

Diaquabis(μ -4-hydroxybenzenecarboxylato- κ^2O,O')disilver(I)(Ag—Ag) tetrahydrate

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Key indicators

Single-crystal X-ray study
 T = 296 K
 Mean $\sigma(C-C)$ = 0.004 Å
 Disorder in main residue
 R factor = 0.025
 wR factor = 0.065
 Data-to-parameter ratio = 16.7

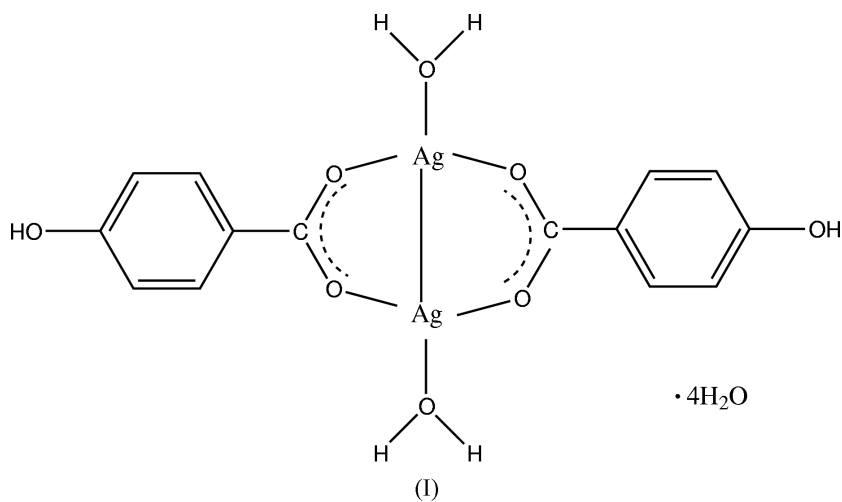
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title complex, $[Ag_2(C_7H_5O_3)_2(H_2O)_2] \cdot 4H_2O$, is a centrosymmetric bis(carboxylato- κ^2O,O')-bridged binuclear dimer with a strong Ag—Ag interaction. Each Ag^I atom has a four-coordinate square-planar geometry, in which it is bonded to two carboxylate O atoms, one water O atom and the other Ag^I atom. All the coordinated and uncoordinated water molecules are disordered; they form a cluster around the dimer through intermolecular hydrogen-bond networks, linking the complex molecules to each other.

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Comment

Silver complexes are used widely as effective antimicrobial agents to combat pathogens (bacteria, viruses and eukaryotic microorganisms) in the clinic and for public health hygiene (Silver, 2003). Various silver complexes with carboxylic acid derivatives have been structurally characterized (Smith *et al.*, 1990, 1994; Sun *et al.*, 2004; Kristiansson, 2001). The majority of these complexes are based on a bis(carboxylato- κ^2O,O')-bridged dimer, which may be discrete or extended into polymeric forms.



Among the carboxylic acid derivatives, some metabolites are of considerable interest, not only for bioinorganic chemistry but also for their stereochemistry. We have successfully synthesized silver complexes with 4-hydroxybenzenecarboxylic acid (*p*-hydroxybenzoic acid, 4-HB), which is an important metabolite of phenol in the process of anaerobic metabolism activated by CoA (Lack & Fuchs, 1992; Gallert & Winter, 1994). It has also been tested as an active ingredient in an energy-enhancing supplement for increasing the cellular formation of ATP (Smith & Griffin, 2002). 4-HB appears in the ordinary metabolic map to be one of the tyrosine metab-

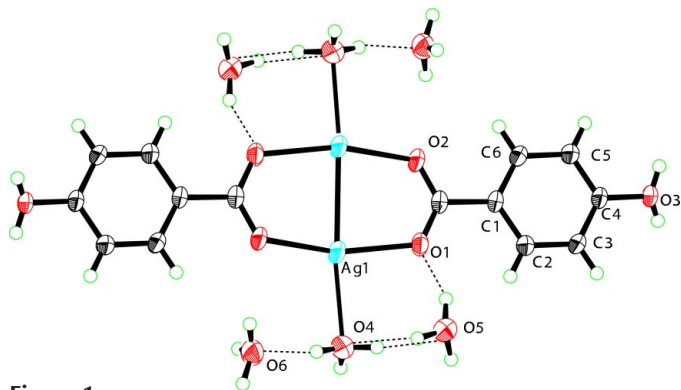


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. Unlabelled atoms are related to labelled atoms by the symmetry code $(1-x, 1-y, 1-z)$. All disorder components are shown for the water molecules.

