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Trisilver(I) citrate

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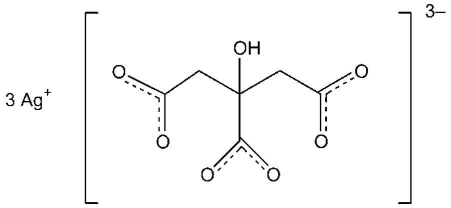
Key indicators: single-crystal X-ray study; T = 299 K; mean σ(C–C) = 0.006 Å; R factor = 0.032; wR factor = 0.051; data-to-parameter ratio = 13.6.

Trisilver(I) citrate, $3Ag^+\cdot C_6H_5O_7^{3-}$, was obtained by evaporation of a saturated aqueous solution of the raw material that had been obtained from sodium dihydrogen citrate and silver nitrate. It features one formula unit in the asymmetric unit. There is an intramolecular O—H⋯O hydrogen bond between the OH group and one of the terminal carboxylate groups. Different citrate groups are linked *via* the three Ag^+ ions, yielding a three-dimensional network with rather irregular $[AgO_4]$ polyhedra.

Related literature

For the preparation and structure of ammonium disilver(I) citrate monohydrate, see: Sagatys *et al.* (1993) and for tetraammonium copper(II) bis(citrate), see: Bott *et al.* (1991). For ^{109}Ag solid-state NMR studies on different silver salts, including commercial silver citrate, see: Penner & Li (2004).



Experimental

Crystal data

$3Ag^+\cdot C_6H_5O_7^{3-}$
M_r = 512.71
Orthorhombic, *Pbca*
a = 6.6181 (7) Å
b = 11.8477 (11) Å
c = 22.386 (2) Å
V = 1755.3 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 6.65 mm^{-1}
T = 299 K
0.12 × 0.05 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.631, T_{max} = 0.876
15238 measured reflections
2008 independent reflections
1493 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.051
S = 1.10
2008 reflections
148 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.21 e Å^{-3}
$\Delta\rho_{min}$ = −1.21 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ag1—O6^{i}	2.275 (3)	Ag2—O7^{ii}	2.550 (3)
Ag1—O3	2.416 (3)	Ag2—O2^{ii}	2.566 (3)
Ag1—O6^{ii}	2.539 (3)	Ag3—O4	2.197 (3)
Ag1—O7^{ii}	2.555 (3)	Ag3—O1^{iii}	2.340 (3)
Ag2—O2^{iii}	2.300 (3)	Ag3—O5^{iv}	2.404 (3)
Ag2—O3	2.477 (4)	Ag3—O4^{iv}	2.519 (4)

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

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O5—H5*O*⋯O7	0.81 (2)	1.90 (3)	2.636 (5)	152 (5)

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2301).

References

Bott, R. C., Sagatys, D. S., Lynch, D. E., Smith, G., Kennard, C. H. L. & Mak, T. C. W. (1991). *Aust. J. Chem.* **44**, 1495–1498.
Brandenburg, K. (2007). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Penner, G. H. & Li, W. (2004). *Inorg. Chem.* **43**, 5588–5597.
Sagatys, D. S., Smith, G., Bott, R. C., Lynch, D. E. & Kennard, C. H. L. (1993). *Polyhedron*, **12**, 709–713.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supplementary materials

Acta Cryst. (2011). E**67**, m255 [**doi:10.1107/S160053681100239X**]

Trisilver(I) citrate

A. Fischer

Comment

The structures of many citrates of common metal ions are surprisingly sparsely investigated. Of the citrates of coinage metal cations, only ammonium disilver citrate monohydrate (Sagatys *et al.*, 1993) and tetraammonium copper(II) bis(citrate) (Bott *et al.* 1991) have been reported. Here, we report the crystal structure of trisilver citrate, which was obtained from mixing solutions of sodium dihydrogen citrate and silver nitrate.

The basic structural of the 3D-polymeric structure shows an intramolecular hydrogen bond O–H···O bond between O5 and O7 (Fig. 1). As expected from the charges, all three carboxy groups are deprotonated. The coordination polyhedra about the Ag^+ cations are quite irregular, the Ag–O distances are in the range 2.275 (3) to 2.566 (3) Å (Table 1). The Ag2–Ag3 contact of 2.8801 (6) Å is the shortest one in the structure. It can be noted that significantly shorter distances Ag^+–Ag^+ are observed in many silver coordination compounds.

