

## A two-dimensional network formed by self-associating silver(I) perchlorate with 3-[4-(2-thienyl)-2H-cyclopenta[*d*]pyridazin-1-yl]benzotrile

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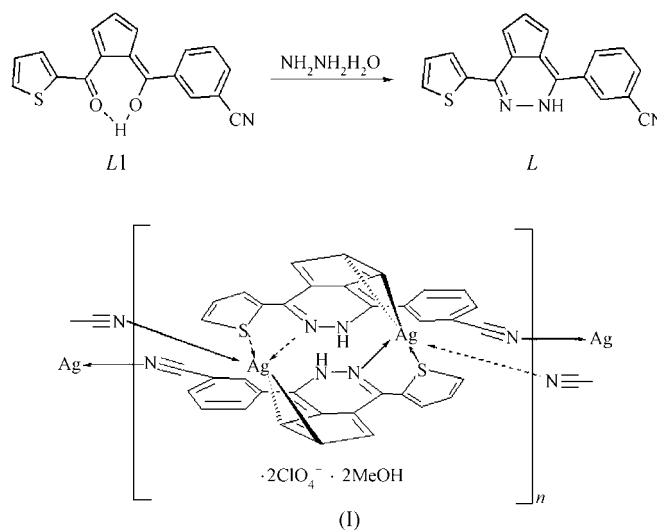
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In the organometallic silver(I) supramolecular complex poly[[silver(I)- $\mu_3$ -3-[4-(2-thienyl)-2H-cyclopenta[*d*]pyridazin-1-yl]benzotrile] perchlorate methanol solvate],  $\{[\text{Ag}(\text{C}_{18}\text{H}_{11}\text{N}_3\text{S})](\text{ClO}_4) \cdot \text{CH}_3\text{OH}\}_n$ , there is only one type of  $\text{Ag}^{\text{I}}$  center, which lies in an  $\{\text{AgN}_2\text{S}\pi\}$  coordination environment. Two unsymmetric multidentate 3-[4-(2-thienyl)-2H-cyclopenta[*d*]pyridazin-1-yl]benzotrile (*L*) ligands link two  $\text{Ag}^{\text{I}}$  atoms through  $\pi$ - $\text{Ag}^{\text{I}}$  interactions into an organometallic box-like unit, from which two 3-cyanobenzoyl arms stretch out in opposite directions and bind two  $\text{Ag}^{\text{I}}$  atoms from neighboring box-like building blocks. This results in a novel two-dimensional network extending in the crystallographic *bc* plane. These two-dimensional sheets stack together along the crystallographic *a* axis to generate parallelogram-like channels. The methanol solvent molecules and the perchlorate counter-ions are located in the channels, where they are fixed by intermolecular hydrogen-bonding interactions. This architecture may provide opportunities for host-guest chemistry, such as guest molecule loss and absorption or ion exchange. The new fulvene-type multidentate ligand *L* is a good candidate for the preparation of Cp- $\text{Ag}^{\text{I}}$ -containing (Cp is cyclopentadienyl) organometallic coordination polymers or supramolecular complexes.

### Comment

The design and synthesis of supramolecular complexes exhibiting novel structures and properties have provided exciting new prospects for chemists (Fujita *et al.*, 1995; Hagrman *et al.*, 1999; Dong *et al.*, 2000; Kitagawa *et al.*, 2004). It is well known that fulvene is one of the most important classes of ligands in organometallic chemistry, and it is widely used in the construction of organometallic complexes (Little, 1961; Knox & Pauson, 1961; Stone & Little, 1984). In principle, the abundant coordination chemistry of fulvene could afford us an

