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catena-Poly[[[diacetonitrilesilver(I)]-μ-2,11-dithia[3.3]paracyclophane-κ^2S:S'] hydrogenoctafluoroadipate]

Shu Qin Liu,[a] Hisashi Konaka,[a] Takayoshi Kuroda-Sowa,[a] Masahiko Maekawa,[a] Yusaku Suenaga,[a] Gui Ling Ning[b] and Megumu Munakata[a]*

[a]Department of Science, Kinki University, Higashi-Osaka, Osaka 577-8502, Japan, and [b]Department of Chemistry, Dalian University of Technology, Dalian 116012, People's Republic of China

Correspondence e-mail:
munakata@chem.kindai.ac.jp

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The title compound, $\{[Ag(C_{16}H_{16}S_2)(C_2H_3N)_2](C_6HF_8O_4)\}_n$, forms two infinite chains, which are approximately perpendicular to each other. One chain consists of $[Ag(C_{16}H_{16}S_2)(C_2H_3N)_2]_n^{n+}$, and the other is formed from HOFA$^-$ (HOFA$^-$ is hydrogen octafluoroadipate) units *via* $O_c—H\cdots O_c$ (c is carboxy) hydrogen-bonding interactions, with an $H\cdots A$ distance of 1.66 (5) Å. Each silver(I) cation lies on a crystallographic twofold rotation axis and has a tetrahedral geometry, defined by two N atoms belonging to two acetonitrile molecules and two S atoms from two 2,11-dithia[3.3]paracyclophane molecules. The cyclophanes have inversion symmetry.

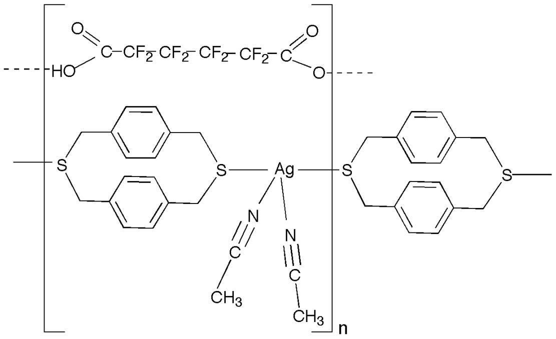
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.067
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.

Comment

The chemistry of cyclophanes, especially [2.2]- and [3.3]paracyclophane, has attracted much attention in organometallic chemistry (Schmidbaur *et al.*, 1986*a*,*b*; Schmidbaur *et al.*, 1989; Swann *et al.*, 1986; Cohen-Addad *et al.*, 1988). Conversely, relatively little is known about the coordination chemistry of the structurally related thia-bridged paracyclophanes. In particular, reports on polymeric metal complexes of thia-bridged compounds are rare. Recently, we have reported four copper(I) complexes and one silver(I) complex of 2,11-dithia[3.3]paracyclophane (dtpcp) (Munakata *et al.*, 1996; Yamanoto *et al.*, 1997). To further our work in this field, we report here the crystal structure of the title dtpcp complex with silver(I) octafluoroadipate generated *in situ*, $\{[Ag(C_{16}H_{16}S_2)(C_2H_3N)_2](C_6HF_8O_4)\}_n$, (I) (Fig. 1).



(I)

The X-ray analysis shows that the crystal structure of (I) is centrosymmetric. Each silver(I) cation lies on a twofold rotation axis and has a four-coordinate environment, composed of two S atoms belonging to distinct dtpcp molecules and two N atoms from different acetonitrile molecules. The geometry around the silver(I) cation is tetrahedral. The

