

Diaquabis(L-serinato)copper(II) 0.1-hydrate at 120 K

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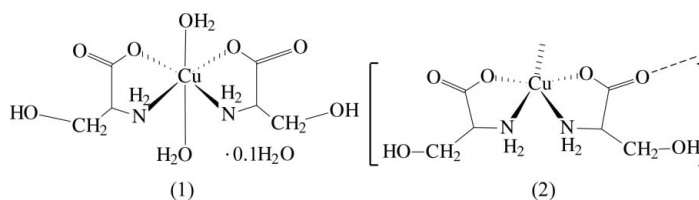
Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in solvent or counterion
 R factor = 0.019
 wR factor = 0.052
Data-to-parameter ratio = 15.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Cu}(\text{C}_3\text{H}_6\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 0.1\text{H}_2\text{O}$, is isostructural with the nickel analogue. The octahedral Cu^{II} ion lies on a twofold axis, with *cis* chelating *O,N*-serine groups and *trans* aqua ligands. Small amounts of a solvent water molecule form hydrogen bonds to link the molecules along the [010] direction, while a number of strong hydrogen bonds combine to form sheets in the (110) plane.

Comment

As part of our continuing study of Cu complexes with amino acids (Felcman & de Miranda, 1997; de Miranda & Felcman, 2001; de Miranda *et al.*, 2002; Felcman *et al.*, 2003), we have isolated and characterized the diaquabis(L-serinato)-copper(II) complex, (1), from an aqueous reaction mixture containing (*L*)-serine (ser), guanidinoacetic acid (gaa) and Cu^{II} (1:1:1). Crystals of (1) were obtained after several months. No crystalline complex containing gaa, either alone or in a mixed complex with ser, appeared in a similar time. van der Helm & Franks (1969) reported the structure of the unhydrated complex, [bis(L-serinato)copper(II)], (2), obtained from Cu^{II} and (*L*)-serine in methanol containing a little water.



Complex (1), isostructural with the analogous nickel complex, diaquabis(L-serinato)nickel(II) hydrate, (3), (van der Helm & Hossain, 1969), has an octahedrally coordinated Cu^{II} ion with *cis* chelating *O,N*-ser groups and *trans* aqua ligands (Fig. 1). A similar *cis* arrangement of ser units arises in square-pyramidal (2), in which a carboxylate O atom, from an adjacent molecule, occupies the apical position. A distant O atom is sited 3.632 (6) Å from Cu *trans* to the apical ligand in (2), but this can at most be considered only a very weak interaction. Comparison of the serine–Cu bond lengths in (2) [Cu–O 1.952 (5) and 1.970 (5) Å; Cu–N 1.975 (6) and 1.988 (6) Å] and in (1) (Table 1) indicates that the weaker interactions occur in the higher coordinate complex, (1). The serine chelate rings in (1) have envelope conformations with flaps at the N atoms. The Cu^{II} ion and the four serine binding atoms are essentially co-planar.

Small amounts of additional water molecules are present in both (1) and (3). The space group and structure of (1) are notably different from those of the unhydrated compound, (2), and although only a very small amount of water was found

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to be present in (1), both the hydrogen-bonding scheme (see below) and the availability of space (PLATON; Spek, 2003) confirm its presence.

The non-isolation of any gaa-containing complex from the reaction mixture probably reflects more their solubility in the reaction media than their non-formation. A number of Cu-gaa complexes have been isolated, including tetrakis(μ -guanidinoacetic acid- $\kappa^2O:O'$)bis[nitrato- κO]copper, [Cu₂(NO₃)₂(gaa)₄], (4) (de Miranda *et al.*, 2002), {aqua[μ -(*N'*-carboxylatomethylguanidino)oxidoacetato](μ -guanidinoacetic acid)dicopper(II)} nitrate dihydrate, [Cu₂(oag)(gaa)(H₂O)]NO₃·2H₂O, (5) (Felcman *et al.*, 2003), and [CuCl₂(gaa)₂] (Silva *et al.*, 2001). Compounds (4) and (5) were obtained from reaction mixtures containing gaa and Cu^{II}, both in the presence and absence of another amino acid, namely aspartine. Furthermore, mixed Cu-L-serine complexes, *e.g.* with glycine, have been reported (D'yakon *et al.*, 1991).

