Di-μ-chloro-bis{[N,N-bis(2-pyridylmethyl)-glycine-$\kappa^4 N,N',N'',O$]copper(II)} diperchlorate acetonitrile tetrasolvate

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The title compound, $[Cu_2Cl_2(C_{14}H_{15}N_3O_2)_2](ClO_4)_2 \cdot 4C_2H_3N$, contains dichloro-bridged dicopper(II) complexes lying on centres of inversion. The crystal examined was twinned by a 180° rotation about c^*.

Comment

Reaction of bis(2-pyridylmethyl)glycine (bpgH) and $CuCl_2 \cdot 2H_2O$ in acidic methanol results in immediate precipitation of the title compound, (I). Compound (I) contains dichloro-bridged dicopper(II) complexes (Fig. 1) lying on centres of inversion, with the carboxylate groups protonated. The coordination geometry around the Cu^{II} atom (Table 1) is approximately octahedral, but exhibits significant elongation of the Cu1—O1 and Cu1—Cl1^i bonds [symmetry code: (i) $1 - x, 1 - y, 1 - z$] on account of the Jahn–Teller distortion associated with Cu^{II}. The protonated carboxyl groups form hydrogen bonds to perchlorate anions (Table 2).

(I)
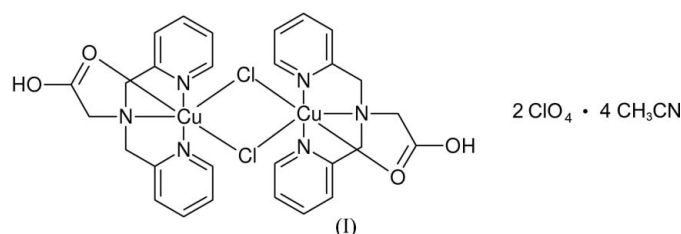
Experimental

Bis(2-pyridylmethyl)glycine (0.1573 g, 0.611 mmol) and $CuCl_2 \cdot 2H_2O$ (0.1047 g, 0.614 mmol) were dissolved in methanol (5 ml) and $HClO_4$ (0.25 ml of a 70% aqueous solution) was added. A turquoise powder (yield 0.2662 g, 93%) precipitated immediately. Recrystallization from hot acetonitrile afforded crystals of (I).

Crystal data

$[Cu_2Cl_2(C_{14}H_{15}N_3O_2)_2](ClO_4)_2 \cdot 4C_2H_3N$	$\gamma = 97.159\ (4)°$
$M_r = 1075.68$	$V = 1127.58\ (17)$ Å³
Triclinic, $P\bar{1}$	$Z = 1$
$a = 7.1238\ (6)$ Å	$D_x = 1.584$ Mg m⁻³
$b = 10.6609\ (10)$ Å	Mo $K\alpha$ radiation
$c = 14.9894\ (13)$ Å	$\mu = 1.25$ mm⁻¹
$\alpha = 92.919\ (4)°$	$T = 180\ (2)$ K
$\beta = 91.266\ (4)°$	Plate, turquoise
	$0.24 \times 0.20 \times 0.05$ mm

Data collection

Bruker–Nonius X8APEX-II CCD diffractometer	26597 measured reflections
thin–slice ω and φ scans	8342 independent reflections
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2004)	4142 reflections with $I > 2\sigma(I)$
$T_{min} = 0.768$, $T_{max} = 0.940$	$R_{int} = 0.076$
	$\theta_{max} = 26.6°$

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Refinement on F^2		H-atom parameters constrained	
$R[F^2 > 2\sigma(F^2)] = 0.073$		$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2]$	
$wR(F^2) = 0.191$		where $P = (F_o^2 + 2F_c^2)/3$	
$S = 1.01$		$(\Delta/\sigma)_{max} < 0.001$	
8342 reflections		$\Delta\rho_{max} = 1.11$ e Å^{-3}	
289 parameters		$\Delta\rho_{min} = -0.65$ e Å^{-3}	