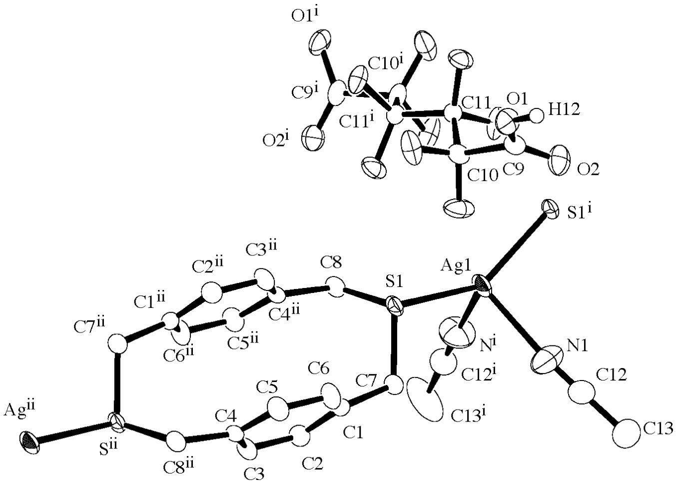


Figure 1
Part of the structure of (I), with the atom-numbering scheme, showing displacement ellipsoids at the 50% probability level. Aromatic H atoms have been omitted for clarity. Atoms F1–F4 and F1^{i}–F4^{i} have been omitted for clarity. [Symmetry codes: (i) $2-x, y, \frac{3}{2}-z$; (ii) $1-x, 1-y, 1-z$.]

Ag—S bond length in (I) [2.4787 (5) Å] is slightly shorter than those in (μ_2-dtpcp)nitritosilver(I) [2.534 (2) and 2.510 (2) Å; Munakata *et al.*, 1996]. The Ag—N bond length in (I) [2.355 (3) Å] is much longer than those found in silver(I) complexes with pyridine derivatives (Jung *et al.*, 2000; Muthu *et al.*, 2002) but close to those in silver(I) polynitrile complexes (Min & Suh, 2000).

The two symmetry-related acetonitrile ligands bonded to Ag have an N1—Ag1—N1^{i} bond angle of 89.8 (1)° [symmetry code: (i) $2-x, y, \frac{3}{2}-z$], indicating their perpendicular nature. The dtpcp ligand is centrosymmetric and bridges two symmetry-related silver centres, utilizing its two S atoms. An infinite one-dimensional chain of $[Ag(C_{16}H_{16}S_2)(C_2H_3N)_2]_n^{n+}$ is thus formed by the silver(I) cations, linking dtpcp ligands and terminal acetonitrile molecules. Interestingly, the HOFA$^-$ anions do not take part in coordination with silver(I) cations but are connected to each other in a head-to-tail mode to give an infinite anion chain, in a perpendicular direction, *via* hydrogen-bond interactions, with an $O_c \cdots O_c$ (c is carboxy) distance of 2.447 (3) Å (Table 2).

There are two kinds of sheets in (I), as shown in Fig. 2. One kind of sheet is formed by parallel $[Ag(C_{16}H_{16}S_2)(C_2H_3N)_2]_n^{n+}$ chains, with an interchain Ag1$^{i}\cdots$Ag1^{ii} distance of 8.79 Å [symmetry codes: (i) $x+1, 1-y, z+\frac{1}{2}$; (ii) $x+1, y, z+1$], while the other kind is given by parallel HOFA$^-$ anion chains with an interchain C9$^{iii}\cdots$C10^{iv} distance of 7.65 Å [symmetry codes: (iii) $\frac{3}{2}+x, \frac{3}{2}-y, z-\frac{1}{2}$; (iv) $\frac{5}{2}-x, \frac{3}{2}-y, 1-z$]. No significant interaction was found between chains or sheets.

Experimental

A solution (3 ml) of mesitylene containing dtpcp (0.03 mmol, 8.1 mg) was introduced into a glass tube and layered with acetonitrile solution (3 ml) containing $AgCF_3CO_2$ (0.04 mmol, 8.8 mg) and octafluoroadipic acid (0.1 mmol, 29.0 mg). The glass tube was sealed under argon. After standing at room temperature for 5 d, colourless block crystals of (I) were isolated at the interface between the two solutions

