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Weak antiferromagnetic interactions in hydronium diaqua-1κ*O*,2κ*O*-trichloro-1κ*Cl*,$2\kappa^2$*Cl*-*μ*-dimethylglycinato-1κ*O*:$2\kappa^2$*O*′,*N*-dimethylglycinato-$1\kappa^2$*N*,*O*-dicuprate(II)

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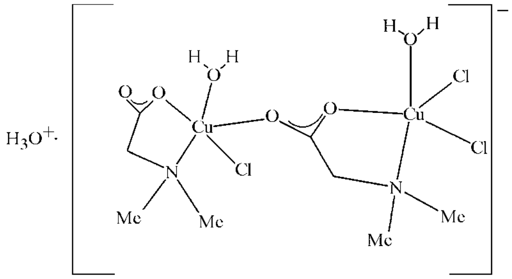
The crystal structure of the title compound, $(H_3O)[Cu_2(C_4H_8NO_2)_2Cl_3(H_2O)_2]$, contains two Cu^{II} ions bridged by the carboxylate group of a dimethylglycinate ion in an *anti–anti* configuration. The Cu^{II} atoms both have an approximately square-pyramidal conformation geometry and are 5.977 (2) Å apart. The two dimethylglycinate ligands have similar conformations, although they play different roles in the structure. A weak antiferromagnetic interaction between the two copper ions could be inferred from the magnetic susceptibility measurements.

Comment

The establishment of a relationship between the magnetic and structural properties, leading to a better understanding of the fundamental factors governing magnetic properties, has been the aim of much recent scientific work (Khan, 1993). Such knowledge would allow the design and production of new molecular-based magnets, and provide an understanding of the structure and function of the paramagnetic active sites in metalloproteins. Metalloproteins justify the great interest in metal–carboxylate complexes, since in these systems the metal ions are chelated by carboxylate groups supplied by amino acid chains. Carboxylate is a versatile anion that can display several types of bridging conformation, such as monoatomic or triatomic *syn–syn*, *syn–anti* and *anti–anti*. A soft correlation has been found between the magnetic interaction of the metallic ions and the carboxylate conformation. The triatomic *syn–syn* conformation usually mediates strong interactions, medium–weak interactions are found with the *syn–anti* conformation, and the *anti–anti* conformation favours very weak magnetic exchange interactions. The crystal structure of the title compound, (I), contains two Cu^{II} ions with different environments bridged by the carboxylate group of a dimethylglycinate ion in an *anti–anti* configuration (Fig. 1). According to the procedure described by Addison *et al.* (1984), the shapes of the polyhedra can be considered as square-based pyramidal since the τ values [$\tau = (\theta1 - \theta2)/60°$, where $\theta1$ and $\theta2$ are the largest angles in the coordination sphere] are 0.30 for atom Cu1 and 0.08 for atom Cu2. (τ is 1 for trigonal–bypyramidal D_{3h} and 0 for square-based-pyramidal C_{4v} geometries.)



(I)

Four short bonds occupy the basal positions, and they are of the same type for both Cu1 and Cu2, involving a carboxylate O atom, a water O atom, an N atom and a Cl atom. As seen in Fig. 1, atom Cu1 is coordinated by a Cl atom in the apical position, with a bond distance of 2.5986 (8) Å. Atom Cu2 has a carboxylate O atom in that position, with a distance of 2.272 (2) Å. As usual, both copper ions deviate from their mean basal plane towards the apical atom [0.2511 (11) Å for Cu1 and 0.2250 (12) Å for Cu2].

The mean basal planes of the pyramids make an angle of 82.24 (5)°. The atoms in the pyramid bases are not equally spaced. The O2—Cu1—O5 angle is 90.19 (9)° and O5—Cu1—Cl2 is 90.10 (8)°, but the Cl2—Cu1—N1 angle is 96.19 (7)° and N1—Cu1—O2 is 82.46 (8)°; a similar situation is found around atom Cu2. The smaller angle, N1—Cu1—O2, is certainly a result of the incapacity of the organic moiety to stretch further. The distances in the basal plane range between 1.972 (2) and 2.2367 (8) Å for atom Cu1, and between 1.9636 (19) and 2.2131 (8) Å for atom Cu2 (Table 1). The two Cu atoms are separated by almost 6 Å. The dimethylglycine molecules crystallize in their ionic form with a total charge of −1. The carboxylate groups are deprotonated, and the C—O