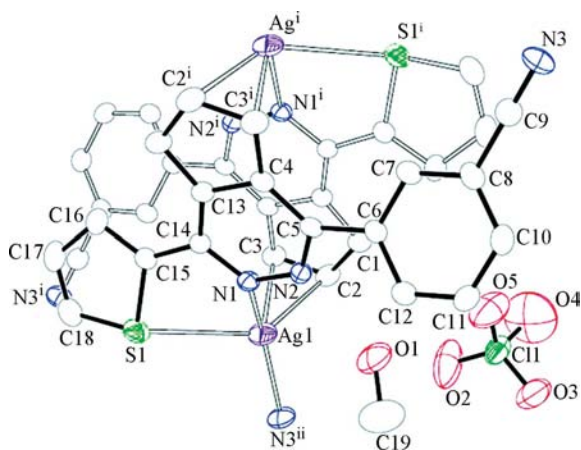
excellent opportunity to construct organic-inorganic hybrid materials that might be different in topology and physical and chemical properties from those based on common organic spacers. A continuing project in our laboratory has been the development of organometallic coordination frameworks generated from conjugated symmetric and unsymmetric fulvene ligands, which can adopt either *cis* or *trans* conformations to bind the soft acid  $\text{Ag}^{\text{I}}$  ion through not only the terminal  $-\text{CN}$  and furan or thiophene functional groups but also the fulvene C atoms into organometallic coordination polymers or discrete complexes (Dong *et al.*, 2002, 2003; Dong, Jin *et al.*, 2004; Dong, Wang *et al.*, 2004; Wang *et al.*, 2005). In this paper, we report a novel two-dimensional network which was formed by the self-assembly reaction of a new fulvene ligand with silver perchlorate. We have recently synthesized the new multidentate thiophene- and benzotrile-containing unsymmetric fulvene ligand 3-[4-(2-thienyl)-2H-cyclopenta[*d*]pyridazin-1-yl]benzotrile (*L*) and investigated its self-assembly reaction with  $\text{Ag}^{\text{I}}$  salts. Crystallization of *L* with  $\text{AgClO}_4$  in a methylene chloride/methanol mixed solvent system at room temperature afforded a new organometallic supramolecular complex, (I).



There is only one type of  $\text{Ag}^{\text{I}}$  center in (I), which lies in an  $\{\text{AgN}_2\text{S}\pi\}$  coordination environment (Fig. 1). Two N atoms [N1 and N3<sup>ii</sup>; symmetry code: (ii)  $-x, y - \frac{1}{2}, -z + \frac{1}{2}$ ] from the pyridazine ring and  $-\text{CN}$  donors of different ligands [ $\text{Ag1}-\text{N1} = 2.313(5) \text{ \AA}$  and  $\text{Ag1}-\text{N3}^{\text{ii}} = 2.171(6) \text{ \AA}$ ], one S atom from a thiophene ring, which comes from the same ligand as the pyridazine group [ $\text{Ag1}-\text{S1} = 2.935(2) \text{ \AA}$ ], and one  $\pi$ -donor from a coordinated cyclopentadienyl (Cp) ring of a third neighboring ligand constitute the  $\text{Ag}^{\text{I}}$  coordination environment. The two  $\text{Ag}-\text{C}$  bond lengths [2.624(7) and 2.650(7)  $\text{ \AA}$ ] lie in the range of normal  $\text{Ag}-\text{C}$  distances (2.47–2.86  $\text{ \AA}$ ), while the remaining  $\text{Ag}-\text{C}$  contacts are greater than 3.12  $\text{ \AA}$ , which is beyond the limit commonly observed in  $\text{Ag}^{\text{I}}$ -aromatic complexes. Thus, the substituted five-membered Cp ring in *L* coordinates to the  $\text{Ag}^{\text{I}}$  ion with an  $\eta^2$  binding mode, which is typical of arene-silver complexes (Munakata *et al.*,

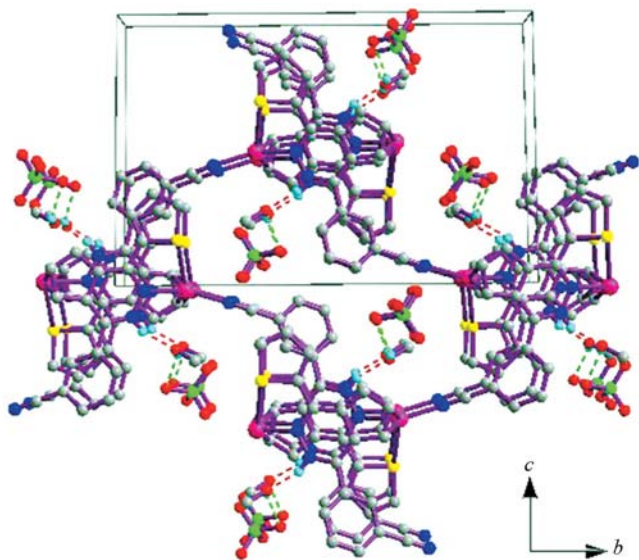
2000). In our previous work, some similar fulvene-type ligands, such as 4-[2-phenyl-4-(2-thienyl)-2*H*-cyclopenta[*d*]-pyridazin-1-yl]benzotrile (Dong *et al.*, 2006) and 4-[4-(furan-2-yl)-2*H*-cyclopenta[*d*]pyridazin-1-yl]benzotrile (Dong *et al.*, 2005), displayed different coordination modes with Ag<sup>I</sup> ions. In particular, the S atom from the thiophene ring or the O atom from the furan ring of the ligand did not coordinate to the Ag<sup>I</sup> ion.

