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Poly[di-μ-aqua-bis(μ_8-3-carboxylato-4-hydroxybenzenesulfonato)tetrasilver(I)]

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.026
wR factor = 0.068
Data-to-parameter ratio = 12.8

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

In the polymeric title compound, $[Ag_4(C_7H_4O_6S)_2(H_2O)_2]_n$, the 3-carboxylato-4-hydroxybenzenesulfonate anion uses its hydroxy (–OH) unit to bind to an Ag atom and its sulfonyl ($–SO_3$) unit to bind to five Ag atoms; it uses its carboxylate ($–CO_2$) group to bridge an Ag—Ag [Ag—Ag = 2.7778 (8) Å] unit. The bonding mode gives rise to a three-dimensional network structure that is consolidated by hydrogen bonds involving the coordinated water molecules. The four Ag atoms in the asymmetric unit all lie on special positions of site symmetry 2.

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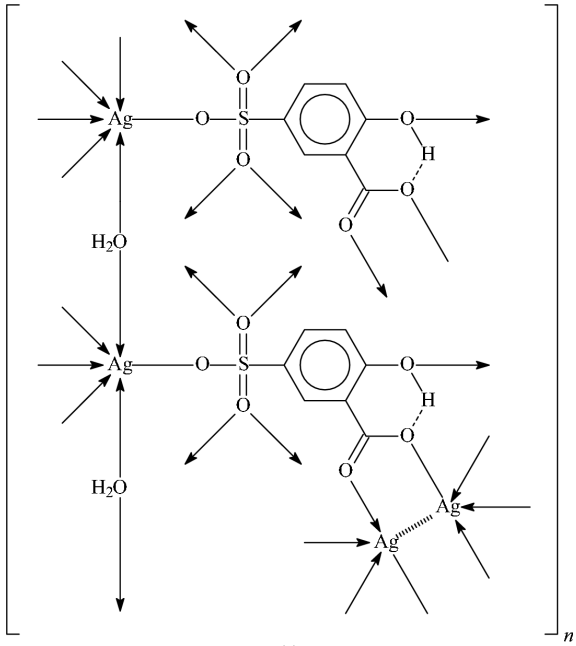
Comment

The preceeding report, by introducing aspects of the structural chemistry of the silver derivatives of sulfosalicylic acid, details the structure of a compound having the empirical silver(I) 3-carboxy-4-hydroxybenzenesulfonate dihydrate formulation (Gao *et al.*, 2005). The negative charge of the anion formally resides on the sulfonate group. A slight variation of the reaction conditions has yielded a compound formulated as tetrasilver(I) bis(3-carboxy-4-hydroxybenzenesulfonate) dihydrate, (I), a tetranuclear compound exhibiting an Ag—Ag bond.



(I)

The asymmetric unit of the polymeric structure consists of one 3-carboxylato-4-hydroxybenzenesulfonate dianion, one water molecule and four Ag atoms that all lie on special

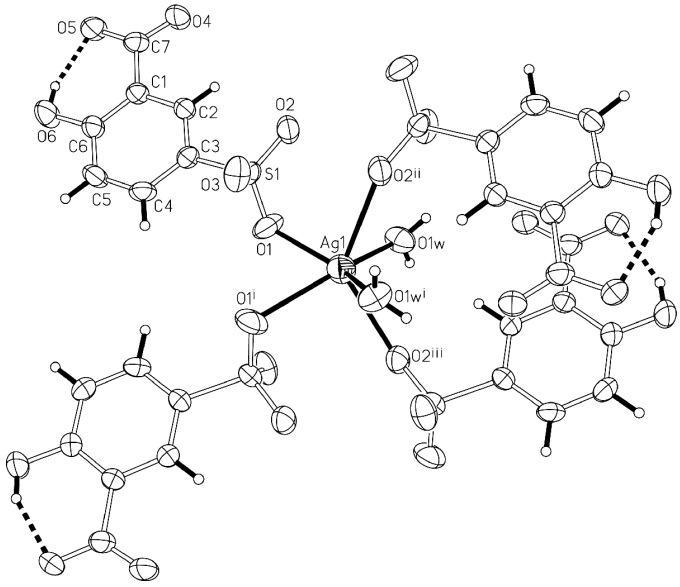


Figure 1
ORTEPII plot (Johnson, 1976) illustrating the coordination geometry of atom Ag1. Displacement ellipsoids are drawn at the 70% probability level and H atoms are drawn as spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. Symmetry codes are as given in Table 1.

