

Conformational flexibility of tricine as a chelating agent in *catena*-poly[[*N*-(2-hydroxy-1,1-bis(hydroxymethyl)ethyl)glycinato-*O,N,O'*]copper(II)]- μ -chloro]

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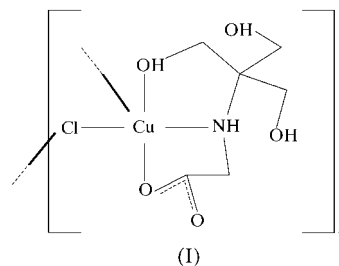
In the polymeric title compound, *catena*-poly[[*N*-(2-hydroxy-1,1-bis(hydroxymethyl)ethyl)glycinato-*O,N,O'*]copper(II)]- μ -chloro], [CuCl(C₆H₁₂NO₅)_n], the Cu²⁺ ions are chelated by tridentate tricine anions and bridged by chloride ions. The metal ion is five-coordinated, with an approximately square-pyramidal geometry. The [CuCl(C₆H₁₂NO₅)] units form infinite zigzag chains running parallel to the *c* axis, with Cu—Cl distances of 2.2209 (14) and 2.7792 (19) Å. The tricine anion adopts a conformation intermediate between that found in the crystal structure of the neutral molecule and those reported for the Ni²⁺ and Zn²⁺ complexes.

Comment

Some of the best studied polynuclear copper compounds are planar dihydroxo-bridged copper(II) dimers in which the terminal groups are bidentate nitrogen-containing ligands. It was shown by Crawford *et al.* (1976) that the energy gap *J* between the singlet and triplet states of the Cu²⁺ dimer could be directly related to the bridging Cu—O—Cu angle; a difference of 1° in the bridging angle would result in a variation of about 74 cm⁻¹ in the singlet–triplet separation. Much effort has been expended in correlating the magnitude of the exchange interactions in halide-bridged copper(II) dimers or chains with their structural features, but a general magneto-structural correlation similar to the simple one detected for the di- μ -hydroxo-bridged copper dimers should not be expected (Rojo *et al.*, 1987). The nature of the ligands *trans* to the bridging ligand is also important. Dimers having a chloride ligand in a *trans* position generally show greater anti-ferromagnetic interactions (Rojo *et al.*, 1987). The linear chain compound [CuCl₂(pyridine)₂] has been studied extensively and it is generally accepted that this complex exhibits magnetic properties that can be explained by the one-dimensional Heisenberg model (Crawford & Hatfield, 1977). Another interesting chloride-bridged chain is found in cyclohexylammonium trichlorocopper(II), which exhibits meta-magnetic behaviour and has chain-bridging angles of 85.3 and

86°. In zero field, the ground state is antiferromagnetic, but in an applied field greater than 100 G (1 G = 10⁻⁴ T), the ground state becomes ferromagnetic-like (Kahn, 1993).

The title compound, (I), was synthesized as part of a study of the magnetic properties of Cu^{II} compounds, in particular dimers and polymeric chains where the transition metal ions are bridged through unsubstituted or substituted amino acids, providing a superexchange pathway *via* the carboxy groups. Tricine [*N*-(tris(hydroxymethyl)methyl)glycine] is a good complexation agent for divalent alkaline-earth and transition metal cations (Good *et al.*, 1966). Potentiometric studies have shown that stable complexation of several transition metal, rare earth and actinide atoms occurs in solution. The stability constants of Th⁴⁺, Ce³⁺, La³⁺ and UO₂²⁺ have been determined in aqueous media and evidence was found for the presence of binary complexes of 1:1 and 1:2 proportions (El-Roudy *et al.*, 1997). These studies suggest that tricine may act as a tridentate as well as a bidentate ligand. There is, however, little structural work on the chelating properties of this ligand. A survey of the April 2000 release of the Cambridge Structural Database (Allen & Kennard, 1993) has shown that only two crystal structures, namely of the Zn²⁺ and Ni²⁺ complexes, have been reported. In both, tricine indeed acts as a tridentate ligand (Menabue & Saladini, 1992).