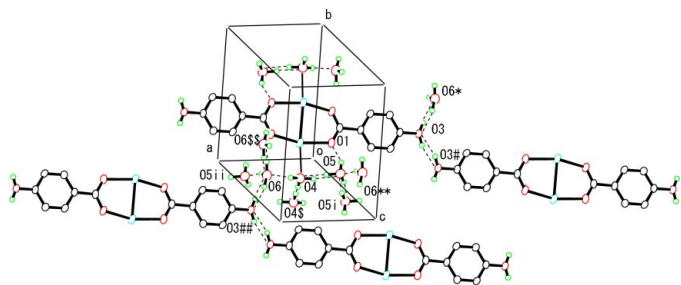


Figure 2
The molecular packing of (I). Hydrogen bonds are indicated by dashed lines. [Symmetry codes: (*) $-1+x, 1+y, 1+z$; (**) $-1+x, y, z$; (\$) $1-x, -y, 1-z$; (§§) $1-x, -y, -z$; (#) $-1-x, 1-y, 2-z$; (##) $1+x, -1+y, -1+z$; (i) $-x, -y, 1-z$; (ii) $1+x, y, z$.]

olites in the coenzyme Q (ubiquinone) synthesis. The present paper reports the structure of a silver complex of 4-HB, (I).

In complex (I), each Ag^{I} atom is four-coordinate, bonded to two carboxylate O atoms from two 4-HB molecules, one water O atom, and one neighbouring Ag^{I} atom, in a distorted square-planar geometry (Fig. 1). The structure is based on a bis(carboxylato- $\kappa^2\text{O}, \text{O}'$)-bridged binuclear dimer with an eight-membered central ring, similar to the structure of disilver(I) disalicylate, which has the same *syn-syn* bridge conformation (Movsumov *et al.*, 1990). In (I), the dimeric molecule is centrosymmetric and the benzene ring is essentially coplanar with the ring $\text{Ag}-\text{O}-\text{C}-\text{O}-\text{Ag}$, the dihedral angle being 3.38 (17) $^\circ$.

In the terminal coordination sites of the dimer, water molecules complete the coordination of the silver centres. Although there are analogous examples in which water is coordinated in the terminal positions of such dimers, most of them are extended into tetrameric or polymeric structures, *e.g.* silver(I) phenoxyacetate hydrate (Smith *et al.*, 1990) and ammonium silver(I) citrate hydrate (Sagatys *et al.*, 1993). Thus, complex (I) is one of a few discrete Ag^{I} dimeric complexes with terminal aqua ligands. Another example (Smith *et al.*, 1994) has a bond length for $\text{Ag}-\text{O}(\text{water})$ of 2.518 (4) \AA , which is very similar to that in complex (I).

The $\text{Ag}-\text{Ag}$ distance demonstrates a very strong metal-metal interaction, compared with the analogous complex disilver(I) disalicylate (Movsumov *et al.*, 1990), with an $\text{Ag}-\text{Ag}$ distance of 2.855 (1) \AA . In the case of disilver(I) disalicylate, the typical intramolecular hydrogen bond between the *ortho*-phenol group and the carboxylate O atom in the salicylic acid molecule results in a slight expansion of the $\text{O}-\text{C}-\text{O}$ angle of the carboxylate group, in conjunction with the longer $\text{Ag}-\text{Ag}$ distance. Moreover, among the $\text{Ag}-\text{Ag}$ distances in the series of other Ag^{I} complexes, such as silver(I) hydrogen maleate, silver(I) maleate and silver(I) fumarate [2.924 (1), 2.925 (1) and 3.090 (1) \AA ; Smith *et al.*, 1995], an Ag^{I} complex of 4-fluorophenoxyacetate [2.886 (2) and 2.836 (2) \AA ; Smith *et al.*, 1990], and *catena*-bis(4-aminobenzoato)disilver(I) [2.953 (1) \AA ; Kristiansson, 2001], complex (I) has the shortest. These results indicate that the positions or types of substituents have a significant influence on the $\text{Ag}-\text{Ag}$ distance.