Experimental

An aqueous solution (0.5 mol/L) of sodium dihydrogen citrate was prepared by dissolving the respecitve amounts of trisodium citrate (Merck, p.a.) and citric acid in demineralised water. 1 mL of this solution was added to 1 mL of a solution of silver nitrate (0.5 mol/L), yielding a white precipitate. The latter was washed with demineralised water. The precipitate was then heated to 323 K with 1 mL of demineralised water. Upon cooling to room remperature, the saturated solution was filtered off and put aside for evaporation. Within a couple of days, small, colourless, rod-like crystals formed, that were suitable for structure determination. It can be noted that crystals of the title compound turned brown during the structure determination; however, no significant decrease in diffraction intensity could be observed. The initial precipitate formed from sodium dihydrogen citrate and silver nitrate was investigated by powder diffraction and it could be confirmed that it consisted of pure trisilver citrate. In addition, this powder pattern is identical with that of commercial "silver citrate hydrate".

Refinement

Methylene-H atoms were placed at calculated positions (C–H=0.97 Å, U_{iso}=1.2 U_{eq} of the respective C atom). The hydroxy-H atom was located from the Fourier map and was refined with a restraint (O–H=0.82 (2) Å) and U_{iso}=1.5 U_{eq}(O)). The largest Fourier peak/hole (1.21 and -1.21 e/Å^3, respectively), are found 0.82 and 0.77Å from Ag2.

Figures

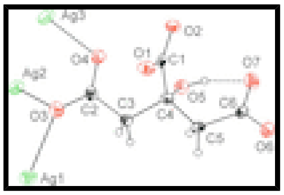

Fig. 1. The molecular structure of the title compound. Thermal ellipsoids at the 50% probability level. H bond as dashed line.

Trisilver citrate

Crystal data

$3Ag^+\cdot C_6H_5O_7^{3-}$

$M_r = 512.71$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 6.6181$ (7) Å

$b = 11.8477$ (11) Å

$c = 22.386$ (2) Å

$V = 1755.3$ (3) Å^3

$Z = 8$

$F(000) = 1904$

$D_x = 3.880$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 53 reflections

$\theta = 4.0–20.0°$

$\mu = 6.65$ mm^{-1}

$T = 299$ K

Rod, colourless

0.12 × 0.05 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD diffractometer

Radiation source: fine-focus sealed tube

φ & ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)

$T_{min} = 0.631$, $T_{max} = 0.876$

15238 measured reflections

2008 independent reflections

1493 reflections with $I > 2\sigma(I)$

$R_{int} = 0.055$

$\theta_{max} = 27.5°$, $\theta_{min} = 4.6°$

$h = -8\rightarrow8$

$k = -14\rightarrow15$

$l = -29\rightarrow29$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.051$

$S = 1.10$

2008 reflections

148 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0117P)^2 + 5.8189P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 1.21$ e Å^{-3}

$\Delta\rho_{min} = -1.21$ e Å^{-3}

1 restraint

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
Ag1	0.10659 (6)	0.25916 (4)	0.431564 (16)	0.02802 (12)
Ag2	0.27992 (6)	0.15476 (4)	0.296424 (16)	0.03187 (12)
Ag3	0.42015 (6)	0.32800 (4)	0.216249 (16)	0.02955 (12)
C1	0.7295 (7)	0.5962 (4)	0.33652 (19)	0.0165 (10)
C2	0.4709 (7)	0.3885 (4)	0.3454 (2)	0.0181 (11)
C3	0.5610 (7)	0.4467 (4)	0.39995 (19)	0.0168 (10)
C4	0.7567 (7)	0.5110 (4)	0.38916 (18)	0.0155 (10)
C5	0.8155 (7)	0.5769 (4)	0.44573 (19)	0.0160 (10)
C6	1.0229 (7)	0.6305 (4)	0.4444 (2)	0.0176 (11)
O1	0.5862 (5)	0.6651 (3)	0.34287 (14)	0.0244 (8)
O2	0.8489 (5)	0.5926 (3)	0.29317 (14)	0.0240 (8)
O3	0.3092 (5)	0.3355 (3)	0.35141 (15)	0.0317 (9)
O4	0.5631 (5)	0.3974 (3)	0.29684 (14)	0.0307 (9)
O5	0.9113 (5)	0.4296 (3)	0.37668 (14)	0.0186 (7)
O6	1.0678 (5)	0.7019 (3)	0.48333 (15)	0.0296 (9)
O7	1.1480 (5)	0.6006 (3)	0.40461 (15)	0.0272 (8)
H3A	0.4617	0.4990	0.4157	0.020*
H3B	0.5856	0.3900	0.4304	0.020*
H5A	0.7161	0.6359	0.4522	0.019*
H5B	0.8089	0.5260	0.4796	0.019*
H5O	1.012 (5)	0.468 (4)	0.379 (2)	0.028*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.0264 (2)	0.0362 (3)	0.02149 (19)	0.00746 (19)	0.00281 (17)	−0.00024 (17)
Ag2	0.0284 (2)	0.0484 (3)	0.01882 (19)	−0.0047 (2)	−0.00075 (17)	−0.00654 (19)
Ag3	0.0383 (3)	0.0327 (3)	0.01763 (18)	−0.0018 (2)	−0.00653 (17)	−0.00150 (17)
C1	0.014 (2)	0.020 (3)	0.016 (2)	−0.005 (2)	−0.004 (2)	−0.003 (2)
C2	0.018 (3)	0.014 (3)	0.022 (2)	−0.002 (2)	−0.004 (2)	0.002 (2)
C3	0.014 (2)	0.021 (3)	0.015 (2)	0.001 (2)	0.0015 (19)	−0.0013 (19)

