)				

Table 3. The equations of least-squares planes for Cu_4O_4, the distances (Å) of some atoms from these planes, and the angles (°) between the planes. Equations of the planes are expressed as $PX + QY + RZ = S$ in direct space.

Plane 1: Cu(1), Cu(3), O(1), O(3)
$-4.92X + 20.24Y - 0.49Z = -4.82$
Cu(1) 0.107, Cu(3) 0.107, O(1) −0.106, O(3) −0.109

Plane 2: Cu(1), Cu(2), O(1), O(4)
$2.83X + 7.70Y + 11.48Z = -1.50$
Cu(1) −0.069, Cu(2) −0.055, O(1) 0.073, O(4) 0.052

Plane 3: Cu(1), Cu(4), O(3), O(4)
$27.05X - 0.11Y - 12.76Z = 0.53$
Cu(1) −0.058, Cu(4) −0.073, O(3) 0.053, O(4) 0.078

Plane 4: Cu(3), Cu(4), O(2), O(3)
$4.57X + 0.46Y + 11.61Z = 2.79$
Cu(3) 0.085, Cu(4) 0.067, O(2) −0.064, O(3) −0.089

Plane 5: Cu(2), Cu(3), O(1), O(2)
$25.43X + 6.57Y - 12.77Z = 0.85$
Cu(2) 0.077, Cu(3) 0.060, O(1) −0.055, O(2) −0.082

Plane 6: Cu(2), Cu(4), O(2), O(4)
$-5.13X + 20.23Y - 0.34Z = -6.74$
Cu(2) −0.119, Cu(4) −0.119, O(2) 0.120, O(4) 0.118

Angles (°) between the planes:

Plane	2	3	4	5	6
1	80.2	80.9	79.2	80.3	0.5
2		88.4	20.6	87.7	80.0
3			88.3	18.9	80.4
4				88.8	79.4
5					80.7

Table 4. The equations of least-squares planes through the atoms N(i1), N(i2), O(i) and O(j), and the distances (Å) of some atoms from these planes. Equations of the planes are expressed as $PX + QY + RZ = S$ in direct space.

Plane 1: N(11), N(12), O(1), O(4)
$1.54X + 10.98Y + 10.97Z = -2.43$
N(11) 0.136, N(12) −0.147, O(1) 0.159, O(4) −0.148
Cu(1) 0.081, O(3) 2.435, O(111) −2.691

Plane 2: N(21), N(22), O(2), O(1)
$23.59X + 9.77Y - 12.09Z = -0.20$
N(21) −0.117, N(22) 0.130, O(2) −0.141, O(1) 0.128
Cu(2) −0.063, O(4) −2.421, O(211) 2.641

Plane 3: N(31), N(32), O(3), O(2)
$4.60X - 3.35Y + 11.43Z = 3.61$
N(31) −0.124, N(32) 0.135, O(3) −0.146, O(2) 0.135
Cu(3) −0.067, O(1) −2.434, O(311) 2.586

Plane 4: N(41), N(42), O(4), O(3)
$26.69X - 3.96Y - 12.02Z = 1.66$
N(41) 0.151, N(42) −0.167, O(4) 0.178, O(3) −0.163
Cu(4) 0.087, O(2) 2.391, O(411) −2.503

distances are noticeably longer than the other four. The copper(II) ions are bridged by an approximately tetrahedral array of oxygen atoms, forming the cubane-type structure Cu_4O_4. The limiting planes of this cube and the angles between the planes are calculated and shown in Table 3. The structure of the array is similar to that of the chloride salt of this cation [3] and resembles the structures of the copper(II) compound of the Shiff base of aminoethanol and acetylacetone,[9] chloro(2-diethylaminoethanolato)copper(II),[10,11] and chloro-, and γ-bromo(2-dibutylaminoethanolato)copper(II).[12] However, the difference between the shortest and longest interatomic copper(II) ion distances is smaller in the present cation than in those just mentioned, so that the coupling in the present compound can be thought to have more tetranuclear character. The unit Cu_4O_4 has S_4 pseudosymmetry, and the whole cation $[Cu_4(C_5H_{13}N_2O)_4]^{4+}$ has approximately this symmetry too.

