with $U(H) = 1.2U$, where U is the isotropic displacement parameter of the O or C atom in the O—H or C—H bond. All calculations were performed using the *GX* program package (Mallinson & Muir, 1985), which includes a local modification of *ORTEP* (Johnson, 1971).

We thank SERC for an equipment grant and for a studentship (to ARK).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55898 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1027]

References

Alcock, N. W., Brown, J. M. & Jeffery, J. C. (1976). *J. Chem. Soc. Dalton Trans.* pp. 583–588.

Alcock, N. W., Brown, J. M. & Jeffrey, J. C. (1977). *J. Chem. Soc. Dalton Trans.* pp. 888–893.

Branan, D. M., Hoffman, N. W., McElroy, E. A., Prokopuk, N., Salazar, A. B., Robbins, M. J., Hill, W. E. & Webb, T. R. (1991). *Inorg. Chem.* **30**, 1200–1207.

Ceriotti, A., Ciani, G. & Sironi, A. (1983). *J. Organomet. Chem.* **247**, 345–350.

Dahan, F. & Choukroun, R. (1985). *Acta Cryst.* C**41**, 704–706.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, 2nd revision. Oak Ridge National Laboratory, Tennessee, USA.

Mallinson, P. R. & Muir, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.

Peone, J., Flynn, B. R. & Vaska, L. (1974). *Inorg. Synth.* **15**, 68–72.

Rheingold, A. L. & Geib, S. J. (1987). *Acta Cryst.* C**43**, 784–786.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1993). C**49**, 1148–1150

Di-μ-nitrato-bis[bis(triphenylphosphine)-silver(I)], $[(Ph_3P)_2AgNO_3]_2$, at 178 K

PETER G. JONES

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, W-3300 Braunschweig, Germany

(*Received* 10 *August* 1992; *accepted* 25 *November* 1992)

Abstract

The title compound possesses crystallographic twofold symmetry. The coordination at silver is distorted tetrahedral, the donor atoms being two phosphine P atoms and one O atom from each of the two nitrate ligands; the O atoms each bridge the two Ag atoms, forming a central Ag_2O_2 ring. The twofold axis passes through each N atom and each coordinating O atom. Most bond lengths and angles are essentially as expected, except that the Ag—O bonds are short (2.34 Å) and the non-coordinated N—O bonds are long (1.29 Å).

Comment

The title compound (1) arose fortuitously during a study of ylide complexes of silver. Nitratobis(triphenylphosphine)silver(I), the monomeric form corresponding to the dimeric title compound, has previously been studied as two modifications: the unsolvated form (Barron, Dyason, Healy, Engelhardt, Skelton & White, 1986) and a benzene solvate (Harker & Tiekink, 1989). A dimer (2), structurally analogous to the title compound, has also been characterized; this involves trimethylphosphite rather than triphenylphosphine (Meiners, Clardy & Verkade, 1975).

Atomic coordinates of (1) are given in Table 1 with selected bond lengths and angles in Table 2. The molecule (Fig. 1) possesses crystallographic twofold symmetry, the axis passing through the atoms N(1), O(2), N(2) and O(4), whereas the corresponding complex (2) (Meiners *et al.*, 1975) displayed inversion symmetry; in both cases the central four-membered ring is exactly planar. In (1), the nitrate ions are also planar by imposed symmetry and are almost coplanar with the central ring [dihedral angles 6 and 4° for the nitrates at N(1) and N(2), respectively].

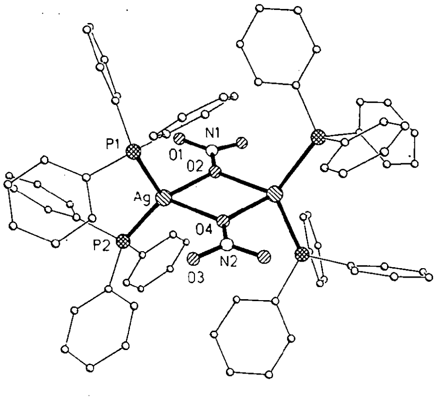

Fig. 1. The molecule of the title compound (1) in the crystal. Radii are arbitrary; H atoms are omitted for clarity.

The nitrate ligands in (1) each bridge both Ag atoms, whereby only one O atom per ligand acts as a donor; this contrasts with the monomeric forms (Barron *et al.*, 1986; Harker & Tiekink, 1989) in which distorted η^2-coordination by the nitrate ligands is observed. The angles in the four-membered ring thus formed [75.7 (1)° at Ag and 104.3, 104.4 (2)° at O] differ appreciably from those in (2) [67.0 (3)° at Ag, 113.0 (3)° at O].