C4	0.015 (2)	0.016 (3)	0.016 (2)	0.003 (2)	0.001 (2)	0.0021 (19)
C5	0.019 (3)	0.015 (3)	0.014 (2)	0.002 (2)	0.0004 (19)	0.0012 (19)
C6	0.017 (3)	0.020 (3)	0.016 (2)	0.002 (2)	−0.004 (2)	0.003 (2)
O1	0.0250 (19)	0.023 (2)	0.0250 (17)	0.0080 (17)	0.0029 (15)	0.0076 (15)
O2	0.0222 (18)	0.034 (2)	0.0162 (16)	0.0004 (16)	0.0039 (15)	0.0037 (15)
O3	0.029 (2)	0.040 (2)	0.0260 (18)	−0.013 (2)	0.0013 (16)	−0.0050 (17)
O4	0.029 (2)	0.044 (2)	0.0188 (17)	−0.0117 (18)	0.0016 (17)	−0.0080 (16)
O5	0.0197 (19)	0.0140 (19)	0.0220 (16)	0.0030 (16)	0.0001 (15)	−0.0033 (14)
O6	0.031 (2)	0.034 (2)	0.0232 (17)	−0.0112 (18)	0.0018 (16)	−0.0115 (16)
O7	0.0223 (19)	0.030 (2)	0.0296 (19)	−0.0022 (17)	0.0038 (16)	−0.0077 (16)

Geometric parameters (Å, °)

Ag1—O6^{i}	2.275 (3)	C3—C4	1.522 (6)
Ag1—O3	2.416 (3)	C4—O5	1.433 (6)
Ag1—O6^{ii}	2.539 (3)	C4—C5	1.538 (6)
Ag1—O7^{ii}	2.555 (3)	C5—C6	1.513 (7)
Ag2—O2^{iii}	2.300 (3)	C6—O6	1.251 (6)
Ag2—O3	2.477 (4)	C6—O7	1.266 (6)
Ag2—O7^{ii}	2.550 (3)	O1—Ag3^{vi}	2.340 (3)
Ag2—O2^{ii}	2.566 (3)	O2—Ag2^{vi}	2.300 (3)
Ag2—Ag3	2.8801 (6)	O2—Ag2^{vii}	2.566 (3)
Ag2—Ag3^{iv}	3.1563 (7)	O4—Ag3^{v}	2.519 (4)
Ag3—O4	2.197 (3)	O5—Ag3^{v}	2.404 (3)
Ag3—O1^{iii}	2.340 (3)	O6—Ag1^{i}	2.275 (3)
Ag3—O5^{iv}	2.404 (3)	O6—Ag1^{vii}	2.539 (3)
Ag3—O4^{iv}	2.519 (4)	O7—Ag2^{vii}	2.550 (3)
Ag3—Ag2^{v}	3.1563 (7)	O7—Ag1^{vii}	2.555 (3)
C1—O2	1.252 (5)	C3—H3A	0.9700
C1—O1	1.260 (6)	C3—H3B	0.9700
C1—C4	1.562 (6)	C5—H5A	0.9700
C2—O3	1.248 (6)	C5—H5B	0.9700
C2—O4	1.252 (6)	O5—H5O	0.81 (2)
C2—C3	1.523 (6)		
O6^{i}—Ag1—O3	145.89 (13)	O4—C2—C3	117.8 (4)
O6^{i}—Ag1—O6^{ii}	95.88 (6)	C4—C3—C2	115.6 (4)
O3—Ag1—O6^{ii}	88.17 (12)	O5—C4—C3	107.6 (4)
O6^{i}—Ag1—O7^{ii}	132.00 (12)	O5—C4—C5	108.8 (4)
O3—Ag1—O7^{ii}	75.34 (12)	C3—C4—C5	109.8 (3)
O6^{ii}—Ag1—O7^{ii}	51.10 (11)	O5—C4—C1	111.7 (3)
O2^{iii}—Ag2—O3	137.63 (12)	C3—C4—C1	110.2 (4)
O2^{iii}—Ag2—O7^{ii}	144.77 (12)	C5—C4—C1	108.8 (4)
O3—Ag2—O7^{ii}	74.39 (11)	C6—C5—C4	115.2 (4)
O2^{iii}—Ag2—O2^{ii}	103.78 (10)	O6—C6—O7	121.6 (4)