The coordination around the copper(II) ions is distorted octahedral $(4+2)$-coordination. The two nitrogen atoms and the oxygen atom of one amine (i) and the oxygen atom of another amine (j) lie almost in a plane with the cop-

per(II) ion. The least-squares planes through the nitrogen and oxygen atoms are calculated and are given in Table 4. The copper(II) ions are situated $0.063-0.087$ Å from the planes toward the oxygen atom of the third amine (k). The bond distances (Tables 2 and 5) in the plane correspond to typical coordination bonds: (mean values) $Cu(i)-N(i1)$ 1.99 Å, $Cu(i)-N(i2)$ 2.02 Å, $Cu(i)-O(i)$ 1.95 Å and $Cu(i)-O(j)$ 1.98 Å. The apices of the octahedron are occupied by the oxygen atom of the third amine, having an interatomic distance 2.59 Å (mean value), and an oxygen atom of the NO_3 group having the $Cu(i)-O(i11)$ distance 2.70 Å (mean value). These longer distances can be considered semicoordination bonds and they are in agreement with the bond extension in the axial direction of copper(II) octahedral coordination.[13] The coordination of the copper(II) ion in this cation differs from the coordinations in other compounds described earlier, where it is bipyramidal $(3+2)$-coordination with two oxygen atoms in axial positions and a nitrogen atom and two oxygen atoms of different ligands in equatorial positions or distorted square pyramidal coordination.[9-12]

The amine configuration is similar to that of

Table 5. Bond lengths (Å) between the atoms in the amine rings and in the NO_3 ions. The shortest interatomic distances (Å) from the oxygens of water molecules to other atoms. Estimated standard deviations are given in parentheses.

	i = 1	i = 2	i = 3	i = 4	i = 5
$Cu(i)-N(i1)$	1.99(2)	2.01(1)	1.98(2)	2.01(1)	
$Cu(i)-N(i2)$	2.03(1)	2.03(1)	2.01(1)	2.03(1)	
$N(i1)-C(i1)$	1.53(2)	1.51(2)	1.52(2)	1.48(2)	
$C(i1)-C(i2)$	1.54(3)	1.56(3)	1.56(3)	1.56(3)	
$C(i2)-C(i3)$	1.56(3)	1.52(2)	1.52(3)	1.55(2)	
$C(i3)-N(i2)$	1.49(2)	1.50(2)	1.50(2)	1.48(2)	
$N(i2)-C(i4)$	1.48(3)	1.49(2)	1.53(3)	1.51(2)	
$C(i4)-C(i5)$	1.50(2)	1.53(2)	1.46(2)	1.56(2)	
$C(i5)-O(i)$	1.42(2)	1.45(2)	1.42(2)	1.47(2)	
$Cu(i)-O(i11)$	2.80(2)	2.72(3)	2.66(1)	2.59(2)	
$N(i11)-O(i11)$	1.21(2)	1.16(18)	1.19(2)	1.24(2)	1.28(3)
$N(i11)-O(i12)$	1.21(3)	1.47(13) [a]	1.29(2)	1.25(2)	1.14(4)
$N(i11)-O(i13)$	1.17(3)	1.13(17)	1.20(2)	1.24(2)	1.29(4)
$O(6)\cdots O(511)$	2.67(4)				
$O(6)\cdots O(212)$	2.92(4)				
$O(7)\cdots O(511)$	2.86(4)				
$O(8)\cdots O(312)$	2.49(7)				

[a] The interatomic distance $O(212)$ $[1/2-x, 1/2-y,\bar{z}]\cdots N(211)$ is 1.33 Å and the distance $N(211)\cdots N(211)$ $[1/2-x,1/2-y,\bar{z}]$ is 0.40 Å.

