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trans-Bis(glycinato-$\kappa^2 N,O$)copper(II) 4-bromophenol solvate

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Key indicators

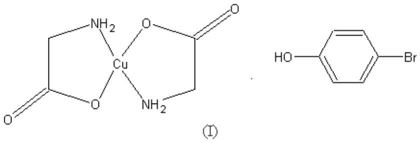
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.017 Å
R factor = 0.043
wR factor = 0.104
Data-to-parameter ratio = 7.0

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

The title compound, *trans*-[Cu(gly)$_2$]·4-BrC$_6$H$_4$OH, (I), crystallized in the non-centrosymmetric orthorhombic space group $Pca2_1$ when *trans*-bis(glycinato-N,O)copper(II) and 4-bromophenol were allowed to stand in water for several days. Structural analysis reveals that the 4-bromophenol is not coordinated to the copper and that the glycinato units are *trans* in N,O-bidentate binding mode. The packing of the molecules shows well defined units of (I), interlocked *via* a network of secondary covalent and non-covalent bonds, with the Cu atom in a [4 + 2] coordination mode.

Comment

Copper complexes of glycine have been studied extensively for their bioactivity and physicochemical properties (Beattie *et al.*, 1976; Percy, 1976; Gillard *et al.*, 1980; Goodman *et al.*, 1981; Szabo-Planka, 1985; Efstathiou & Woodruff, 2003; El-Saadani *et al.*, 1993; Farkas *et al.*, 2000; Gasque *et al.*, 1992; Murakami *et al.*, 2002; Thomas & Zacharia, 1985). In particular, the unusual *cis–trans*-isomer conversion in the solid state of bis(glycinato-N,O)copper(II) (Delf *et al.*, 1979; Moussa *et al.*, 2002; Tautermann *et al.*, 2004) and its biomimetic behavior in water (Davies *et al.*, 2003), along with its anti-ulcer activity (El-Saadani *et al.*, 1993), have been reported and the self-assembly (*i.e.* surface modification) of glycine on copper surfaces has been studied (Efstathiou & Woodruff, 2003). Although structural studies on the bis(glycinato-N,O)copper(II) compounds *cis*-[Cu(gly)$_2$]·H$_2$O, *trans*-[Cu(gly)$_2$]·2AgNO$_3$ and *trans,trans*-[Cu(gly)$_2$Cl$_2$]·[Mg(H$_2$O)$_6$]·H$_2$O and other compounds of the type [Cu(gly)$_2$]·2X, where X is a neutral solvent, and the copper mono-glycinato compounds [Cu(gly)(OH$_2$)$_4$]$^+$ and [Cu(gly)(NO$_3$)(OH$_2$)], along with the hexanuclear copper(II) complex Na[NaCu$_6$(gly)$_8$(H$_2$O)$_2$]-(ClO$_4$)$_6$·2H$_2$O, have been reported (Freeman *et al.*, 1964; Davies *et al.*, 1992; Davies *et al.*, 2003; Hu *et al.*, 2001), to our knowledge the structure of the title compound, (I), is not already known.



(I)

As early as the 1940s, it was realised that the addition of phenols to copper glycine mixtures led to the precipitation of dark blue salts of the type [Cu(gly)$_2$]·2X, where X = phenol or substituted phenols (Wieland & Wirth, 1949; Puzari & Baruah, 2000). The nature of these compounds was not determined, and attempts to grow single crystals suitable for X-ray analysis

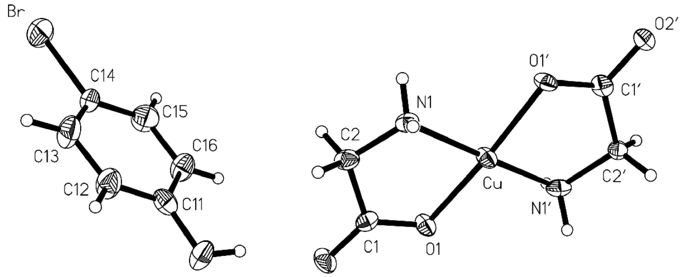


Figure 1
A view of the molecular structure of (I), with dispacement ellipsoids drawn at the 30% probability level.

