

# A cyclic tetramer of [Ag(1,4,7-trithia-cyclononane)]<sup>+</sup>, *cyclo-tetrakis*( $\mu$ -1,4,7-trithiacyclononane- $\kappa^3S^1, S^4, S^7$ : $\kappa S^1$ )-tetrasilver(I) tetrakis(trifluoromethanesulfonate) nitromethane disolvate

Tadashi Yamaguchi,\* Fumie Yamazaki and Tasuku Ito

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan  
Correspondence e-mail: yamaguchi@agnus.chem.tohoku.ac.jp

Received 2 November 2001

Accepted 21 January 2002

Online 12 March 2002

(1,4,7-Trithiacyclononane)silver trifluoromethanesulfonate crystallizes in a tetrameric form from nitromethane, to give the title compound, [Ag<sub>4</sub>(C<sub>6</sub>H<sub>12</sub>S<sub>3</sub>)<sub>4</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>·2CH<sub>3</sub>NO<sub>2</sub>. The complex cation consists of four [AgL]<sup>+</sup> units (*L* is 1,4,7-trithiacyclononane), with four Ag—S—Ag bridges forming a cyclic tetramer. The almost planar Ag<sub>4</sub>S<sub>4</sub> ring takes an octagonal form.

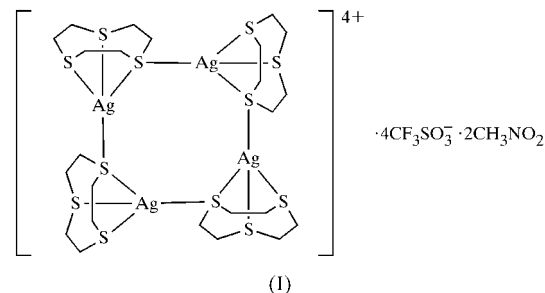
## Comment

Recently, molecular squares and related cyclic oligomers of metal complexes constructed by self-assembly have attracted much attention in supramolecular chemistry (Fujita & Ogura, 1996; Leininger *et al.*, 2000). Thia-macrocyclic ligands have a tendency to form oligomeric complexes with metal ions such as Ag<sup>+</sup> (Blower *et al.*, 1989; Blake *et al.*, 2000). A cyclic trimer of [AgL]<sup>+</sup> (*L* is 1,4,7-trithiacyclononane) was reported to be present in a crystal obtained from a reaction between AgClO<sub>4</sub> and *L* in methanol, *i.e.* [Ag<sub>3</sub>L<sub>3</sub>][AgL<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (Küppers *et al.*, 1987). The <sup>1</sup>H NMR spectrum of this complex indicates a rapid ligand-exchange equilibrium in solution, and the possibility of another type of oligomer was considered. In this paper, we report the tetrameric structure of [AgL]<sup>+</sup> observed in [AgL]<sub>4</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>·2CH<sub>3</sub>NO<sub>2</sub>, (I). By changing the counter-anion, solvent and metal–ligand ratio, it is possible to form the tetramer rather than the previously reported trimer.

The complex cation in (I) consists of four [AgL]<sup>+</sup> units (Fig. 1), with the macrocyclic ligand *L* coordinating to Ag<sup>+</sup>. One of the three S atoms in each [AgL]<sup>+</sup> unit acts as a bridging ligand to another [AgL]<sup>+</sup> unit, forming an approximately octagonal skeletal structure comprised of four Ag<sup>+</sup> and four S atoms. All the angles at the corners of the Ag<sub>4</sub>S<sub>4</sub> octagon are close to 135°. There is a crystallographic inversion centre at

the centre of the complex cation, and therefore two non-equivalent [AgL]<sup>+</sup> units exist.

The Ag<sub>4</sub>S<sub>4</sub> ring is almost flat, with a maximum deviation from the mean plane of 0.11 Å for atom S1. It is interesting to compare (I) with the cyclic trimer, which also has a planar Ag<sub>3</sub>S<sub>3</sub> ring, with a corner angle of *ca* 120°.