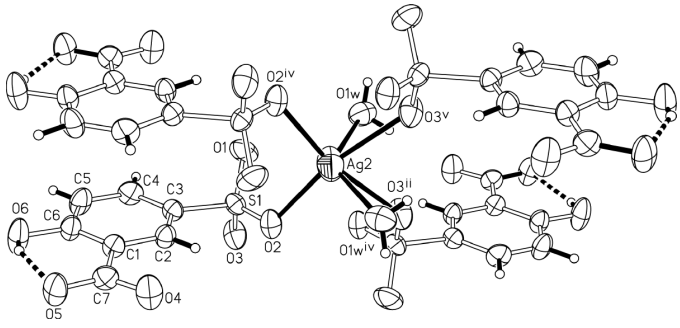


Figure 2
*ORTEP*II plot (Johnson, 1976) illustrating the coordination geometry of atom Ag2. Displacement ellipsoids are drawn at the 70% probability level and H atoms are drawn as spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. Symmetry codes are as given in Table 1.

positions of site symmetry 2. The dianion uses its hydroxy (–OH) unit to bind to an Ag atom and its sulfonyl ($-SO_3$) unit to bind to five Ag atoms; it uses its negatively charged carboxylate ($-CO_2$) group to bridge an Ag—Ag [Ag—Ag = 2.7778 (8) Å] unit (Figs. 1–3).

The Ag—Ag distance is short, almost as short as the shortest [2.750 (2) Å in tetrasilver tris(dimethylaminopyridinioacetate) perchlorate (Wei *et al.*, 1997)] known for a dinuclear dicarboxylate complex, and is of the order of the bond lengths found in three cytotoxic silver carboxylates reported recently (Zhu *et al.*, 2003).

Experimental

5-Sulfosalicylic acid (1.10 g, 5 mmol) and sodium hydroxide (0.40 g, 10 mmol) dissolved in water (10 ml) were mixed with silver nitrate (1.70 g, 10 mmol) dissolved in water (20 ml). The solution was filtered; colorless crystals were obtained from the filtrate after several days. Elemental analysis found (calculated): C 18.54 (18.69), H 1.38% (1.34%).

Crystal data

$[Ag_4(C_7H_4O_6S)_2(H_2O)_2]$
M_r = 899.94
Monoclinic, $P2/n$
a = 7.493 (2) Å
b = 16.237 (3) Å
c = 8.253 (2) Å
β = 92.91 (3)°
V = 1002.8 (3) Å^3
Z = 2
D_x = 2.980 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9456 reflections
θ = 3.0–27.5°
μ = 4.13 mm^{-1}
T = 295 (2) K
Block, colorless
0.32 × 0.25 × 0.17 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.294, T_{max} = 0.495
8593 measured reflections
2158 independent reflections
2015 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 27.5°
$h = -8 \rightarrow 9$
$k = -21 \rightarrow 21$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.068
S = 1.06
2158 reflections
168 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 2.4683P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.91 e Å^{-3}
$\Delta\rho_{min}$ = −1.25 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ag1—O1	2.537 (3)	Ag2—O1w	2.657 (3)
Ag1—O1^{i}	2.537 (3)	Ag2—O1w^{iv}	2.657 (3)
Ag1—O2^{ii}	2.612 (3)	Ag3—O5	2.317 (2)
Ag1—O2^{iii}	2.612 (3)	Ag3—O5^{vi}	2.317 (2)
Ag1—O1w	2.455 (3)	Ag3—O6^{vii}	2.536 (3)
Ag1—O1w^{i}	2.455 (3)	Ag3—O6^{viii}	2.536 (3)
Ag2—O2	2.404 (3)	Ag4—O3^{ix}	2.573 (3)
Ag2—O2^{iv}	2.404 (3)	Ag4—O3^{x}	2.573 (3)
Ag2—O3^{ii}	2.512 (3)	Ag4—O4	2.139 (3)
Ag2—O3^{v}	2.512 (3)	Ag4—O4^{vi}	2.139 (3)
O1—Ag1—O1^{i}	76.9 (1)	O2^{iv}—Ag2—O3^{v}	86.1 (1)
O1—Ag1—O2^{ii}	94.5 (1)	O2^{iv}—Ag2—O1w	106.4 (1)
O1—Ag1—O2^{iii}	127.6 (1)	O2^{iv}—Ag2—O1w^{iv}	100.6 (1)
O1—Ag1—O1w	82.7 (1)	O3^{ii}—Ag2—O3^{v}	81.2 (1)
O1—Ag1—O1w^{i}	147.8 (1)	O3^{ii}—Ag2—O1w	69.8 (1)
O1^{i}—Ag1—O2^{ii}	127.6 (1)	O3^{ii}—Ag2—O1w^{iv}	75.8 (1)
O1^{i}—Ag1—O2^{iii}	94.5 (1)	O3^{v}—Ag2—O1w	75.8 (1)
O1^{i}—Ag1—O1w	147.8 (1)	O3^{v}—Ag2—O1w^{iv}	69.8 (1)
O1^{i}—Ag1—O1w^{i}	82.7 (1)	O1w—Ag2—O1w^{iv}	134.1 (1)
O2^{ii}—Ag1—O2^{iii}	127.9 (1)	O5—Ag3—O5^{vi}	164.5 (1)
O2^{ii}—Ag1—O1w	78.3 (1)	O5—Ag3—O6^{vii}	75.5 (1)
O2^{ii}—Ag1—O1w^{i}	78.5 (1)	O5—Ag3—O6^{viii}	116.0 (1)
O2^{iii}—Ag1—O1w	78.5 (1)	O5^{vi}—Ag3—O6^{vii}	116.0 (1)
O2^{iii}—Ag1—O1w^{i}	78.3 (1)	O5^{vi}—Ag3—O6^{viii}	75.5 (1)
O1w—Ag1—O1w^{i}	125.4 (1)	O6^{vii}—Ag3—O6^{viii}	91.1 (1)
O2—Ag2—O2^{iv}	106.7 (1)	O3^{ix}—Ag4—O3^{x}	78.9 (1)
O2—Ag2—O3^{ii}	86.1 (1)	O3^{ix}—Ag4—O4	96.6 (1)
O2—Ag2—O3^{v}	167.2 (1)	O3^{ix}—Ag4—O4^{vi}	93.3 (1)
O2—Ag2—O1w	100.6 (1)	O3^{x}—Ag4—O4	93.3 (1)
O2—Ag2—O1w^{iv}	106.4 (1)	O3^{x}—Ag4—O4^{vi}	96.6 (1)
O2^{iv}—Ag2—O3^{ii}	167.2 (1)	O4—Ag4—O4^{vi}	167.2 (1)