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.970 (5)	Cu1—O1	2.316 (4)
Cu1—N2	2.076 (5)	Cu1—Cl1	2.2397 (17)
Cu1—N3	1.976 (5)	Cu1—Cl1^i	3.1116 (18)
N1—Cu1—N2	83.0 (2)	N3—Cu1—O1	91.58 (18)
N1—Cu1—N3	164.4 (2)	Cl1—Cu1—O1	100.18 (12)
N2—Cu1—N3	82.3 (2)	N1—Cu1—Cl1^i	84.87 (14)
N1—Cu1—Cl1	97.10 (15)	N2—Cu1—Cl1^i	84.60 (15)
N2—Cu1—Cl1	179.18 (17)	N3—Cu1—Cl1^i	88.40 (14)
N3—Cu1—Cl1	97.50 (15)	Cl1—Cu1—Cl1^i	94.61 (5)
N1—Cu1—O1	91.33 (17)	O1—Cu1—Cl1^i	165.08 (11)
N2—Cu1—O1	80.62 (18)		

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

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯O2D^{ii}	0.84	1.88	2.720 (7)	176

Symmetry code: (ii) $-x, -y, -z + 1$.

The crystal was twinned by 180° rotation about c^*. The diffraction pattern was indexed using *CELL_NOW* (Bruker–Nonius, 2004) and integrated as a two-component twin using *SAINT-Plus* (Bruker, 2003). 8445 data (2549 unique; R_{int} = 0.077) were associated with component 1 only, 8423 data (2539 unique; R_{int} = 0.084) were associated with component 2 only, and 9729 data (3277 unique; R_{int} = 0.076) were overlapped. Refinement was performed using the HKLF5 format in *SHELXTL* (Sheldrick, 2000). H atoms bound to C atoms were positioned geometrically and allowed to ride during subsequent refinement, with C—H = 0.95 Å for Csp^2 or 0.99 Å for the methylene groups, and with U_{iso}(H) = 1.2U_{eq}(C). The methyl groups of the acetonitrile molecules were positioned geometrically, with C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C), and allowed to rotate about their local threefold axes. In the final cycles of refinement, rotation was not permitted to aid convergence. The H atom of the hydroxyl group was
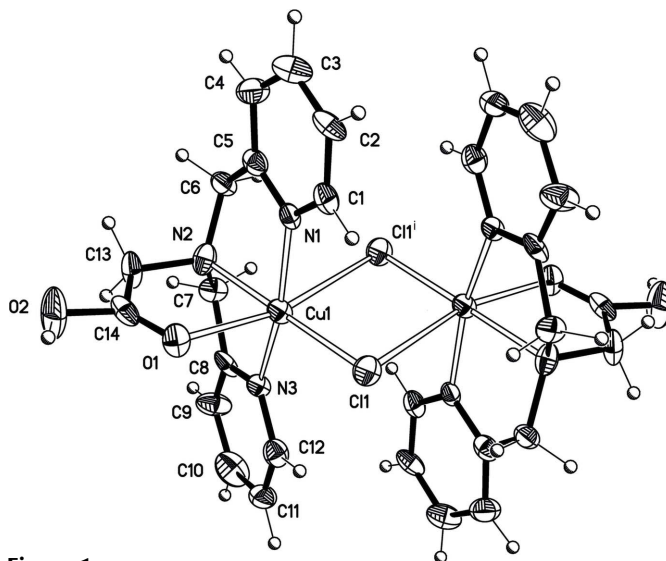

Figure 1
The dichloro-bridged dicopper(II) cationic complex in (I), showing displacement ellipsoids at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radius. [Symmetry code (i) $1 - x$, $1 - y, 1 - z$.]

placed in the plane of the carboxyl group, so as to form the best hydrogen bond (AFIX 83 in *SHELXTL*), with O—H = 0.84 Å and U_{iso}(H) = 1.5U_{eq}(O). The largest peak in the difference density lies in the vicinity of the perchlorate anion.

Data collection: *APEX2* (Bruker–Nonius, 2004); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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