There are four uncoordinated water molecules for each dimer complex, and they form a cluster around the dimer. All the water molecules, including the coordinated ones, are disordered and are involved in the intermolecular hydrogen-bond network. As shown in Fig. 2, the hydrogen-bond network seems to be complicated because of the disorder. All possible H atoms, however, are bonded to the available acceptor O atoms (Table 2). Moreover, in the packing, the complex molecules are connected to each other and stabilized by other hydrogen bonds provided by the phenol atom O3 (Table 2).

Experimental

Colourless prismatic crystals of (I) were obtained by slow evaporation of an aqueous methanol solution of a mixture of 4-hydroxybenzenecarboxylic acid and AgNO_3 (molar ratio 1:1) at room temperature.

Crystal data

$[\text{Ag}_2(\text{C}_7\text{H}_5\text{O}_3)_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$
 $M_r = 598.06$
 Triclinic, $P\bar{1}$
 $a = 6.635$ (5) \AA
 $b = 9.239$ (7) \AA
 $c = 9.359$ (8) \AA
 $\alpha = 115.53$ (3) $^\circ$
 $\beta = 107.51$ (2) $^\circ$
 $\gamma = 95.60$ (2) $^\circ$
 $V = 476.2$ (7) \AA^3

$Z = 1$
 $D_x = 2.085$ Mg m^{-3}
 Mo $K\alpha$ radiation
 Cell parameters from 4290 reflections
 $\theta = 3.3$ – 27.5 $^\circ$
 $\mu = 2.11$ mm^{-1}
 $T = 296.1$ K
 Prism, colourless
 $0.30 \times 0.10 \times 0.10$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\text{min}} = 0.590$, $T_{\text{max}} = 0.810$
 4695 measured reflections

2149 independent reflections
 1950 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$
 $\theta_{\text{max}} = 27.5$ $^\circ$
 $h = -8 \rightarrow 8$
 $k = -11 \rightarrow 11$
 $l = -12 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.065$
 $S = 1.07$
 2149 reflections
 129 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.2921P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.96$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.83$ e \AA^{-3}

Table 1
Selected geometric parameters (Å, °).

Ag1—O2 ⁱ	2.190 (2)	Ag1—O4	2.552 (3)
Ag1—O1	2.214 (2)	Ag1—Ag1 ⁱ	2.761 (2)
O2 ⁱ —Ag1—O1	162.24 (7)	O2 ⁱ —Ag1—Ag1 ⁱ	81.79 (5)
O2 ⁱ —Ag1—O4	98.58 (7)	O1—Ag1—Ag1 ⁱ	83.75 (5)
O1—Ag1—O4	93.51 (7)	O4—Ag1—Ag1 ⁱ	168.31 (5)

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

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

D—H...A	D—H	H...A	D...A	D—H...A
O3—H31...O6 ⁱⁱ	0.82	1.92	2.729 (4)	171
O3—H32...O3 ⁱⁱⁱ	0.82	1.93	2.701 (3)	157
O4—H41...O5	0.94	1.86	2.782 (4)	166
O4—H42...O6	0.91	1.87	2.756 (4)	165
O4—H43...O4 ^{iv}	0.93	1.86	2.777 (4)	177
O5—H51...O1	0.92	1.91	2.754 (2)	155
O5—H52...O4	0.95	1.84	2.782 (4)	169
O5—H53...O5 ^v	0.93	1.90	2.793 (4)	165
O6—H61...O3 ^{vi}	0.91	1.87	2.729 (4)	157
O6—H62...O5 ^{vii}	0.92	1.92	2.823 (3)	164
O6—H63...O6 ^{viii}	0.93	2.15	2.858 (4)	133

Symmetry codes: (ii) x - 1, 1 + y, 1 + z; (iii) -1 - x, 1 - y, 2 - z; (iv) 1 - x, -y, 1 - z; (v) -x, -y, 1 - z; (vi) 1 + x, y - 1, z - 1; (vii) 1 + x, y, z; (viii) 1 - x, -y, -z.

All H atoms, except those of water, were located in difference Fourier maps and were then regenerated at ideal positions and treated as riding, with C—H = 0.93 Å, phenol O—H = 0.82 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$. The positional parameters of the disordered water H atoms were calculated on the basis of the positions of the other H atoms and treated as riding, with O—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Data collection: *RAPID-AUTO* (Rigaku, 2003); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2004) and *CRYSTALS* (Watkin *et al.*, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999) and *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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