Table 6. Bond angles (°) in the amine rings and in the NO_3 ions. The interatomic angles (°) from the oxygens water molecules. Estimated standard deviations are given in parentheses.

	i=1	i=2	i=3	i=4	i=5
N(i1)−Cu(i)−N(i2)	94.2(6)	93.2(5)	94.3(6)	92.9(4)	
N(i1)−Cu(i)−O(i)	175.9(4)	175.9(5)	175.9(4)	175.0(6)	
N(i1)−Cu(i)−O(j)	94.5(5)j=3	96.1(5)j=4	94.9(5)j=1	95.0(4)j=2	
N(i1)−Cu(i)−O(k)	94.1(5)k=4	95.2(4)k=1	93.9(5)k=2	94.9(4)k=3	
N(i1)−Cu(i)−O(i11)	97.8(5)	94.6(7)	94.1(5)	92.0(6)	
N(i2)−Cu(i)−O(i)	84.9(5)	84.8(4)	85.0(5)	85.5(4)	
N(i2)−Cu(i)−O(j)	120.0(3)j=3	117.8(5)j=4	120.1(3)j=1	121.6(5)j=2	
N(i2)−Cu(i)−O(k)	164.6(5)k=4	166.4(4)k=1	165.9(5)k=2	163.9(5)k=3	
N(i2)−Cu(i)−O(i11)	78.6(4)	78.7(6)	79.8(4)	81.1(5)	
O(i)−Cu(i)−O(i11)	86.0(5)	89.0(6)	89.8(5)	92.4(5)	
O(j)−Cu(i)−O(i11)	156.9(3)j=3	159.6(6)j=4	157.3(4)j=1	155.6(3)j=2	
O(k)−Cu(i)−O(i11)	87.5(4)k=4	89.8(6)k=1	88.3(4)k=2	84.5(5)k=3	
Cu(i)−N(i1)−C(i1)	117.3(12)	113.4(10)	117.3(12)	117.6(9)	
N(i1)−C(i1)−C(i2)	110.7(18)	111.5(17)	113.7(17)	112.0(13)	
C(i1)−C(i2)−C(i3)	111.1(13)	110.0(20)	113.0(12)	114.2(17)	
C(i2)−C(i3)−N(i2)	110.6(13)	111.2(14)	111.2(11)	109.8(13)	
C(i3)−N(i2)−Cu(i)	119.8(12)	120.3(9)	120.7(12)	122.6(8)	
Cu(i)−N(i2)−C(i4)	107.3(8)	107.9(10)	105.8(8)	108.2(9)	
C(i3)−N(i2)−C(i4)	111.9(12)	109.8(11)	111.1(11)	109.4(11)	
N(i2)−C(i4)−C(i5)	108.6(13)	106.8(11)	108.2(14)	106.8(11)	
C(i4)−C(i5)−O(i)	108.8(16)	106.6(9)	107.6(17)	105.8(10)	
C(i5)−O(i)−Cu(i)	110.3(9)	110.9(9)	111.0(9)	110.5(9)	
C(i5)−O(i)−Cu(j)	124.5(11)j=2	121.8(7)j=3	123.8(10)j=4	120.0(7)j=1	
C(i5)−O(i)−Cu(k)	122.9(7)k=3	120.7(9)k=4	122.2(6)k=1	126.1(10)k=2	
Cu(i)−O(i11)−N(i11)	121(2)	151(6) a	134(1)	139(1)	
O(i11)−N(i11)−O(i12)	120(2)	84(9) a	113(1)	121(1)	116(3)
O(i11)−N(i11)−O(i13)	119(3)	160(10) a	130(2)	118(2)	120(3)
O(i12)−N(i11)−O(i13)	120(2)	87(9) a	116(1)	121(1)	123(3)
O(212)···O(6)···O(511)	97(1)				
O(511)···O(7)···O(511) b	99(−)				

a Disordered.   b Equivalent position $\bar{x},y,1/2-z$.

tetrameric {2-[(3-aminopropyl)amino]ethanolato}copper(II) chloride monohydrate.[3] The bond lengths (Table 5) in both amine rings are typical single bond values, and the (3-aminopropyl)amino ring has chair conformation. Both the bond length and angles (Table 6) are in agreement with those of (3-aminopropyl)-amines reported earlier.[14] The mean value of the bond angles around the oxygen atom is 109°. This corresponds to sp^3 hybridization. The coordination is rather distorted, however.

