

Poly[[[(1,2- η)-benzene]silver(I)]- μ -tri-
fluoromethanesulfonate-O;O';O'';O''']

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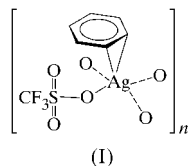
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The title compound, $[\text{Ag}(\text{CF}_3\text{O}_3\text{S})(\text{C}_6\text{H}_6)]$, has been synthesized and characterized by low-temperature single-crystal X-ray diffraction. The complex is polymeric, with a network of trifluoromethanesulfonate anions bridging the silver cations. The terminal planar benzene ligand is asymmetrically η^2 -coordinated to the Ag.

Comment

Complexes of benzene with Ag^{I} have been extensively studied since the very beginning of modern-day transition metal arene chemistry (Quinn & Tsai, 1969). Recent renewed interest in such systems has been driven mainly by potential applications for crystal engineering and electroactive materials design (Munakata *et al.*, 1997, 1998, 1999; Ning *et al.*, 1999).

Several crystalline 'binary' adducts of the form $\text{Ag}^{\text{I}}\text{X}-\text{C}_6\text{H}_6$ are known, with stoichiometric ratios of 2:1 ($\text{X} = \text{CF}_3\text{CO}_2$; Hunt *et al.*, 1974), 1:1 [$\text{X} = \text{ClO}_4$ (Rundle & Goring, 1950; Smith & Rundle, 1958; McMullan *et al.*, 1997), $\text{X} = \text{AlCl}_4$ (Turner & Amma, 1966) and $\text{X} = \text{N}(\text{SO}_2\text{F})_2$ (Begley *et al.*, 1994)], 1:2 [$\text{X} = \text{CB}_{11}\text{H}_{11}\text{F}$ (Ivanov *et al.*, 1995) and $\text{X} = \text{CB}_9\text{H}_8\text{F}_2$ (Ivanov *et al.*, 1996)] and 1:3 ($\text{X} = \text{BF}_4$; Batsanov *et al.*, 1998), depending on the nature of the anion. The coordination mode of the arene to the Ag^{I} ion is also variable, between η^1 and η^2 , with benzene acting as a terminal or bridging ligand. Bridging arenes have recently been the subject of a renaissance of interest in organic transition metal chemistry (Wadepohl, 1992).



The preparation of crystalline $\text{C}_6\text{H}_6(\text{AgCF}_3\text{SO}_3)_2$ was reported by Dines (1974), but the structure of this adduct was not determined. From equilibrium ligand vapour-pressure measurements in the benzene– AgCF_3SO_3 system, the formation of two stable species of the form $\text{C}_6\text{H}_6(\text{AgCF}_3\text{SO}_3)_n$ (n is

1 or 2) was established (Yanagihara *et al.*, 1996). We report here the structure of the 1:1 adduct, the title complex, (I). This material was obtained by slow crystallization from a dilute solution of AgCF_3SO_3 in absolute benzene.

Complex (I) is polymeric. The most salient feature is the terminal coordination mode of the benzene ligands, in contrast with the bridging coordination which was found in the AgClO_4 (Smith & Rundle, 1958; McMullan *et al.*, 1997) and $\text{AgN}(\text{SO}_2\text{F})_2$ adducts (Begley *et al.*, 1994). A section of the polymer structure is depicted in Fig. 1. The structure can be

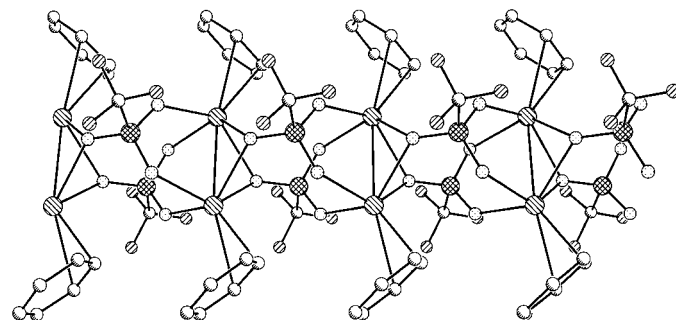


Figure 1

A view of the polymeric structure of (I). The crystal b axis runs vertically.

formally grouped into $[\text{Ag}(\text{benzene})]_2$ 'dimers', held together by the trifluoromethanesulfonate anions *via* two O and two OSO bridges. The $\text{Ag}\cdots\text{Ag}$ distance is rather long [3.2415 (3) Å] and is indicative of minimal, if any, metal–metal bonding. An unambiguous (non-bridged) $\text{Ag}-\text{Ag}$ bond of comparable length (3.293 Å) was reported in the $[\text{Ag}(\text{CN})_2]_2$ dianion (Kappenstein *et al.*, 1988). The 'dimers' in (I) are linked together by the bridging trifluoromethanesulfonate moieties to form chains along the direction of the crystal b axis. Of the three O atoms of every trifluoromethanesulfonate group, one (O1) is three-coordinate and bridges two Ag atoms, whilst the other two are two-coordinate and each bond to one Ag atom only.