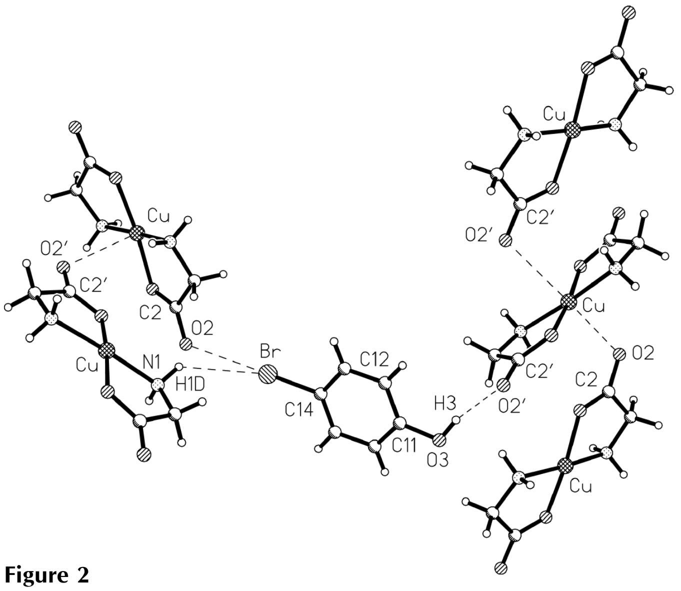


Figure 2
A view of the secondary and non-covalent bonds (dashed lines) in *trans*-[Cu(gly)$_2$]·4-bromophenol.

were unsuccessful. In the case of picric acid, crystals of Cu(gly)$_2$·2picric acid·6H$_2$O were isolated, in which the glycine was found to bind in a unidentate coordination mode (Davies *et al.*, 2003). Our interest in the interactions between α-amino acids and metal ions led to this study, which reports the first structure of its type.

The molecular structure of (I) is shown in Fig. 1; it can be seen that the 4-bromophenol is not coordinated to copper, and that the glycinato units are *trans* in *N,O*-bidentate binding mode. Copper is coordinated by two N and two O atoms of glycinate ligands in a square planar geometry. The *O,N*-bidentate glycinato ligands form two planar fused five-membered metallacyclic rings (Cu—N—C—C—O) with coordinated O and N atoms in a *trans* geometry. The bond distances and angles are normal (see Table 1) and similar to those reported for a variety of Cu^{II}–glycinato compounds. For example, an O—Cu—N bite angle of 84.90 ° and Cu—O and Cu—N bond distances of 1.94 and 1.98 Å have been reported for [Cu(gly)(NO$_3$)(H$_2$O)] (Davies *et al.*, 1992). In the case of *cis*-[Cu(gly)$_2$]·H$_2$O, an average O—Cu—N bite angle of 85.20 (2)° and Cu—O and Cu—N bond distances of 1.94 (2) and 2.00 (2) Å have been reported (Freeman *et al.*, 1964).

The molecular packing shows well defined *trans*-[Cu(gly)$_2$]·4-bromophenol units, interlocked *via* a network of secondary covalent and non-covalent bonds to form a polymer (see Table 2 and Fig. 2). The coordination mode of copper in the polymer is six and of the [4 + 2] type, with the equatorial sites occupied by the covalent binding of *N,O*-bidentate glycinato units and the axial sites occupied by the O atoms of the carboxylates of adjacent *trans*-[Cu(gly)$_2$] units (see Fig. 2). The axial Cu—O bonds are not equivalent, Cu—O2^{i} being 2.487 (8) Å [symmetry code: (i) $x - \frac{1}{2}, -y, z$] and Cu—O2$'^{ii}$ being 2.829 (8) Å [symmetry code: (ii) $\frac{1}{2} + x, 1 - y, z$]. These distances are of the same order as those observed in *cis*-[Cu(gly)$_2$(OH$_2$)] and other related compounds. For example, axial Cu—O distances of 2.40 and 2.74 Å have been reported for *cis*-[Cu(gly)$_2$(OH$_2$)] (Freeman *et al.*, 1964). The 4-bromophenol molecules interlock adjacent strands of *trans*-[Cu(gly)$_2$] units *via* bifurcated non-covalent interactions, as shown in Fig. 2. The distances and angles of the non-covalent interactions are normal, and similar to those reported for a variety of compounds containing such interactions. For example, in *cis*-[Cu(L-isoLeu)$_2$], where L-isoLeu is L-isoleucine, hydrogen-bond parameters $d_{(\mathrm{HA})}$, $d_{(DA)}$ and $<(D\mathrm{H}A)$ of 2.22 (3), 2.87 (2), 156 (5) and 2.24 (2), 3.00 (2), 149 (4) were reported for O—H···O and N—H···O, respectively (Weeks *et al.*, 1969).

