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# *catena*-Poly[[[diacetonitrilesilver(I)]-$\mu$-2,11-dithia[3.3]paracyclophane-$\kappa^2S$:$S'$] tetrafluoroterephthalate tetrafluoroterephthalic acid acetonitrile tetrasolvate]

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The title compound, $\{[Ag_2(C_{16}H_{16}S_2)_2(C_2H_3N)_4](C_8F_4O_4)\cdot 2C_8H_2F_4O_4\cdot 4C_2H_3N\}_n$, has been prepared from the reaction of 2,11-dithia[3.3]paracyclophane (dtpcp) and *in situ* silver(I) tetrafluoroterephthalate ($TFTP^{2-}$) using an interface method. In the solid state the title compound forms two infinite chains, which are parallel to one another. One chain consists of $[Ag_2(C_{16}H_{16}S_2)_2(C_2H_3N)_4]_n^{2n+}$, and the other is formed from $TFTP^{2-}$ and $H_2TFTP$ *via* $O_c—H\cdots O_c$ ($c$ is carboxy) hydrogen- bonding interactions, with $H\cdots A$ distances of 1.72 (2) and 1.774 (19) Å. The $Ag^I$ ion is tetrahedrally coordinated by two acetonitrile N atoms and two dtpcp S atoms. The cyclophanes have inversion symmetry.

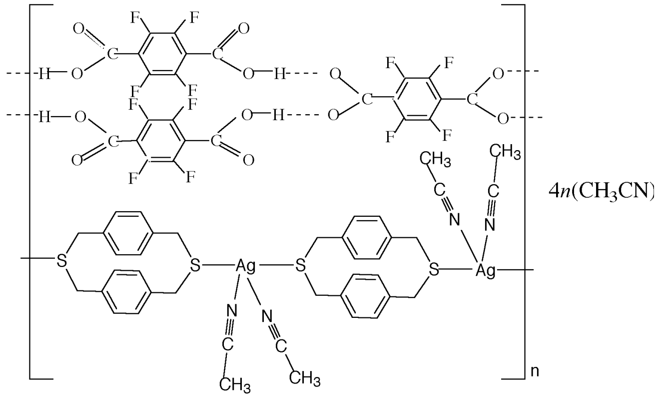
**Key indicators**

Single-crystal X-ray study
$T$ = 150 K
Mean $\sigma$(C–C) = 0.003 Å
$R$ factor = 0.033
$wR$ factor = 0.073
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 design and synthesis of supramolecular frameworks has received much attention in recent years owing to their intriguing structural diversity and their potential applications as functional materials (Eddaoudi *et al.*, 2001; Kitagawa & Kondo, 1998; Seo *et al.*, 2000). Bi- or multidentate ligands containing heteroatoms are often used to coordinate to metal centers (Fujita & Ogura, 1996; Mori & Takamizawa, 2000). 2,11-Dithia[3.3]paracyclophane (dtpcp), involving two S atoms, is a good bridging ligand that can sometimes be used to generate unexpected and interesting coordination polymers (Munakata *et al.*, 1996; Yamanoto *et al.*, 1997; Liu *et al.*, 2004). We report here the crystal structure of the title dtpcp complex, (I), with silver(I) tetrafluoroterephthalate, generated *in situ*.



(I)

Single-crystal X-ray diffraction analysis of (I) reveals that the title compound crystallizes in a triclinic unit cell and consists of $[Ag_2(C_{16}H_{16}S_2)_2(C_2H_3N)_4]_n^{2n+}$ cation chains, $[(TFTP)(2H_2TFTP)]_n^{2n-}$ anion chains (TFTP is tetrafluoroterephthalate) and acetonitrile solvent molecules. Similar to

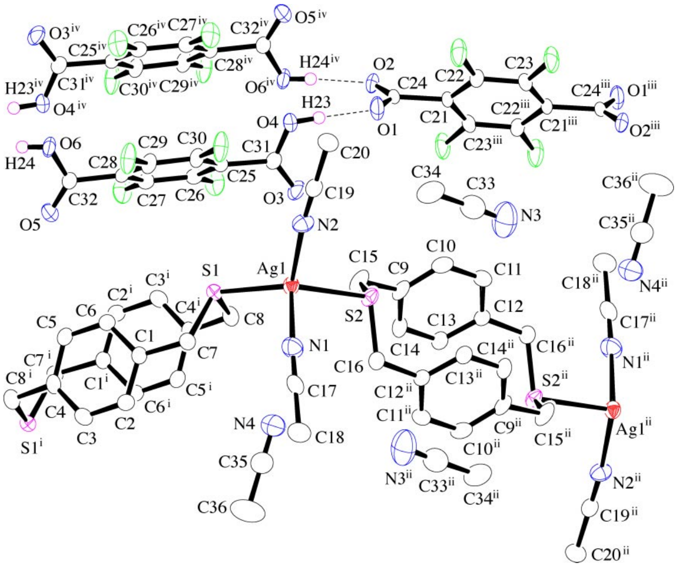


**Figure 1**

Part of the structure of (I), with the atom-numbering scheme, showing displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity. Atoms labels of F atoms have been omitted for clarity. [Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+1, -y+2, -z+2$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x+1, -y+1, -z+1$.]