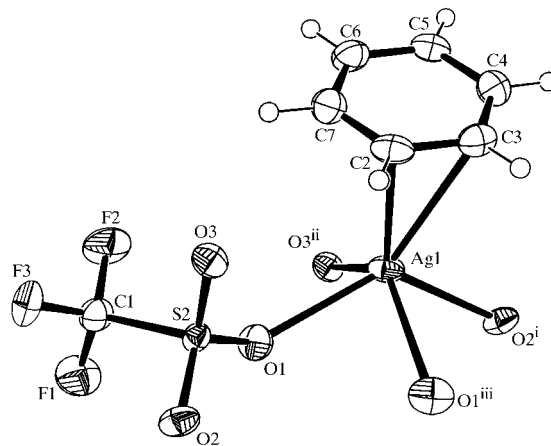


Figure 2

The structure of the repeat unit of (I), showing the coordination around Ag. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii; symmetry codes are as given in Table 1.

Each of the Ag atoms bonds to two adjacent C atoms of the planar (r.m.s. deviation 0.009 Å) benzene ligand in an asymmetric fashion (Fig. 2). Asymmetric bidentate coordination of arene ligands is very common for d^{10} metal ions, but the symmetric η^2 -bonding mode has also been observed in a few cases (Griffith & Amma, 1974; Begley *et al.*, 1994). The Ag—C bonds [2.387 (2) and 2.698 (2) Å] are not exactly perpendicular to the ring plane, but tilted outward toward the H atoms by 6°. The lengths of the C—C bonds within the η^2 benzene vary only little [1.379 (3)–1.395 (4) Å]; there is no significant systematic lengthening of the metal coordinated bond. Such an effect was discussed in the structure of $C_6H_6(AgClO_4)$ (McMullan *et al.*, 1997).

Every Ag atom in (I) is essentially five-coordinate. The coordination polyhedron resembles a distorted square pyramid, with all oxygen ligands occupying basal positions.

Experimental

Colourless needles of (I) were grown from a solution of $AgCF_3SO_3$ in benzene at 278 K. The product crystallized in the form of long needles, which could not be cut without destruction.

Crystal data

$[Ag(CF_3O_3S)(C_6H_6)]$	$D_x = 2.273 \text{ Mg m}^{-3}$
$M_r = 335.05$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 8907 reflections
$a = 25.4244$ (5) Å	$\theta = 2.1\text{--}28.2^\circ$
$b = 5.05600$ (10) Å	$\mu = 2.300 \text{ mm}^{-1}$
$c = 18.9045$ (4) Å	$T = 173$ (2) K
$\beta = 126.3270$ (10)°	Needle, colourless
$V = 1957.80$ (7) Å ³	$1.25 \times 0.14 \times 0.08 \text{ mm}$
$Z = 8$	

Data collection

Bruker AXS SMART 1000 diffractometer	2420 independent reflections
ω scans	2248 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{int} = 0.035$
$T_{min} = 0.551$, $T_{max} = 0.862$	$\theta_{max} = 28.28^\circ$
12 969 measured reflections	$h = -33 \rightarrow 36$
	$k = 0 \rightarrow 6$
	$l = 0 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 3.092P]$
$R[F^2 > 2\sigma(F^2)] = 0.023$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.060$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.085$	$\Delta\rho_{max} = 0.86 \text{ e } \text{Å}^{-3}$
2420 reflections	$\Delta\rho_{min} = -0.47 \text{ e } \text{Å}^{-3}$
160 parameters	
All H-atom parameters refined	

Refined C—H distances are in the range 0.89 (3)–0.99 (3) Å.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT+ (Bruker, 1999); data reduction: SAINT+; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXTL (Sheldrick, 1999).

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Table 1

Selected geometric parameters (Å, °).