The bond lengths and angles for NO_3 groups are shown in Tables 5 and 6. These values are normal except those for the disordered $NO_3(2)$. Three types of NO_3 groups can be distinguished. $NO_3(2)$ and $NO_3(4)$ are located in special positions (0, −0.3166, 1/4) and (1/4, −1/4, 0), having the Cu(i)−O(i11) distance 2.65 Å (mean value). These NO_3 groups form bridges between tetrameric [Cu$_4$-(C$_5$H$_{13}$N$_2$O)$_4$]$^{4+}$ units in the direction $\vec{a}-\vec{c}$. $NO_3(1)$ and $NO_3(3)$ are semicoordinated to copper(II) ions, having the mean value Cu(i)−O(i11) distance 2.73 Å. There is a possible hydrogen bond from the atom O(312) to the lattice water molecule O(8) [O(312)···O(8) 2.49 Å]. $NO_3(5)$ is probably joined to the structure through hydrogen bonds. Oxygen atom O(6) is at a distance 2.67 Å from oxygen atom O(511) and at a distance 2.92 Å from oxygen atom O(212), and the angle O(511)···O(6)···O(212) is 97°. Thus water (6) joins together $NO_3(2)$ and $NO_3(5)$ groups. Oxygen atom O(7) is located on the *two*-fold axis. The interatomic
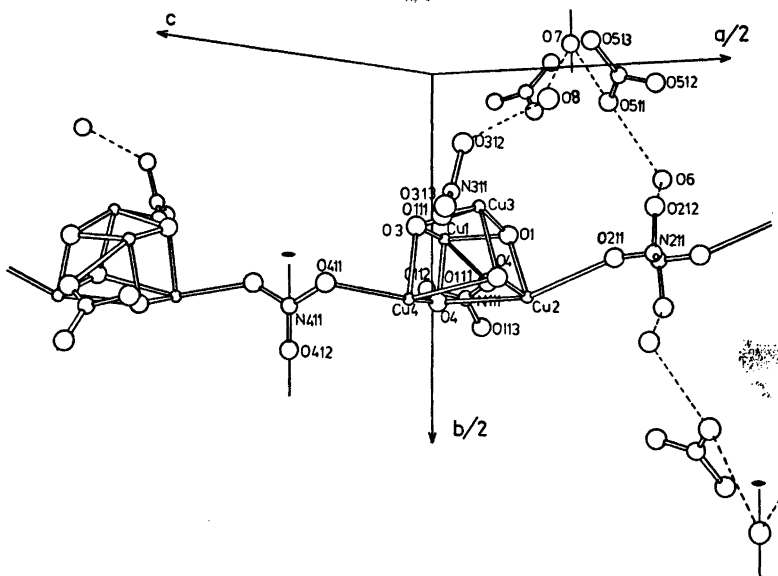
Fig. 2. Perspective view of the chain.

$O(7) \cdots O(511)$ distances are 2.86 Å and the angle $O(511) \cdots O(7) \cdots O(511)'$ is 99°, which values probably indicate hydrogen bonds. The bridges formed by water molecules and nitrate ions join $\{[Cu_4(C_5H_{13}N_3O)_4](NO_3)_3\}_n^+$ chains together in the direction $\vec{a} + \vec{c}$. A view of the chain is shown in Fig. 2 (the amine rings are omitted for clarity).

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