In compound (I), the Cu²⁺ ion is five-coordinated with an approximately square-pyramidal geometry (Fig. 1). The basal atoms of the pyramid are a Cl⁻ ion, a carboxy O atom, the glycine N atom and an O atom of one of the hydroxymethyl groups, which form a distorted square plane around the Cu atom [r.m.s. deviation 0.0682 (6) Å]. A symmetry-related Cl⁻ ion [Clⁱ; symmetry code: (i) *x*, 1 - *y*, *z* - ½] occupies the apical position of the pyramid. The Cu²⁺ ion lies 0.1015 (4) Å out of

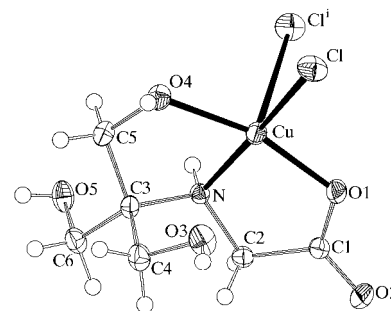


Figure 1

An ORTEP (Johnson, 1976) plot of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) *x*, 1 - *y*, *z* - ½].

the least-squares plane of the pyramid base. The maximum deviation from the ideal value of 90° of the valency angles involving the transition metal atom is $7.70(5)^\circ$ for $O1-Cu-Cl$. The complex units form infinite zigzag chains parallel to the c axis, bridged through the Cl^- ions with asymmetric $Cu-Cl$ distances of 2.2209(14) and 2.7792(19) Å (Fig. 2). The $Cu-Cl-Cu^{II}$ bridging angle is $122.08(3)^\circ$ [symmetry code: (ii) $x, 1 - y, \frac{1}{2} + z$].

Tricine is present in (I) in the anionic form, with a carboxylate group. Despite the fact that this group is ionized, there is considerable asymmetry between the carboxy $C-O$ bond lengths, which may be explained by the chelating bond between $O1$ and Cu that lengthens the $O1-C1$ bond. Bond distances and angles within the anion compare well with those reported by Menabue & Saladini (1992) for the zinc and nickel complexes. In these compounds, the tricine ion is heavily folded (see below) to accommodate two symmetrical ions coordinating to the metal atom; in the present structure, only one tricine ion bonds to the Cu^{2+} ion and the conformation of the tricine ion is closer to that of the neutral molecule (Ramos Silva *et al.*, 2001). It is important to note that, whereas in the nickel and zinc complexes the metal ion is bonded to one of the hydroxymethyl groups further away from the main skeleton ($C1-C2-N-C3$), in (I), the chelating hydroxymethyl group is the closest to the main skeleton (the chelating $O4$ atom is less than 0.6 Å away from the least-squares plane of $C1-C2-N-C3$). In the zinc and nickel complexes, the metal ions are six-coordinated in a distorted octahedral environment and the $O1-metal-O4$ angles are 88.21 and 85.77° , respectively, while for copper the angle is $164.92(5)^\circ$, showing that here the ligand bridges the *trans* rather than the *cis* positions.

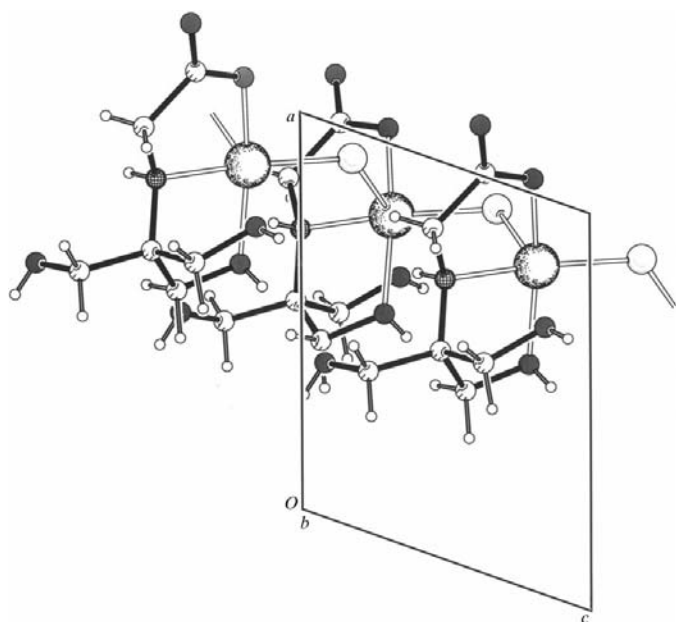


Figure 2
Projection of the structure of (I) along the b axis showing one of the chloride-bridged chains.

The main skeleton of the tricine molecule in (I) deviates from planarity, in contrast with the neutral molecule, but not by as much as in the nickel and zinc complexes, as shown by the $C1-C2-N-C3$ torsion angles [$-134.13(12)$, 90.57 , -82.21 and $177.57(7)^\circ$, for the copper, nickel and zinc complexes, and pure tricine, respectively]. As shown by the $C2-N-C3-C4$, $C2-N-C3-C5$ and $C2-N-C3-C6$ torsion angles, the tris(hydroxymethyl)methyl group is rotated as a rigid group around the $N-C3$ bond by approximately 9° , much less than the rotation found in the nickel and zinc complexes or in pure tricine (where the rotation is 20 , 25 and 22° , respectively). The $N-C3-C5-O4$, $N-C3-C4-O3$ and $N-C3-C6-O5$ torsion angles [$-50.25(15)$, $40.23(17)$ and $-59.75(16)^\circ$, respectively] show that the three hydroxymethyl groups bonded to the N atom do not adopt the propeller-like conformation seen in the neutral molecule.