Each Ag<sup>+</sup> ion in the tetramer has a distorted tetrahedral geometry, with one short [Ag1—S4<sup>i</sup> 2.460 (2) Å and Ag2—S1 2.443 (2) Å; symmetry code: (i)  $-x, -y, 1-z$ ] and three long [2.560 (2)–2.660 (2) Å] Ag—S distances, with the shortest distance involving the bridging S atoms. These Ag—S distances are slightly longer than normal, but similar silver complexes with *L* have comparable Ag—S distances (2.58–2.70 Å; Küppers *et al.*, 1987; Blower *et al.*, 1989). The shortest Ag—S bond in each unit is tilted slightly, away from a pseudo-threefold axis based on the macrocyclic ligand, and three S—Ag—S(adjacent) angles, which involve the unique Ag—S bond, are not equal and are classified as one small [119.15 (6) and 123.01 (6)°] and two large angles [131.98 (6)–134.47 (6)°]. A similar distortion has been observed in tetrahedral [AgL] moieties in the trimer (Küppers *et al.*, 1987) and in [AgLCl] (Blower *et al.*, 1989), and the distortion in (I) is small relative to that in other complexes.

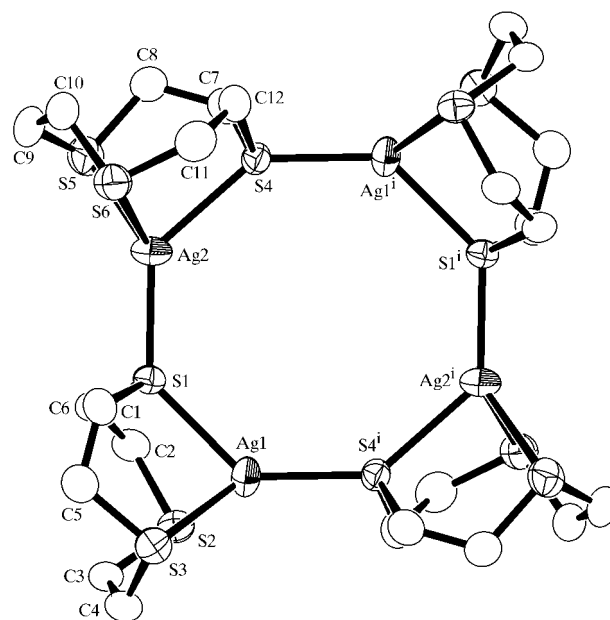


Figure 1

A view of the molecular structure of the tetrameric complex cation in (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

One of the two large S—Ag—S(adjacent) angles in each unit is involved in the Ag<sub>4</sub>S<sub>4</sub> octagon, whereas in the trimer, the unique small S—Ag—S(adjacent) angle is involved in the Ag<sub>3</sub>S<sub>3</sub> ring. Concomitantly, the Ag—S—Ag angles in (I) are larger [134.02 (7) and 139.36 (7)°] than that in the trimer [126.0 (1)°].

## Experimental

[AgL](CF<sub>3</sub>SO<sub>3</sub>) was synthesized according to the published method of Blower *et al.* (1989). A crystal of (I) was obtained by slow evaporation of a nitromethane solution of [AgL](CF<sub>3</sub>SO<sub>3</sub>).