In the solid state in (I), two *L* ligands link two Ag<sup>I</sup> atoms through  $\pi$ -Ag<sup>I</sup> and heteroatom-Ag<sup>I</sup> interactions into an organometallic box-like unit (Fig. 1), from which two 3-cyanobenzoyl arms stretch out in opposite directions and bind two Ag<sup>I</sup> atoms in neighboring box-like building blocks. This results in a novel two-dimensional network extending in



**Figure 1**

A view of (I), with displacement ellipsoids drawn at the 30% probability level. For the sake of clarity, only the major component of the anion is shown. H atoms have been omitted. [Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $-x, y - \frac{1}{2}, -z + \frac{1}{2}$ ]



**Figure 2**

The crystal packing of (I), viewed along the *a* axis. Methanol solvent molecules and perchlorate counter-ions are located in channels, where they are fixed by intermolecular hydrogen-bonding interactions (dashed lines).

the crystallographic *bc* plane (Fig. 2). The Ag $\cdots$ Ag distance within an individual cage is 6.796 (2) Å. Similar organometallic cages with related fulvene ligands have been observed previously, linked into one-dimensional chains (Dong *et al.*, 2005). By contrast, we obtained here a novel two-dimensional network by linking these box-like units.

This two-dimensional network contains a parallelogram-like macrocycle with approximate (crystallographic) dimensions of 16.2  $\times$  7.7 Å (Fig. 2). The sheets stack along the crystallographic *a* axis, thus propagating the parallelogram-like channels in this direction. The methanol solvent molecules and perchlorate anions are located in the channels, where they are held in place by hydrogen bonds. The first hydrogen bond (O $\cdots$ H–N) consists of the O atom of the methanol solvent molecule and the NH group in the pyridazine ring of the ligand *L*. The second hydrogen bond (O–H $\cdots$ O) involves the OH group of the methanol molecule and an O atom of the perchlorate ion. The guest methanol molecules and perchlorate counter-ions are thus fixed in place by intermolecular hydrogen-bonding interactions. Self-assembled coordination polymers containing cavities or channels play an important role in materials science because of their potential applications in adsorption and desorption and host–guest chemistry. The intriguing architecture and topology in (I) may provide opportunities for this type of behavior.

To date, a number of Ag<sup>I</sup>-containing coordination polymers have been successfully generated from inorganic silver salts and various types of rigid and flexible organic spacers based on Ag–heteroatom (Hagrman *et al.*, 1999; Blake *et al.*, 1999; Dong *et al.*, 2002) or Ag– $\pi$  interactions (Batten & Robson, 1998; Li *et al.*, 2000). In contrast, the chemistry of supramolecular architectures based on fulvene molecules has received considerably less attention. In our previous work (Dong *et al.*, 2005), we synthesized some fulvene-type ligands and obtained a series of coordination polymers by self-assembly of fulvene ligands with various silver salts. In general, these ligands linked Ag atoms through cyclopentadienyl  $\pi$ -Ag and pyridazine N–Ag interactions into one-dimensional zigzag chains. However, in (I), the ligands bind Ag atoms through cyclopentadienyl  $\pi$ -Ag and cyano group N–Ag interactions to form one-dimensional wavy chains. These wavy chains are then linked by the pyridazine N–Ag interactions into a two-dimensional network. Thus, the fulvene organic spacer reported here appears to be a good candidate for the preparation of Cp–Ag<sup>I</sup>-containing organometallic coordination supramolecular complexes. This encourages us to undertake further studies on fulvene ligands of this type and explore their interesting coordination chemistry.

## Experimental

The fulvene ligand *L1* (see reaction scheme in *Comment*) was prepared according to the method of Dong *et al.* (2005). A solution of *L1* (0.4 g) in anhydrous EtOH (20 ml) and a large excess of hydrazine hydrate was heated to reflux for about 7 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure to give a red–orange solid. The product was recrystallized

from EtOH to give orange crystals of *L*. A solution of AgClO<sub>4</sub> (20.7 mg, 0.10 mmol) in MeOH (10 ml) was layered on to a solution of *L* (29.1 mg, 0.10 mmol) in methylene chloride (10 ml). The solutions were left for about one week at room temperature, and yellow single crystals of (**1**) suitable for single-crystal X-ray diffraction were obtained after that time.