The solvent water molecule forms hydrogen bonds (Table 2) with the O atom of the aqua ligand in the main molecule (Fig. 2), leading to chains along [010]. Together with the other strong hydrogen bonds (Table 2), these form sheets in the (110) plane (Fig. 2).

Experimental

To a hot solution (333 K) of guanidinoacetic acid (0.3513 g, 3 mmol) and serine (0.3153, 3 mmol) in deionized water (100 ml) was slowly added a solution of copper(II) nitrate (0.7248 g, 3 mmol) in deionized water (5 ml). The reaction mixture was stirred at 333 K for 8 h, cooled slowly to 277 K, and the pH adjusted to 6.0 with KOH (3 M). The white precipitate which formed was filtered off and the filtrate was stored in a covered vessel. Thin blue plate-like crystals began to be formed after the fifth month and were collected after six months, washed with absolute ethanol and dried at 323 K.

Crystal data

[Cu(C₃H₆NO₃)₂(H₂O)₂].0.1H₂O $D_x = 1.837 \text{ Mg m}^{-3}$
 $M_r = 309.55$ Mo $K\alpha$ radiation
 Monoclinic, $C2$ Cell parameters from 673 reflections
 $a = 7.5866(2) \text{ \AA}$ $\theta = 2.9\text{--}27.5^\circ$
 $b = 8.5684(2) \text{ \AA}$ $\mu = 1.99 \text{ mm}^{-1}$
 $c = 8.8257(2) \text{ \AA}$ $T = 120(2) \text{ K}$
 $\beta = 102.7701(15)^\circ$ Plate, pale blue
 $V = 559.52(2) \text{ \AA}^3$ $0.40 \times 0.30 \times 0.08 \text{ mm}$
 $Z = 2$

Data collection

Bruker Nonius KappaCCD area-detector diffractometer 1220 independent reflections
 φ and ω scans 1214 reflections with $I > 2\sigma(I)$
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003) $R_{\text{int}} = 0.026$
 $T_{\text{min}} = 0.666$, $T_{\text{max}} = 0.853$ $\theta_{\text{max}} = 27.5^\circ$
 3347 measured reflections $h = -7 \rightarrow 9$
 $l = -11 \rightarrow 10$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0104P)^2 + 0.5389P]$
 $R[F^2 > 2\sigma(F^2)] = 0.019$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.053$ $(\Delta/\sigma)_{\text{max}} < 0.001$
 $S = 1.10$ $\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
 1220 reflections $\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$
 81 parameters Absolute structure: Flack (1983),
 H-atom parameters constrained with 536 Friedel pairs
 Flack parameter: 0.071 (12)

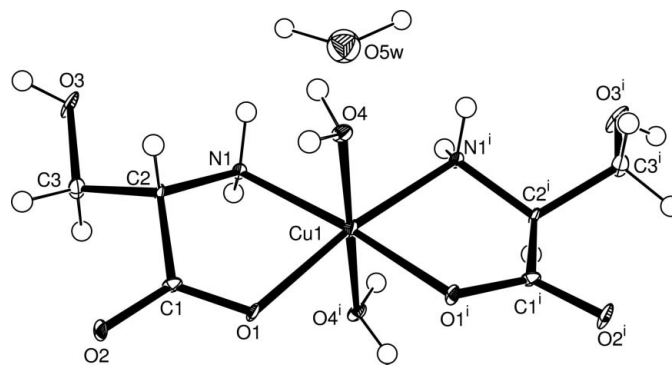


Figure 1
 The molecular structure of (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as open circles. [Symmetry code: (i) 1 - x, y, -z.]

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—O1	2.032 (2)	Cu1—O4	2.1044 (11)
Cu1—N1	2.079 (2)		
O1—Cu1—O1 ⁱ	91.50 (11)	O1—Cu1—O4 ⁱ	87.95 (8)
O1—Cu1—N1 ⁱ	172.11 (9)	N1—Cu1—O4 ⁱ	89.99 (8)
O1—Cu1—N1	81.16 (7)	N1—Cu1—O4	89.49 (8)
N1—Cu1—N1 ⁱ	106.31 (13)	O4—Cu1—O4 ⁱ	179.14 (14)
O1—Cu1—O4	92.65 (8)		