### Crystal data

[Ag <sub>4</sub> (C <sub>6</sub> H <sub>12</sub> S <sub>3</sub> ) <sub>4</sub> ](CF <sub>3</sub> SO <sub>3</sub> ) <sub>4</sub> · 2CH <sub>3</sub> NO <sub>2</sub>	$D_x = 2.015 \text{ Mg m}^{-3}$
$M_r = 1871.17$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 24 reflections
$a = 14.877 (4) \text{ \AA}$	$\theta = 11.0\text{--}12.4^\circ$
$b = 14.775 (3) \text{ \AA}$	$\mu = 1.88 \text{ mm}^{-1}$
$c = 15.581 (4) \text{ \AA}$	$T = 296.2 \text{ K}$
$\beta = 115.80 (2)^\circ$	Prismatic, colourless
$V = 3083 (1) \text{ \AA}^3$	$0.15 \times 0.15 \times 0.10 \text{ mm}$
$Z = 2$	

### Data collection

Rigaku AFC-7S diffractometer	3810 reflections with $F^2 > 2\sigma(F^2)$
$\omega/2\theta$ scans	$R_{\text{int}} = 0.021$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$\theta_{\text{max}} = 25^\circ$
$T_{\text{min}} = 0.753$ , $T_{\text{max}} = 0.828$	$h = -17 \rightarrow 0$
5904 measured reflections	$k = 0 \rightarrow 17$
5433 independent reflections	$l = -16 \rightarrow 18$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ag1—S1	2.596 (2)	Ag2—S1	2.443 (2)
Ag1—S2	2.660 (2)	Ag2—S4	2.645 (2)
Ag1—S3	2.571 (2)	Ag2—S5	2.560 (2)
Ag1—S4 <sup>i</sup>	2.460 (2)	Ag2—S6	2.577 (2)
S1—Ag1—S2	82.71 (5)	S1—Ag2—S5	131.98 (6)
S1—Ag1—S3	84.21 (5)	S1—Ag2—S6	123.01 (6)
S1—Ag1—S4 <sup>i</sup>	133.82 (5)	S4—Ag2—S5	83.76 (6)
S2—Ag1—S3	83.96 (5)	S4—Ag2—S6	83.47 (5)
S2—Ag1—S4 <sup>i</sup>	119.15 (6)	S5—Ag2—S6	85.60 (6)
S3—Ag1—S4 <sup>i</sup>	134.47 (6)	Ag1—S1—Ag2	134.02 (7)
S1—Ag2—S4	132.32 (5)	Ag1 <sup>i</sup> —S4—Ag2	139.36 (7)

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

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R(F) = 0.047$	$w = 1/[\sigma^2(F_o^2) + \{0.059[\max(F_o^2, 0) + 2F_c^2]/3\}^2]$
$wR(F^2) = 0.133$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.18$	$\Delta\rho_{\text{max}} = 1.15 \text{ e \AA}^{-3}$
5433 reflections	$\Delta\rho_{\text{min}} = -0.53 \text{ e \AA}^{-3}$
361 parameters	

H atoms were placed in calculated positions, with C—H = 0.95  $\text{\AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  of the bonded C atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Rigaku, 1999); program(s) used to solve structure: *DIRDIF92* (Beurskens *et al.*, 1992); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

This work was supported by Grants-in-Aid for Scientific Research (No. 12640531 and Priority Areas 'Metal-assembled Complexes' No. 10149102) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1126). Services for accessing these data are described at the back of the journal.

## References

- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., García-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Blake, A. J., Champness, N. R., Howdle, S. M. & Webb, P. B. (2000). *Inorg. Chem.* **39**, 1035–1038.
- Blower, P. J., Clarkson, J. A., Rawle, S. C., Hartman, J. R., Wolf, R. E. Jr, Yagbasan, R., Bott, S. G. & Cooper, S. R. (1989). *Inorg. Chem.* **28**, 4040–4046.
- Fujita, M. & Ogura, G. (1996). *Bull. Chem. Soc. Jpn.* **69**, 1471–1482.
- Küppers, H.-J., Wieghardt, K., Tsay, Y.-H., Kruger, K., Nuber, B. & Weiss, J. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 575–576.
- Leininger, S., Olenyuk, B. & Stang, P. J. (2000). *Chem. Rev.* **100**, 853–907.
- Molecular Structure Corporation (1994). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Rigaku (1999). *TEXSAN*. Version 1.10. Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.