The polymers are linked together by an extended three-dimensional network of hydrogen bonds. Full saturation of every strong donor involved in hydrogen bonding is observed. The hydroxyl groups act as donors to three neighbouring tricine ions linking the polymeric chains, whereas a weak interaction between the NH group and the Cl^- ion occurs within the chain.

The magnetic susceptibility of (I) was measured as a function of temperature using a SQUID magnetometer on a powder sample which was free to rotate under the applied field. Unexpectedly, paramagnetic behaviour was found from room temperature down to the lowest attainable temperature of 2 K. A linear fit of the inverse susceptibility as a function of the temperature yielded an effective magnetic moment of $1.8 \mu_B$ per Cu atom. The fact that the susceptibility obeys the paramagnetic Curie law down to such a low temperature shows that the magnetic exchange interaction between the Cu^{2+} ions is very small and that the Cl^- ions do not provide an effective superexchange pathway through the chain. This might be explained by the wide $Cl-Cu-Cl^{II}$ bridging angle and the fact that the magnetic planes of adjacent metal ions (planes with the four most strongly bound ligands, where the unpaired electron exists) do not share the bridging Cl atom.

Experimental

Copper(II) chloride dihydrate (10 mmol) was added to tricine (10 mmol; Aldrich, 99%) in a solution of ethanol (50 ml). After a few days, blue crystals had formed.

Crystal data

$[CuCl(C_6H_{12}NO_5)]$
 $M_r = 277.16$
 Monoclinic, Cc
 $a = 7.8836(12)$ Å
 $b = 20.134(3)$ Å
 $c = 6.089(4)$ Å
 $\beta = 109.32(3)^\circ$
 $V = 912.0(6)$ Å³
 $Z = 4$

$D_x = 2.019$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 9.87-16.16^\circ$
 $\mu = 2.683$ mm⁻¹
 $T = 293(2)$ K
 Prism, intense blue
 $0.27 \times 0.17 \times 0.14$ mm

Table 1

Selected geometric parameters (Å, °).

Cu—O1	1.9444 (11)	Cu—Cl ⁱ	2.7792 (19)
Cu—N	1.9943 (16)	O1—C1	1.2830 (18)
Cu—O4	2.0302 (12)	O2—C1	1.2301 (18)
Cu—Cl	2.2209 (14)		
O1—Cu—N	85.04 (6)	O1—Cu—Cl	97.70 (5)
O1—Cu—O4	164.92 (5)	N—Cu—Cl	174.81 (4)
N—Cu—O4	83.58 (6)	O4—Cu—Cl	92.94 (5)
C2—N—C3—C4	50.83 (16)	C2—N—C3—C6	−68.88 (15)
C2—N—C3—C5	171.51 (11)		

Symmetry code: (i) $x, 1 - y, z - \frac{1}{2}$.**Data collection**

Enraf–Nonius CAD-4 diffractometer
 Profile data from $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.652$, $T_{\max} = 0.687$
 2843 measured reflections
 1336 independent reflections (plus 1326 Friedel-related reflections)

2603 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$
 $\theta_{\max} = 29.96^\circ$
 $h = -11 \rightarrow 11$
 $k = -28 \rightarrow 28$
 $l = -8 \rightarrow 8$
 3 standard reflections
 frequency: 180 min
 intensity decay: 7%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.016$
 $wR(F^2) = 0.042$
 $S = 1.070$
 2662 reflections
 139 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 0.3297P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1983)
 Flack parameter = -0.004 (6)

All H atoms could be located in a difference Fourier map at an intermediate stage of the refinement. The coordinates of the H atoms bonded to O or N atoms were refined freely with an isotropic displacement parameter constrained to that of the parent atom. H atoms bonded to C atoms were refined as riding on their parent atoms, using *SHELXL97* (Sheldrick, 1997) defaults.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97*; molecular graphics:

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N—H0 \cdots Cl ⁱⁱ	0.89 (2)	2.74 (2)	3.3671 (16)	127.9 (18)
O5—H5 \cdots O1 ⁱⁱⁱ	0.78 (3)	2.02 (3)	2.7703 (19)	160 (3)
O3—H3 \cdots O2 ^{iv}	0.72 (3)	2.07 (3)	2.7908 (19)	178 (3)
O4—H4 \cdots O5 ^v	0.69 (3)	2.05 (3)	2.741 (2)	171 (3)

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

ORTEPII (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: *JZ1425*). Services for accessing these data are described at the back of the journal.

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