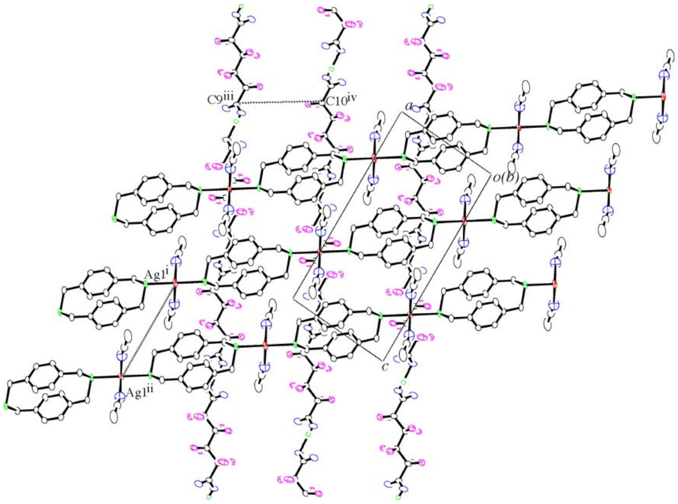


Figure 2
A packing plot of (I), viewed along the *b* axis. Aromatic H atoms have been omitted for clarity. [Symmetry codes: (i) $1+x, 1-y, \frac{1}{2}+z$; (ii) $1+x, y, 1+z$; (iii) $\frac{3}{2}+x, \frac{3}{2}-y, z-\frac{1}{2}$; (iv) $\frac{5}{2}-x, \frac{3}{2}-y, 1-z$.]

(yield 44%). Analysis calculated for $C_{26}H_{23}AgF_8N_2O_4S_2$: C 41.56, H 3.08, N 3.73%; found: C 41.52, H 3.01, N 3.64%.

Crystal data

$[Ag(C_{16}H_{16}S_2)(C_2H_3N)_2]$-
($C_6HF_8O_4$)
$M_r = 751.45$
Monoclinic, $C2/c$
$a = 8.748$ (1) Å
$b = 19.503$ (2) Å
$c = 17.247$ (2) Å
$\beta = 94.842$ (5)°
$V = 2932.2$ (6) Å^3
$Z = 4$

$D_x = 1.702$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 4112 reflections
$\theta = 3.2$–27.5°
$\mu = 0.91$ mm^{-1}
$T = 150.2$ K
Block, colourless
0.20 × 0.20 × 0.15 mm

Data collection

Rigaku/MSC Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1995–1998)
$T_{min} = 0.778$, $T_{max} = 0.872$
11 413 measured reflections

3352 independent reflections
2847 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 11$
$k = -25 \rightarrow 24$
$l = -22 \rightarrow 19$

Refinement

Refinement on F^2
$R(F) = 0.035$ [$I > 2\sigma(I)$]
$wR(F^2) = 0.067$
$S = 1.10$
3352 reflections
223 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 2.7139P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ag1—S1	2.4787 (5)	Ag1—N1	2.355 (3)
Ag1—S1^{i}	2.4787 (5)	Ag1—N1^{i}	2.355 (3)
S1—Ag1—S1^{i}	143.43 (3)	S1^{i}—Ag1—N1	99.61 (7)
S1—Ag1—N1	106.12 (8)	S1^{i}—Ag1—N1^{i}	106.12 (8)
S1—Ag1—N1^{i}	99.61 (7)	N1—Ag1—N1^{i}	89.8 (1)

Symmetry code: (i) $2-x, y, \frac{3}{2}-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H12···O1^{v}	0.79 (5)	1.66 (5)	2.447 (3)	175 (10)

Symmetry code: (v) $\frac{3}{2} - x, \frac{3}{2} - y, 2 - z$.

The acetonitrile H atoms were allowed for as riding atoms at distances of 0.96 Å, with U_{iso}(H) values set at $1.2U_{eq}$(parent atom), while the coordinates of the other H atoms were found in a difference Fourier map and subsequently refined with a common fixed U_{iso}(H) = 0.05 Å^2.

Data collection: *CrystalClear*; cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corportation, 1999); program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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