The coordination geometry at the Ag atom is distorted tetrahedral, the major angular distortion being introduced by the four-membered ring (see above). The other angles at Ag range from 101.2–122.1°. The Ag—P bond lengths [2.425 (1) and 2.448 (1) Å] are similar to those in all the above-mentioned complexes. In contrast, the Ag—O bonds are much shorter [2.340, 2.341 (3) Å] than those of the other complexes [*cf.* 2.454, 2.456 (8) Å in (2)].

The N—O bond lengths to the coordinated O atoms are not equal [1.288 (7), 1.248 (8) Å], although the difference may not be very significant; the values are broadly comparable with that observed in (2) [1.277 (12) Å]. Unexpectedly, the non-coordinated N—O bonds are much longer than in (2) [1.290 (4), 1.295 (5) Å compared with 1.216 (11), 1.208 (12) Å]. There is no obvious reason for this apparent discrepancy.

There are no Ag···O contacts shorter than 3.4 Å.

Experimental

Crystal data

$C_{72}H_{60}Ag_2N_2O_6P_4$
M_r = 1388.8
Orthorhombic
$P2_12_12$
a = 14.904 (5) Å
b = 23.169 (7) Å
c = 9.262 (3) Å
V = 3198 (2) Å^3
Z = 2
D_x = 1.442 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 50 reflections
θ = 10–11.5°
μ = 0.77 mm^{-1}
T = 178 K
Prism
0.4 × 0.35 × 0.3 mm
Colourless

Data collection

Siemens *R*3 diffractometer
ω scans
Absorption correction: ψ scans
T_{min} = 0.84, T_{max} = 0.88
7422 measured reflections
7365 independent reflections
5363 observed reflections [$F>4\sigma(F)$]

R_{int} = 0.016
θ_{max} = 27.5°
$h = 0 \rightarrow 19$
$k = -30 \rightarrow 30$
$l = -12 \rightarrow 1$
3 standard reflections monitored every 197 reflections
intensity variation: ±1.5%

Refinement

Refinement on F
Final R = 0.040
wR = 0.035
S = 1.1
5363 reflections
390 parameters
H atoms riding
$w = 1/[\sigma^2(F)+0.0002F^2]$