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1A...O2 ⁱⁱ	0.92	2.39	3.154 (3)	141
N1—H1B...O1 ⁱⁱⁱ	0.92	2.25	3.071 (2)	149
O3—H3...O2 ^{iv}	0.84	1.84	2.671 (2)	172
O4—H4A...O3 ^v	0.82	1.90	2.701 (3)	168
O4—H4B...O2 ⁱⁱ	0.81	1.94	2.747 (3)	177
O5W—H5...O4 ^{vi}	0.82	2.18	2.807 (4)	134

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

Systematic absences permitted $C2$, Cm and $C2/m$ as possible space groups; $C2$ was selected and confirmed by the subsequent structure analysis. In this space group, atoms Cu1 and O5W of the low-occupancy solvent water molecule (see below) lie on crystallographic twofold axes. Therefore, the asymmetric unit comprises, in addition to these two atoms, one of each of a complete serinate and aqua ligand and a single H atom of the solvent water molecule. The small amount of solvent water was clearly identified from the difference map. During the structure solution, and prior to the location of the water molecule, the difference map revealed two electron-density peaks close to one another, which suggested disorder of the water over two sites. However, the two positions could not be refined simultaneously and indeed, once one O atom was refined, the peak in the difference map corresponding to the 'second site' disappeared. Approximate positions for the H atoms of the aqua ligand and of the low-occupancy solvent water molecule were then obtained from difference maps and modified to provide acceptable O—H distances (0.81–0.82 \AA) and H—O—H angles (103°). Owing to correlation with the isotropic displacement parameter, the occupancy of the solvent water

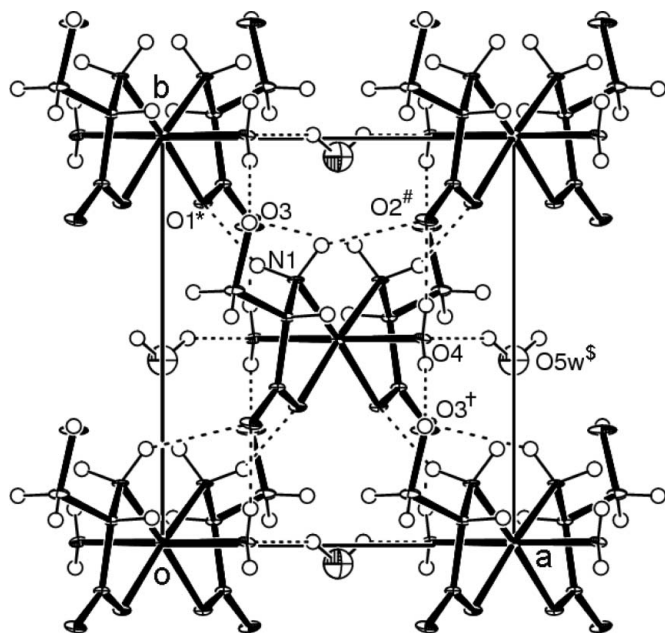


Figure 2

Part of the crystal structure of (1), showing the formation of sheets in the (110) plane built from N—H...O and O—H...O hydrogen bonds (dashed lines). Atoms labelled with a hash (#), asterisk (*) or plus sign (+) are at the symmetry positions $(\frac{1}{2} + x, \frac{1}{2} + y, z)$, $(\frac{1}{2} - x, \frac{1}{2} + y, -z)$ and $(\frac{1}{2} + x, -\frac{1}{2} + y, z)$, respectively. The solvent water molecule is linked to the main molecule by the symmetry operation $(\frac{3}{2} - x, \frac{1}{2} + y, -z)$. The O3—H3...O2^{iv} hydrogen bond is not visible in this orientation but forms behind atom O3.

molecule could only be established by trial and error. The value of 0.10 finally chosen was such as to provide a reasonable value for the freely refined isotropic displacement parameter of the O atom (O5W). All other H atoms were placed in calculated positions, with X—H distances of 0.99 (CH₂), 1.00 (aliphatic CH), 0.92 (NH₂) or 0.84 Å (OH). The torsion angle of the OH group was also refined. All H atoms were refined, finally, with a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ or $1.5U_{\text{eq}}(\text{O})$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL-X* (McArdle, 1994, 2005) and *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *OSCAIL-X* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1997).

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