Ag1—C2	2.387 (2)	S2—O3	1.4478 (16)
Ag1—O2 ⁱ	2.4103 (16)	S2—O1	1.4512 (16)
Ag1—O3 ⁱⁱ	2.4247 (15)	S2—C1	1.823 (2)
Ag1—O1	2.4779 (18)	F1—C1	1.325 (3)
Ag1—O1 ⁱⁱⁱ	2.5904 (17)	F2—C1	1.335 (3)
Ag1—C3	2.698 (2)	F3—C1	1.322 (3)
S2—O2	1.4438 (16)		
C2—Ag1—O2 ⁱ	123.34 (8)	O3 ⁱⁱ —Ag1—O1 ⁱⁱⁱ	131.84 (5)
C2—Ag1—O3 ⁱⁱ	125.22 (7)	O1—Ag1—O1 ⁱⁱⁱ	73.82 (8)
O2 ⁱ —Ag1—O3 ⁱⁱ	85.14 (6)	S2—O1—Ag1	129.28 (11)
C2—Ag1—O1	104.21 (7)	S2—O1—Ag1 ⁱⁱⁱ	128.81 (11)
O2 ⁱ —Ag1—O1	128.49 (6)	Ag1—O1—Ag1 ⁱⁱⁱ	79.48 (5)
O3 ⁱⁱ —Ag1—O1	82.57 (6)	S2—O2—Ag1 ^{iv}	133.79 (10)
C2—Ag1—O1 ⁱⁱⁱ	101.30 (7)	S2—O3—Ag1 ^v	124.79 (9)
O2 ⁱ —Ag1—O1 ⁱⁱⁱ	78.24 (6)		

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1018). Services for accessing these data are described at the back of the journal.

References

- Batsanov, A. S., Crabtree, S. P., Howard, J. A. K., Lehmann, C. W. & Kilner, M. (1998). *J. Organomet. Chem.* **550**, 59–61.
- Begley, M. J., Sowerby, D. B., Verma, R. D. & Vig, A. (1994). *J. Organomet. Chem.* **481**, 243–246.
- Bruker (1998). SMART. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). SAINT+. Version 6.01. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dines, M. B. (1974). *J. Organomet. Chem.* **67**, C55–58.
- Griffith, E. A. H. & Amma, E. L. (1974). *J. Am. Chem. Soc.* **96**, 743–749.
- Hunt, G. W., Lee, T. C. & Amma, E. L. (1974). *Inorg. Nucl. Chem. Lett.* **10**, 909–913.
- Ivanov, S. V., Lupinetti, A. J., Miller, S. M., Anderson, O. P., Solntsev, K. A. & Strauss, S. H. (1995). *Inorg. Chem.* **34**, 6419–6420.
- Ivanov, S. V., Rockwell, J. J., Miller, S. M., Anderson, O. P., Solntsev, K. A. & Strauss, S. H. (1996). *Inorg. Chem.* **35**, 7882–7891.
- Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kappenstein, C., Quali, A., Guerin, M., Cernak, J. & Chomic, J. (1988). *Inorg. Chim. Acta*, **147**, 189.
- McMullan, R. K., Koetzle, T. F. & Fritchie, C. J. Jr (1997). *Acta Cryst.* **B53**, 645–653.
- Munakata, M., Wu, L. P. & Kuroda-Sowa, T. (1997). *Bull. Chem. Soc. Jpn.* **70**, 1727–1743.
- Munakata, M., Wu, L. P. & Kuroda-Sowa, T. (1998). *Adv. Inorg. Chem.* **46**, 173–303.
- Munakata, M., Wu, L. P., Sugimoto, K., Kuroda-Sowa, T., Maekawa, M., Suenaga, Y., Maeno, N. & Fujita, M. (1999). *Inorg. Chem.* **38**, 5674–5680.
- Ning, G. L., Munakata, M., Wu, L. P., Maekawa, M., Kuroda-Sowa, T., Suenaga, Y. & Sugimoto, K. (1999). *Inorg. Chem.* **38**, 1376–1377.
- Quinn, H. W. & Tsai, J. H. (1969). *Adv. Inorg. Radiochem.* **12**, 217–373.
- Rundle, R. E. & Goring, J. H. (1950). *J. Am. Chem. Soc.* **72**, 5337.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
- Sheldrick, G. M. (1999). SHELXTL. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Smith, H. G. & Rundle, R. E. (1958). *J. Am. Chem. Soc.* **80**, 5075–5080.
- Turner, R. W. & Amma, E. L. (1966). *J. Am. Chem. Soc.* **88**, 3243–3247.
- Wadepohl, H. (1992). *Angew. Chem. Int. Ed. Engl.* **31**, 247–262.
- Yanagihara, N., Gotoh, T. & Ogura, T. (1996). *Polyhedron*, **15**, 4349–4354.