O3—Ag2—O2^{ii}	100.80 (12)	O6—C6—C5	119.1 (4)
O7^{ii}—Ag2—O2^{ii}	77.04 (10)	O7—C6—C5	119.4 (4)
O2^{iii}—Ag2—Ag3	78.71 (9)	C1—O1—Ag3^{vi}	119.0 (3)
O3—Ag2—Ag3	70.64 (8)	C1—O2—Ag2^{vi}	115.5 (3)
O7^{ii}—Ag2—Ag3	135.29 (8)	C1—O2—Ag2^{vii}	124.9 (3)
O2^{ii}—Ag2—Ag3	83.01 (8)	Ag2^{vi}—O2—Ag2^{vii}	106.72 (12)
O2^{iii}—Ag2—Ag3^{iv}	81.39 (9)	C2—O3—Ag1	138.1 (3)
O3—Ag2—Ag3^{iv}	62.71 (9)	C2—O3—Ag2	116.7 (3)
O7^{ii}—Ag2—Ag3^{iv}	112.94 (8)	Ag1—O3—Ag2	90.13 (12)
O2^{ii}—Ag2—Ag3^{iv}	155.01 (8)	C2—O4—Ag3	118.2 (3)
Ag3—Ag2—Ag3^{iv}	73.958 (16)	C2—O4—Ag3^{v}	122.1 (3)
O4—Ag3—O1^{iii}	141.33 (13)	Ag3—O4—Ag3^{v}	100.73 (13)
O4—Ag3—O5^{iv}	122.24 (13)	C4—O5—Ag3^{v}	121.5 (2)
O1^{iii}—Ag3—O5^{iv}	85.60 (11)	C6—O6—Ag1^{i}	126.9 (3)
O4—Ag3—O4^{iv}	112.16 (13)	C6—O6—Ag1^{vii}	93.7 (3)
O1^{iii}—Ag3—O4^{iv}	100.76 (12)	Ag1^{i}—O6—Ag1^{vii}	139.37 (15)
O5^{iv}—Ag3—O4^{iv}	73.33 (11)	C6—O7—Ag2^{vii}	136.0 (3)
O4—Ag3—Ag2	83.90 (9)	C6—O7—Ag1^{vii}	92.6 (3)
O1^{iii}—Ag3—Ag2	76.06 (8)	Ag2^{vii}—O7—Ag1^{vii}	85.45 (11)
O5^{iv}—Ag3—Ag2	152.65 (8)	C4—C3—H3A	108.4
O4^{iv}—Ag3—Ag2	90.16 (8)	C2—C3—H3A	108.4
O4—Ag3—Ag2^{v}	89.56 (10)	C4—C3—H3B	108.4
O1^{iii}—Ag3—Ag2^{v}	55.00 (8)	C2—C3—H3B	108.4
O5^{iv}—Ag3—Ag2^{v}	105.44 (8)	H3A—C3—H3B	107.4
O4^{iv}—Ag3—Ag2^{v}	155.43 (9)	C6—C5—H5A	108.5
Ag2—Ag3—Ag2^{v}	80.542 (17)	C4—C5—H5A	108.5
O2—C1—O1	125.8 (4)	C6—C5—H5B	108.5
O2—C1—C4	119.4 (4)	C4—C5—H5B	108.5
O1—C1—C4	114.9 (4)	H5A—C5—H5B	107.5
O3—C2—O4	123.6 (4)	C4—O5—H5O	101 (4)
O3—C2—C3	118.6 (4)	Ag3^{v}—O5—H5O	109 (4)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+3/2, y-1/2, z$; (iii) $-x+1, y-1/2, -z+1/2$; (iv) $x-1/2, y, -z+1/2$; (v) $x+1/2, y, -z+1/2$; (vi) $-x+1, y+1/2, -z+1/2$; (vii) $-x+3/2, y+1/2, z$.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5O···O7	0.81 (2)	1.90 (3)	2.636 (5)	152 (5)

Fig. 1