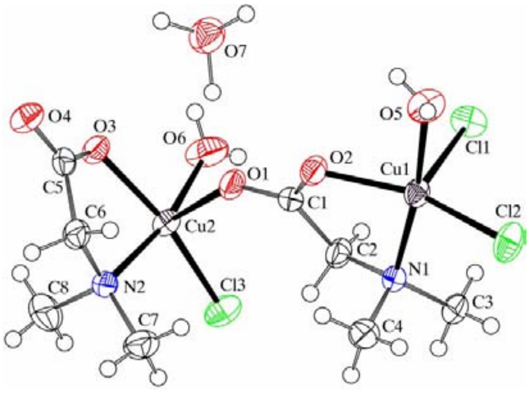


Figure 1
ORTEPII (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

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distances [1.240 (3)–1.279 (3) Å] are slightly elongated because of their metal coordination role. One of the dimethylglycine moieties bridges the two copper ions, while the other coordinates to atom Cu2 only. In spite of having distinct functions in this complex, the conformations of the substituted amino acids are similar, both carboxylate groups being rotated 18° around the C—C bond. Usually, the carboxylate groups of bridging dimethylglycine molecules are rotated less than in the *N*,*O*-coordination mode (Ramos Silva *et al.*, 2005). The molecular skeletons deviate from planarity, as indicated by the C3—N1—C2—C1 [−159.1 (2)°] and C7—N2—C6—C5 [159.4 (2)°] torsion angles. Both chelate rings are significantly non-planar, as illustrated by the N1—C2—C1—O2 [18.0 (3)°] and N2—C6—C5—O3 [−17.5 (3)°] torsion angles. In a related compound, *viz.* aquabis(*N*,*N*-dimethylglycinato)copper dihydrate (Cameron *et al.*, 1973), where amino acid ions chelate each metallic cation in an *N*,*O*-chelating mode and the apical position is occupied by a water O atom, the torsion angles (of the chelate rings) are approximately 18 and 30°. Such a conformation goes against that expected from the results of a density functional study in the gas phase for Cu^+– and Cu^{2+}–glycine bonding (Bertran *et al.*, 1999), using the hybrid three-parameter B3LYP approach. These calculations showed that for Cu^+ the most stable coordination is *N*,*O*-bidentate, with the cation interacting with the N and carbonyl O atoms. For Cu^{2+}, the preferred coordination is *O*,*O*-bidentate, with the metal interacting with the CO_2^- group of the zwitterionic species.

A hydronium cation compensates the negative charge of the complex and links three neighbouring complexes *via* hydrogen bonds (Table 2). The coordination water molecules also share their H atoms with the carboxylate O atoms and atom Cl1, exhausting their potential as donors. Fig. 2 shows the projection of the molecular packing down the *b* axis and the ring patterns formed by the hydronium hydrogen bonds. Perpendicular to the *b* axis, three water H atoms shared with other complexes delineate infinite chains. The remaining H atom participates in rings composed of symmetry-inverted molecules, completing a two-dimensional hydrogen-bond network parallel to the (100) plane. The temperature dependence of the magnetic susceptibility of the title compound was measured using a SQUID magnetometer. An external magnetic field of 100 Oe was applied on a powder sample weighing 0.0277 g. Only a small antiferromagnetic interaction between the sample copper ions could be measured. Indeed, as previous work has pointed out, *anti–anti* bridging is not favourable for an antiferromagnetic interaction, and even weak ferromagnetic coupling has been found (Suarez-Varela *et al.*, 1995).