Symmetry codes: (i) $\frac{3}{2}-x, y, \frac{3}{2}-z$; (ii) $2-x, 1-y, 1-z$; (iii) $x-\frac{1}{2}, 1-y, \frac{1}{2}+z$; (iv) $\frac{3}{2}-x, y, \frac{1}{2}-z$; (v) $x-\frac{1}{2}, 1-y, z-\frac{1}{2}$; (vi) $\frac{5}{2}-x, y, -\frac{1}{2}-z$; (vii) $2-x, 2-y, -z$; (viii) $\frac{1}{2}+x, 2-y, z-\frac{1}{2}$; (ix) $x, y, z-1$; (x) $\frac{5}{2}-x, y, \frac{1}{2}-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6o···O5	0.85 (1)	1.81 (3)	2.589 (4)	151 (6)
O1w—H1w1···O1^{xi}	0.85 (1)	1.97 (2)	2.803 (4)	165 (5)
O1w—H1w2···O3^{xii}	0.85 (1)	2.33 (5)	2.959 (4)	131 (5)
O1w—H1w2···O4^{iii}	0.85 (1)	2.44 (5)	3.114 (4)	137 (6)

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

The three aromatic H atoms were positioned geometrically and were included in the refinement in the riding-model approximation [C—H = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C)]. The water and hydroxyl H atoms were located in a difference Fourier map and were refined with distance restraints of O—H = 0.85 (1) Å and H···H = 1.39 (1) Å.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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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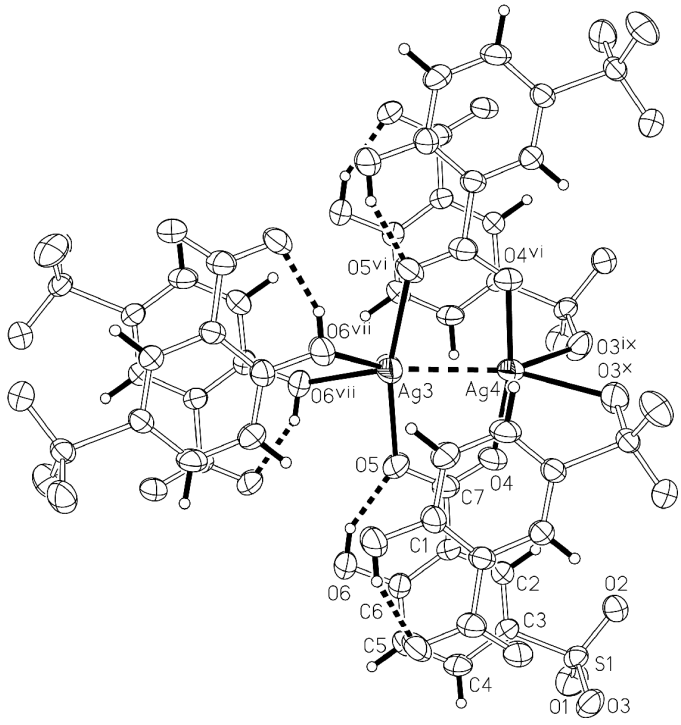

Figure 3
*ORTEP*II plot (Johnson, 1976) illustrating the coordination geometries of atoms Ag3 and Ag4, which which are approximately trigonal bipyramidal. Displacement ellipsoids are drawn at the 70% probability level and H atoms are drawn as spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. Symmetry codes are as given in Table 1.

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