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Tetrakis(μ-6-ammoniohexanoato-1κO:2$\kappa O'$)-bis[chlorocopper(II)] dichloride tetrahydrate

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The title complex, $[Cu_2(C_6H_{13}NO_2)_4Cl_2]Cl_2\cdot4H_2O$, has a centrosymmetric, dimeric and dicationic tetracarboxylatodicopper(II) core with apical positions occupied by chloride. The positive charge is balanced by two non-coordinating chlorides that, together with four uncoordinated water molecules per dimeric unit, are involved in extensive hydrogen bonding, leading to a cohesive crystal structure.

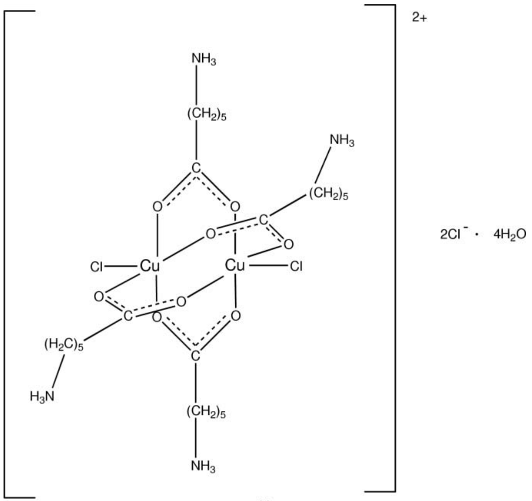
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.036
wR factor = 0.083
Data-to-parameter ratio = 17.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Aliphatic carboxylic acids, bearing an amino group at the terminal end of the hydrocarbon chain, are interesting since they can be used as models for carboxylate and amino side chains present in proteins. So far, several crystal structures of complexes containing terminal amino acids with the general formula $H_2N-(CH_2)_n-COOH$ and copper ions are known. Most contains the essential amino acid glycine (two C atoms) or the next amino acid in the series, *i.e.* β-alanine with three C atoms. Structures with higher terminal amino acids apart from glycine and β-alanine are very rare and reported only for 4-aminobutyric acid (Takenaka *et al.*, 1973; Sabirov *et al.*, 1994), 6-aminohexanoic acid (Sjöberg *et al.*, 1973; Österberg *et al.*, 1970) and 11-aminoundecanoic acid (Mascarenhas *et al.*, 1987). As part of a general study on copper complexes with selected aliphatic carboxylic acids, we present here the structure of a dimeric copper(II) 6-aminohexanoate adduct with chloride, (I).



(I)

The dimeric unit (Fig. 1 and Table 1) exists as a divalent cation with the two Cu atoms bridged by the carboxylate groups of the four 6-aminohexanoate ligands. The net charge of each of the four 6-aminohexanoate bridges is zero as 6-

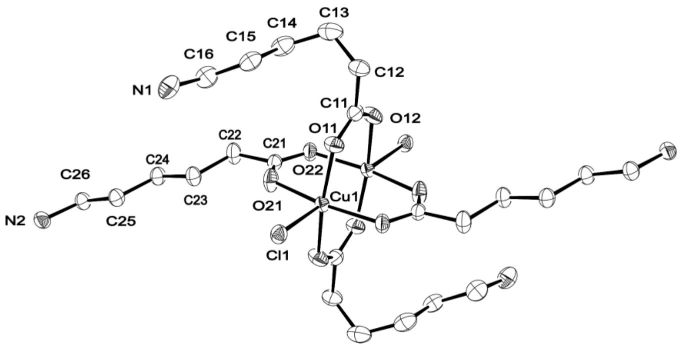


Figure 1

A view of the dimeric cation of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted. Unlabelled atoms are related by the symmetry operation $1 - x, -y, 2 - z$.