$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.8 e Å^{-3}
$\Delta\rho_{min}$ = −1.1 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ag	0.61200 (2)	0.53428 (1)	0.51900 (3)	0.297 (1)
P(1)	0.61043 (8)	0.63755 (4)	0.46307 (11)	0.278 (3)
P(2)	0.75275 (8)	0.48349 (4)	0.55272 (11)	0.269 (3)
C(11)	0.5151 (3)	0.6664 (2)	0.3620 (5)	0.267 (15)
C(12)	0.5226 (3)	0.7000 (2)	0.2398 (5)	0.347 (16)
C(13)	0.4465 (4)	0.7226 (2)	0.1752 (6)	0.476 (20)
C(14)	0.3630 (3)	0.7124 (2)	0.2339 (7)	0.506 (21)
C(15)	0.3547 (3)	0.6785 (3)	0.3534 (6)	0.510 (21)
C(16)	0.4303 (3)	0.6555 (2)	0.4168 (5)	0.425 (18)
C(21)	0.7084 (3)	0.6562 (2)	0.3546 (5)	0.321 (16)
C(22)	0.7211 (3)	0.6244 (2)	0.2286 (5)	0.431 (18)
C(23)	0.7975 (4)	0.6327 (3)	0.1439 (7)	0.572 (24)
C(24)	0.8625 (4)	0.6719 (3)	0.1901 (7)	0.591 (24)
C(25)	0.8514 (3)	0.7024 (2)	0.3164 (7)	0.507 (21)
C(26)	0.7744 (3)	0.6949 (2)	0.4004 (6)	0.404 (17)
C(31)	0.6137 (3)	0.6862 (2)	0.6171 (4)	0.315 (13)
C(32)	0.6033 (3)	0.7453 (2)	0.6032 (5)	0.403 (16)
C(33)	0.6055 (4)	0.7809 (2)	0.7228 (6)	0.480 (18)
C(34)	0.6175 (4)	0.7575 (3)	0.8568 (6)	0.571 (21)
C(35)	0.6267 (4)	0.6995 (3)	0.8732 (5)	0.654 (25)
C(36)	0.6255 (4)	0.6627 (2)	0.7530 (5)	0.471 (19)
C(41)	0.7504 (3)	0.4171 (2)	0.6603 (5)	0.292 (14)
C(42)	0.6752 (3)	0.4062 (2)	0.7419 (5)	0.408 (18)
C(43)	0.6701 (4)	0.3578 (2)	0.8285 (6)	0.527 (21)
C(44)	0.7400 (4)	0.3202 (2)	0.8356 (6)	0.481 (20)
C(45)	0.8155 (4)	0.3308 (2)	0.7560 (6)	0.504 (21)
C(46)	0.8210 (4)	0.3788 (2)	0.6677 (6)	0.448 (18)
C(51)	0.8087 (3)	0.4631 (2)	0.3862 (4)	0.296 (13)
C(52)	0.7547 (3)	0.4545 (2)	0.2632 (5)	0.352 (16)
C(53)	0.7931 (4)	0.4380 (3)	0.1367 (6)	0.497 (21)
C(54)	0.8838 (4)	0.4289 (2)	0.1240 (5)	0.468 (18)
C(55)	0.9377 (4)	0.4376 (2)	0.2440 (5)	0.417 (18)
C(56)	0.9011 (3)	0.4545 (2)	0.3734 (5)	0.332 (15)
C(61)	0.8352 (3)	0.5287 (2)	0.6452 (4)	0.269 (13)
C(62)	0.8601 (3)	0.5189 (2)	0.7873 (5)	0.365 (16)
C(63)	0.9168 (3)	0.5573 (2)	0.8570 (6)	0.440 (18)
C(64)	0.9470 (3)	0.6054 (2)	0.7905 (6)	0.443 (19)
C(65)	0.9218 (3)	0.6155 (2)	0.6477 (6)	0.462 (19)
C(66)	0.8671 (3)	0.5773 (2)	0.5773 (5)	0.388 (17)
N(1)	0.5000	0.5000	0.8129 (7)	0.483 (25)
N(2)	0.5000	0.5000	0.2291 (7)	0.523 (27)
O(1)	0.5644 (2)	0.5253 (2)	0.8813 (3)	0.410 (12)
O(2)	0.5000	0.5000	0.6739 (4)	0.367 (17)
O(3)	0.5664 (2)	0.5218 (2)	0.1575 (3)	0.408 (13)
O(4)	0.5000	0.5000	0.3638 (4)	0.367 (17)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Ag—P(1)	2.448 (1)	Ag—P(2)	2.425 (1)
Ag—O(2)	2.340 (3)	Ag—O(4)	2.341 (3)
P(1)—C(11)	1.828 (5)	P(1)—C(21)	1.824 (5)
P(1)—C(31)	1.818 (4)	P(2)—C(41)	1.833 (5)
P(2)—C(51)	1.816 (4)	P(2)—C(61)	1.828 (4)
N(1)—O(1)	1.290 (4)	N(1)—P(2)	1.288 (7)
N(2)—O(3)	1.295 (5)	N(2)—O(4)	1.248 (8)
P(1)—Ag—P(2)	120.6 (1)	P(1)—Ag—O(2)	117.0 (1)
P(2)—Ag—O(2)	111.9 (1)	P(1)—Ag—O(4)	101.2 (1)
P(2)—Ag—O(4)	122.1 (1)	O(2)—Ag—O(4)	75.7 (1)
Ag—P(1)—C(11)	118.3 (1)	Ag—P(1)—C(21)	109.9 (2)
C(11)—P(1)—C(21)	104.6 (2)	Ag—P(1)—C(31)	116.0 (1)
C(11)—P(1)—C(31)	101.3 (2)	C(21)—P(1)—C(31)	105.3 (2)
Ag—P(2)—C(41)	117.4 (2)	Ag—P(2)—C(51)	114.4 (1)
C(41)—P(2)—C(51)	104.6 (2)	Ag—P(2)—C(61)	111.3 (1)
C(41)—P(2)—C(61)	103.8 (2)	C(51)—P(2)—C(61)	103.8 (2)
O(1)—N(1)—O(2)	119.4 (3)	O(1)—N(1)—O(1)^{i}	121.2 (5)
O(3)—N(2)—O(4)	120.8 (3)	O(3)—N(2)—O(3)^{i}	118.3 (6)
Ag—O(2)—N(1)	127.8 (1)	Ag—O(2)—Ag^{i}	104.4 (2)
Ag—O(4)—N(2)	127.9 (1)	Ag—O(4)—Ag^{i}	104.3 (2)

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

The structure was solved by the heavy-atom method and refined by full-matrix techniques. The absolute structure was determined [η = +1.05(5)].