As a result of the bioactivity of α-amino acids and their metal compounds, and current interest in developing technologies based on biomolecules, work is in progress in our laboratory to prepare single crystals of a variety of metal compounds of biomolecules that include α-amino acids.

Experimental

trans-[Cu(gly)$_2$]·4-bromophenol was synthesized from the reaction of a mixture of [CuSO$_4$·5H$_2$O], glycine and 4-bromophenol in distilled water in a procedure similar to those reported in the literature for the synthesis of a variety of copper-bis-glycinato compounds of the type [Cu(gly)$_2$]·2*X*, where *X* = solvent molecule or salts of group I and II metal compounds (Wieland & Wirth, 1949; Davies *et al.*, 2003). Blue crystals of (I) suitable for X-ray analysis were obtained when a quantity of (I) was allowed to stand in distilled water for several days.

Crystal data

[Cu(C$_2$H$_4$NO$_2$)$_2$]·C$_6$H$_5$BrO
M_r = 384.67
Orthorhombic, $Pca2_1$
a = 9.442 (1) Å
b = 5.063 (1) Å
c = 27.926 (4) Å
V = 1335.0 (4) Å^3
Z = 4
D_x = 1.914 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 61 reflections
θ = 5.8–32.6°
μ = 4.65 mm^{-1}
T = 293 (2) K
Prism, blue
0.26 × 0.16 × 0.06 mm

Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (*XSCANS*; Bruker, 1997)
$T_{\min}$ = 0.191, $T_{\max}$ = 0.308
1691 measured reflections
1214 independent reflections
983 reflections with $I > 2\sigma(I)$

R_{int} = 0.045
$\theta_{\max}$ = 25.0°
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 6$
$l = -1 \rightarrow 33$
3 standard reflections every 97 reflections
intensity decay: none

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.104$
$S = 1.03$
1214 reflections
174 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00013 (9)
Absolute structure: Flack (1983)
Flack parameter = 0.08 (3)

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.951 (6)	O1′—C2′	1.258 (12)
Cu—O1′	1.963 (6)	N1′—C1′	1.476 (13)
Cu—N1′	1.981 (8)	C1′—C2′	1.526 (13)
Cu—N1	1.986 (8)	C2′—O2′	1.229 (12)
O1—C2	1.280 (12)	O3—C11	1.364 (14)
N1—C1	1.459 (12)	C11—C16	1.361 (16)
C1—C2	1.521 (14)	C14—Br	1.903 (11)
C2—O2	1.249 (12)		
O1′—Cu—N1′	83.7 (3)	C1′—N1′—Cu	110.7 (6)
O1—Cu—N1	85.0 (3)	N1′—C1′—C2′	110.6 (8)
O1′—Cu—N1	95.4 (3)	O2′—C2′—O1′	124.8 (9)
C1—N1—Cu	109.6 (6)	O2′—C2′—C1′	118.8 (9)
C1—N1—H1*D*	109.8	O1′—C2′—C1′	116.3 (9)
N1—C1—C2	110.5 (8)	C16—C11—O3	119.0 (10)
O2—C2—O1	123.8 (9)	C16—C11—C12	118.8 (12)
O2—C2—C1	118.8 (9)	C15—C14—Br	119.7 (9)
C2′—O1′—Cu	117.1 (6)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2′	0.82	1.84	2.641 (11)	166
N1—H1*D*···Br^{i}	0.90	3.02	3.732 (9)	137
N1—H1*C*···O1^{ii}	0.90	2.13	3.013 (10)	167
N1′—H1′*C*···O1′^{iii}	0.90	2.10	2.980 (10)	166
N1′—H1′*D*···O3^{iv}	0.90	2.43	3.088 (11)	130

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

The H atoms were included in calculated positions (C—H = 0.97 and 0.93 Å for CH_2 and CH, respectively; N—H = 0.90 Å; O—H = 0.82 Å) and refined as riding, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(parent C and N atoms) or $1.5U_{\rm eq}$(parent O atom).

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990) and *SIR*2002 (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*, *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek, 2004); software used to prepare material for publication: *SHELXTL* and *WinGX* (Farrugia, 1999).

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