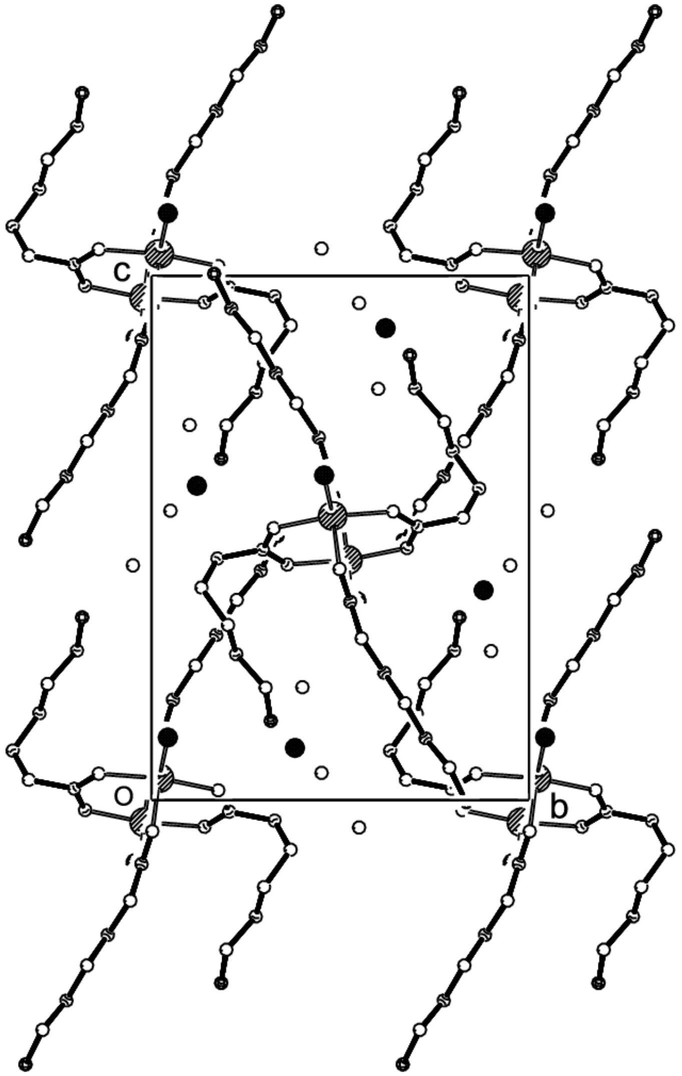


Figure 2

A view of (I) along the *a* axis, showing the arrangement of uncoordinated water molecules (open circles) and chloride ions (black circles).

aminohexanoic acid is present in its zwitterionic form. The apical positions in the centrosymmetric dimer are occupied by chloride. The charge of the dicationic complex is balanced by two non-coordinated chloride anions. Additionally, four water molecules per dimeric unit are present in the crystal structure. The Cu$\cdots$Cu separation of 2.6510 (5) Å is as usually found in other dimeric copper(II) carboxylates. The coordination geometry around the Cu atoms is square pyramidal with four carboxylate O atoms in the basal plane and a Cl atom in the apical site. One pair of the aliphatic chains is in a common plane zigzag conformation, whereas the other pair is distorted by rotation about the C12—C13 bond, giving C11—C12—C13—C14 and C12—C13—C14—C15 torsion angles of 46.3 (3) and 59.4 (3)°, respectively. Only a few chloride adducts that include the cationic copper dimeric core have been reported (Silva *et al.*, 2002; Chen & Mak, 1993 Jezierska *et al.*, 1998; Sabirov *et al.*, 1994). A similar geometry of the dimeric core is observed in all of these related compounds. The Cl—Cu$\cdots$Cu axis is not completely linear, as seen in the the Cl1—Cu$\cdots$Cu^{i} angle of 175.60 (2)°, a result that is consistent with the values found in related compounds [symmetry code: (i) $1 - x, -y, 2 - z$.]

As summarized in Table 2, all components of the structure associate *via* hydrogen-bonding interactions to form a cohesive crystal structure. A view of the unit-cell contents is shown in Fig. 2.

Experimental

$CuCl_2\cdot 2H_2O$ (0.5 mmol) was dissolved in a mixture of water (10 ml) and methanol (5 ml). When 6-aminohexanoic acid (1 mmol) was added to the solution, the colour changed from light blue to green. Green crystals of (I) were obtained by slow evaporation of the solvent at ambient temperature.