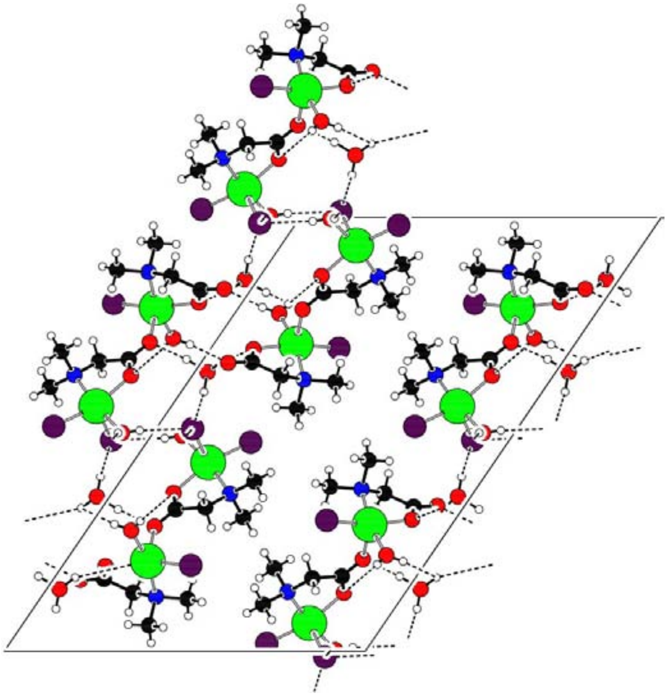

Figure 2
The packing of the anions and cations of (I) projected along *b*. Hydrogen bonds are indicated by dashed lines.

Experimental

Dimethylglycine (5 mmol) was added to an aqueous solution of hydrated copper chloride (2.5 mmol). After a few months at room temperature, small single crystals had grown, and their structure was determined using X-ray analysis (Ramos Silva *et al.*, 2005). After a few weeks, all the crystals had spontaneously dissolved in the solution, and a few weeks later new crystals of the title compound formed and were used for the present determination.

Crystal data

$(H_3O)[Cu_2(C_4H_8NO_2)_2Cl_3(H_2O)_2]$
$M_r = 492.71$
Monoclinic, $P2_1/c$
$a = 15.6775$ (10) Å
$b = 6.2641$ (4) Å
$c = 22.811$ (2) Å
$\beta = 124.292$ (6)°
$V = 1850.8$ (3) Å^3
$Z = 4$
$D_x = 1.768$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.8$–19.8°
$\mu = 2.76$ mm^{-1}
$T = 293$ (2) K
Prism, blue
0.44 × 0.29 × 0.12 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.485$, $T_{\max} = 0.718$
4372 measured reflections
4220 independent reflections
3204 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 20$
$k = -8 \rightarrow 0$
$l = -29 \rightarrow 24$
3 standard reflections
frequency: 180 min
intensity decay: 1%

Table 1
Selected geometric parameters (Å, °).

Cu1—O5	1.972 (2)	Cu2—O3	1.9636 (19)
Cu1—O2	2.0055 (19)	Cu2—O6	1.986 (3)
Cu1—N1	2.012 (2)	Cu2—N2	2.028 (2)
Cu1—Cl2	2.2367 (8)	Cu2—Cl3	2.2131 (8)
Cu1—Cl1	2.5986 (8)	Cu2—O1	2.272 (2)
C1—O1—Cu2	136.87 (19)	O1—C1—O2	123.5 (3)
C1—O2—Cu1	112.19 (17)	O4—C5—O3	123.5 (3)
C4—N1—C2—C1	80.4 (3)	C7—N2—C6—C5	159.4 (2)
C3—N1—C2—C1	−159.1 (2)	C8—N2—C6—C5	−80.6 (3)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.087$
$S = 1.04$
4220 reflections
224 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.8128P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H51···Cl1^{i}	0.89 (4)	2.26 (4)	3.139 (2)	172 (4)
O5—H52···Cl1^{ii}	0.78 (4)	2.31 (4)	3.092 (3)	172 (4)
O6—H61···O2^{iii}	0.62 (5)	2.49 (5)	3.086 (3)	164 (6)
O6—H62···O4^{iv}	0.78 (5)	1.92 (5)	2.690 (3)	172 (5)
O7—H71···O1	1.07 (5)	1.77 (5)	2.841 (3)	172 (4)
O7—H72···O3^{v}	1.05 (5)	1.83 (5)	2.861 (3)	168 (4)
O7—H73···Cl1^{ii}	1.04 (5)	2.26 (5)	3.289 (3)	169 (4)

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

The amino acid H atoms were placed at calculated positions and refined as riding on their parent C atoms, with C—H distances of 0.96 and 0.97 Å, and with U_{iso}(H) values of 1.2 or 1.5 times U_{eq}(C). Water and hydronium H atoms were located in a difference Fourier map and their positions were refined; U_{iso}(H) values were set at 1.2 and 1.5 times U_{eq}(O), respectively. Examination of the crystal structure with *PLATON* (Spek, 2003) showed that there are no solvent-accessible voids.

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* (Sheldrick, 1997); molecular graphics: *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: SK1876). Services for accessing these data are described at the back of the journal.

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