The program system employed was *SHELXTL-Plus* (Sheldrick, 1989).

The crystals were kindly provided by Professor A. Laguna and co-workers, University of Zaragoza, Spain. We thank the Fonds der Chemischen Industrie for financial support.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55893 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1025]

References

Barron, P. F., Dyason, J. C., Healy, P. C., Engelhardt, L. M., Skelton, B. W. & White, A. H. (1986). *J. Chem. Soc. Dalton Trans.* pp. 1965–1970.

Harker, C. S. W. & Tiekink, E. R. T. (1989). *Acta Cryst.* **C45**, 1815–1817.

Meiners, J. H., Clardy, J. C. & Verkade, J. G. (1975). *Inorg. Chem.* **14**, 632–636.

Sheldrick, G. M. (1989). *SHELXTL-Plus.* Version 4.1. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Acta Cryst. (1993). C**49**, 1150–1152

Structure of Sodium Hydrogen (+)-Tartrate Monohydrate

Raymond C. Bott, Dalius S. Sagatys,
Daniel E. Lynch and Graham Smith*

School of Chemistry, Queensland University of Technology, PO Box 2434, Brisbane, 4001, Australia

Colin H. L. Kennard

Department of Chemistry, The University of Queensland, Brisbane, 4072, Australia

(*Received* 18 *May* 1992; *accepted* 30 *November* 1992)

Abstract

The structure of the title compound comprises a network polymer involving all tartrate O atoms (except the protonated carboxyl O atom) in bonding to four separate sodium complex centres. The water molecule completes a distorted bi-face capped trigonal prismatic eight coordination about Na [Na—O range 2.415–2.826 (2), mean 2.57 (14) Å] and is also involved in a number of hydrogen-bonding interactions. In this respect, the structure differs from the isomorphous series of anhydrous univalent cation (K^+, Rb^+, Cs^+, Tl^+, NH_4^+) salts of hydrogen (+)-tartrate.

Comment

The univalent cation hydrogen (+)-tartrates (K^+, Rb^+, Cs^+, Tl^+, NH_4^+) form an isomorphous series (Groth, 1910). Apart from early crystallographic work on the structures including determination of absolute configuration (van Bommel & Bijvoet, 1958), accurate structure determinations have only been completed quite recently [Templeton & Templeton (1978) (Cs); Buschmann & Luger (1985) and Akkurt, Hokelek & Soylu (1987) (K); Templeton & Templeton (1989) (Rb)]. Sodium hydrogen (+)-tartrate is not one of the isomorphous set and although the unit-cell parameters and space group have been reported for the monohydrate† (Zholanov, Umanskii, Barfolomeeva, Eshkova & Zolina, 1956), its crystal structure has not previously been determined. The title compound was isolated during a program of investigation into the stabilizing effect on trivalent Group 15 (As, Sb, Bi) tartrate-anion species using univalent cations (Sagatys, Smith, Lynch & Kennard, 1991) and its crystal structure determined.

The structure of the title compound comprises a three-dimensional network polymer, involving the hydrogen tartrate residues linked by eight-coordinate sodium ion centres (Figs. 1, 2). The NaO_8 stereochemistry is distorted bi-face capped trigonal prismatic, with an Na—O range of 2.415–2.826 (2) Å [mean 2.57 (14) Å]. This compares with a mean value of 2.38 Å over the twelve values for the two coordination centres in the disodium (+)-tartrate dihydrate structure (Ambady & Kartha, 1968) which also forms a network polymer. Also similar to the normal tartrate structure is the incorporation of the water molecule O(1W) in a strong bond to Na [2.420 (2), *cf.* 2.34, 2.42 Å]. The remaining coordination sites in the present structure are occupied by tartrato O atoms, including six from three bidentate chelate hydroxycarboxylate groups, two terminal (α-hydroxy) [$O(2)^a$, $O(12)^a$ ($a = -\frac{1}{2}+x, \frac{1}{2}-y, -z$); $O(3)^c$, $O(41)^c$ ($c = 1-x, -\frac{1}{2}+y, \frac{1}{2}-z$)] and one sub-terminal (β-hydroxycarboxyl) [O(2), O(42)]. In the remaining site, there is a bridging link to another carboxyl O atom [$O(12)^b$ ($b = x-1, y, z$)]. The β-hydroxycarboxyl chelate linkage is unusual in forming a six-membered ring system which expands the

---

† Comparative cell data: $a = 8.663$ (2), $b = 10.580$ (4), $c = 7.230$ (4) Å, space group $P2_12_12_1$.

0108-2701/93/061150-03$06.00