Crystal data

$[Cu_2(C_6H_{13}NO_2)_4Cl_2]Cl_2\cdot 4H_2O$
$M_r = 865.64$
Monoclinic, $P2_1/n$
$a = 9.4122$ (1) Å
$b = 12.1852$ (2) Å
$c = 17.5851$ (2) Å
$\beta = 105.4399$ (6)°
$V = 1944.04$ (4) Å^3
$Z = 2$
$D_x = 1.479$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4519 reflections
$\theta = 2.9$–$27.5°$
$\mu = 1.43$ mm^{-1}
$T = 293$ (2) K
Block, green
0.20 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
ω scans at $\kappa = 55°$
Absorption correction: none
8512 measured reflections
4436 independent reflections
3225 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.083$
$S = 1.02$
4436 reflections
248 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.5397P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O11	1.9602 (16)	C14—C15	1.519 (4)
Cu1—O12^{i}	1.9780 (16)	C15—C16	1.505 (4)
Cu1—O21	1.9667 (16)	C16—N1	1.476 (4)
Cu1—O22^{i}	1.9736 (15)	O21—C21	1.252 (3)
Cu1—Cl1	2.4857 (6)	O22—C21	1.265 (3)
Cu1—Cu1^{i}	2.6510 (5)	C21—C22	1.518 (3)
O11—C11	1.252 (3)	C22—C23	1.507 (3)
O12—C11	1.271 (3)	C23—C24	1.517 (3)
C11—C12	1.503 (3)	C24—C25	1.520 (3)
C12—C13	1.512 (4)	C25—C26	1.507 (3)
C13—C14	1.509 (4)	C26—N2	1.480 (3)
O11—Cu1—O21	91.55 (7)	O21—Cu1—O22^{i}	167.86 (7)
O11—Cu1—O22^{i}	86.93 (7)	O21—Cu1—Cl1	98.15 (5)
O11—Cu1—O12^{i}	167.77 (7)	O22^{i}—Cu1—O12^{i}	91.19 (7)
O11—Cu1—Cl1	93.62 (5)	O22^{i}—Cu1—Cl1	93.97 (5)
O12^{i}—Cu1—Cl1	98.56 (5)	Cl1—Cu1—Cu1^{i}	175.60 (2)
O21—Cu1—O12^{i}	87.75 (8)		

Symmetry code: (i) $1 - x, -y, 2 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯O4	0.79 (3)	2.05 (4)	2.806 (4)	160 (3)
N1—H1B⋯O3	0.90 (4)	1.89 (4)	2.787 (4)	177 (3)
N1—H1C⋯O12^{ii}	0.85 (4)	2.18 (4)	2.926 (3)	146 (3)
N2—H2A⋯O22^{iii}	0.79 (3)	2.59 (3)	3.144 (3)	128 (2)
N2—H2A⋯Cl1^{iv}	0.79 (3)	2.77 (3)	3.456 (3)	147 (2)
N2—H2B⋯Cl1^{v}	0.87 (3)	2.31 (4)	3.174 (3)	173 (3)
N2—H2C⋯Cl2^{iv}	0.97 (4)	2.24 (4)	3.190 (3)	166 (3)
O4—H4A⋯Cl2^{iv}	0.80 (4)	2.52 (4)	3.315 (3)	175 (3)
O4—H4B⋯Cl2^{vi}	0.74 (4)	2.46 (4)	3.196 (3)	173 (5)
O3—H3A⋯Cl1	0.73 (5)	2.58 (5)	3.297 (3)	173 (5)
O3—H3B⋯Cl2^{ii}	0.75 (4)	2.48 (4)	3.228 (3)	174 (4)

Symmetry codes: (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, -\frac{1}{2} - y, z - \frac{1}{2}$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (v) $\frac{1}{2} + x, -\frac{1}{2} - y, z - \frac{1}{2}$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$.

The methylene H atoms were included in the riding-model approximation, with C—H = 0.97 Å and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C). Those of the ammonio groups and the water molecules were freely refined; O—H and N—H distances are given in Table 2.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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