#### Crystal data

[Ag(C <sub>18</sub> H <sub>11</sub> N <sub>3</sub> S)]ClO <sub>4</sub> ·CH <sub>4</sub> O	$V = 1961.3 (8) \text{ \AA}^3$
$M_r = 540.72$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.2729 (17) \text{ \AA}$	$\mu = 1.31 \text{ mm}^{-1}$
$b = 20.340 (5) \text{ \AA}$	$T = 298 (2) \text{ K}$
$c = 13.608 (3) \text{ \AA}$	$0.34 \times 0.24 \times 0.07 \text{ mm}$
$\beta = 103.022 (3)^\circ$	

#### Data collection

Bruker SMART CCD area-detector diffractometer	8044 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3443 independent reflections
$T_{\min} = 0.665$ , $T_{\max} = 0.914$	2713 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.054$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$	3 restraints
$wR(F^2) = 0.181$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 1.74 \text{ e \AA}^{-3}$
3443 reflections	$\Delta\rho_{\text{min}} = -1.06 \text{ e \AA}^{-3}$
272 parameters	

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2A\cdots O1$	0.86	1.91	2.714 (7)	155
$O1-H1A\cdots O5$	0.93	2.30	3.049 (13)	137

H atoms were placed in geometrically idealized positions and included as riding atoms, with C–H distances of 0.93 (aromatic CH;  $sp^2$ ), 0.98 (aromatic CH with C coordinated to Ag;  $sp^3$ ) and 0.96  $\text{\AA}$  (CH<sub>3</sub>), an N–H distance of 0.86  $\text{\AA}$ , and an O–H distance of 0.93  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H})$  values set at  $1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and at  $1.2U_{\text{eq}}(\text{C}, \text{N}, \text{O})$  otherwise.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics:

SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3178). Services for accessing these data are described at the back of the journal.

#### References

- Batten, S. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
- Blake, A. J., Champness, N. R., Hubberstey, P., Li, W.-S., Withersby, M. A. & Schroder, M. (1999). *Coord. Chem. Rev.* **183**, 117–138.
- Bruker (1997). SMART (Version 5.6) and SAINT (Version 5.A06). Bruker AXS Inc., Madison, Wisconsin, USA.
- Dong, Y.-B., Geng, Y., Ma, J.-P. & Huang, R.-Q. (2005). *Inorg. Chem.* **44**, 1693–1703.
- Dong, Y.-B., Geng, Y., Ma, J.-P. & Huang, R.-Q. (2006). *Organometallics*, **25**, 447–462.
- Dong, Y.-B., Jin, G.-X., Smith, M. D., Huang, R.-Q., Tong, B. & zur Loye, H. C. (2002). *Inorg. Chem.* **41**, 4909–4914.
- Dong, Y.-B., Jin, G.-X., Zhao, X., Huang, R.-Q., Smith, M. D., Stitzer, K. E. & zur Loye, H. C. (2004). *Organometallics*, **23**, 1604–1609.
- Dong, Y.-B., Smith, M. D. & zur Loye, H.-C. (2000). *Angew. Chem. Int. Ed.* **39**, 4271–4273.
- Dong, Y.-B., Wang, P., Huang, R.-Q. & Smith, M. D. (2004). *Inorg. Chem.* **43**, 4727–4739.
- Dong, Y.-B., Zhao, X., Jin, G.-X., Huang, R.-Q. & Smith, M. D. (2003). *Eur. J. Inorg. Chem.* **22**, 4017–4024.
- Fujita, M., Kwon, Y. J., Sasaki, O., Yamaguchi, K. & Ogura, K. (1995). *J. Am. Chem. Soc.* **117**, 7287–7288.
- Hagrman, P. J., Hagrman, D. & Zubieta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 2638–2684.
- Kitagawa, S., Kitayra, R. & Noro, S. (2004). *Angew. Chem. Int. Ed.* **43**, 2334–2375.
- Knox, G. R. & Pauson, P. L. (1961). *J. Chem. Soc.* pp. 4610–4614.
- Li, M.-X., Cheung, K.-K. & Mayr, A. (2000). *J. Solid State Chem.* **152**, 247–252.
- Little, W. F. (1961). *J. Org. Chem.* **26**, 3247–3250.
- Munakata, M., Wu, L. P. & Ning, G. L. (2000). *Coord. Chem. Rev.* **198**, 171–203.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Stone, K. J. & Little, R. D. (1984). *J. Org. Chem.* **49**, 1849–1853.
- Wang, P., Dong, Y.-B., Ma, J.-P., Huang, R.-Q. & Smith, M. D. (2005). *Cryst. Growth Des.* **5**, 701–706.