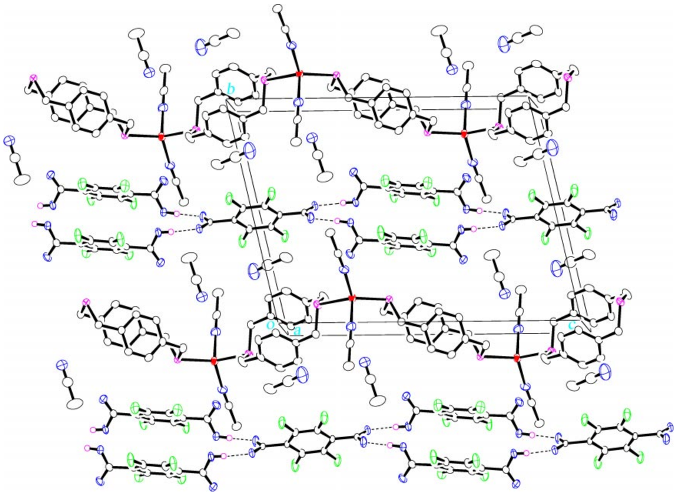


**Figure 2**

A packing plot of (I). Hydrogen bonds are shown as dashed lines. H atoms have been omitted for clarity.

those in $\{[Ag(C_{16}H_{16}S_2)(C_2H_3N)_2](C_6HF_4O_4)\}_n$ (Liu *et al.*, 2004), each $Ag^I$ center is coordinated by two N atoms from different acetonitrile molecules and two S atoms of distinct dtpcp ligands (Fig. 1), and the Ag—S bond lengths [2.5099 (7) and 2.5471 (6) Å] and the Ag—N bond distances [2.369 (2) and 2.306 (2) Å] in (I) are comparable. As shown in Fig. 2, the centrosymmetric dtpcp groups act as *exo*-bidentate ligands, linking four-coordinated $Ag^I$ atoms into a one-dimensional cation chain of $[Ag_2(C_{16}H_{16}S_2)_2(C_2H_3N)_4]_n^{2n+}$, with acetonitrile as terminal ligand. The S1—Ag1—S2 bond angle is 122.13 (3)°, indicative of the presence of a distortion from linearity in the cation chain. On the other hand, an anion chain of $[(TFTP)(2H_2TFTP)]_n^{2n-}$ is formed by an alternate arrangement of one $TFTP^{2-}$ anion and two $H_2TFTP$ molecules, *via* hydrogen-bond interactions, with $O_c\cdots O_c$ (*c* is carboxy) distances of 2.555 (2) and 2.533 (2) Å (Table 2). The cation chains and anion chains are parallel to one another and are alternately arranged along the crystallographic *b* axis (Fig. 2).

## Experimental

A solution (3 ml) of toluene containing dtpcp (0.03 mmol, 8.2 mg) was introduced into a glass tube and layered with an acetonitrile solution (3 ml) containing $AgCF_3CO_2$ (0.04 mmol, 8.8 mg) and tetrafluoroterephthalic acid (0.1 mmol, 23.8 mg). The glass tube was sealed under argon. After standing at room temperature for one week, colorless block crystals of (I) were isolated at the interface between the two solutions (yield 41%).

### *Crystal data*

$[Ag_2(C_{16}H_{16}S_2)_2(C_2H_3N)_4]$-
$(C_8F_4O_4)\cdot 2C_8H_2F_4O_4\cdot 4C_2H_3N$
$M_r = 1801.27$
Triclinic, $P\bar{1}$
$a = 7.416$ (3) Å
$b = 14.319$ (6) Å
$c = 18.883$ (7) Å
$\alpha = 101.449$ (9)°
$\beta = 93.00$ (1)°
$\gamma = 104.107$ (8)°
$V = 1895$ (1) Å$^3$

$Z = 1$
$D_x = 1.578$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 6117 reflections
$\theta = 3.1$–27.5°
$\mu = 0.72$ mm$^{-1}$
$T = 150.2$ K
Block, colorless
0.15 × 0.15 × 0.15 mm

### *Data collection*

Rigaku/MSC Mercury CCD diffractometer
$\omega$ scans
Absorption correction: multi-scan (Jacobson, 1995–1998)
$T_{min} = 0.791$, $T_{max} = 0.898$
14 697 measured reflections

8279 independent reflections
7115 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 18$
$l = -22 \rightarrow 24$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.073$
$S = 1.03$
7115 reflections
554 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 0.5618P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.45$ e Å$^{-3}$
$\Delta\rho_{min} = -0.41$ e Å$^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ag1—S1 | 2.5099 (7) | Ag1—N1 | 2.369 (2) |
| Ag1—S2 | 2.5471 (6) | Ag1—N2 | 2.306 (2) |
| | | | |
| S1—Ag1—S2 | 122.13 (3) | S2—Ag1—N1 | 101.35 (6) |
| S1—Ag1—N1 | 106.50 (6) | S2—Ag1—N2 | 104.74 (6) |
| S1—Ag1—N2 | 119.17 (5) | N1—Ag1—N2 | 99.01 (8) |

**Table 2**

Hydrogen-bonding geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O4—H23$\cdots$O1 | 0.84 (2) | 1.71 (3) | 2.555 (2) | 177 (3) |
| O6$^{iv}$—H24$^{iv}\cdots$O2 | 0.77 (2) | 1.77 (3) | 2.533 (2) | 171 (4) |

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

*Acta Cryst.* (2004). E**60**, m1504–m1506 Liu *et al.* • An Ag–$C_{16}H_{16}S_2$–$C_2H_3N$ polymer **m1505**

The acetonitrile H atoms were treated as riding atoms at a distance of 0.96 Å, with $U_{\rm iso}$(H) values set at $1.2U_{\rm eq}$(parent atom), while the positions of the other H atoms were found in a difference Fourier map and were subsequently refined, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. Atomic coordinates of atoms H23 and H24 were refined freely. Atoms H1–H16 and H23/H24 were refined with a fixed $U_{\rm iso}$ value of 0.036 Å$^2$.

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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