

## (1,4,7,11,14,17-Hexathia-9,9,19,19-tetrahydroxymethylcycloicosane)silver(I) nitrate

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## Key indicators

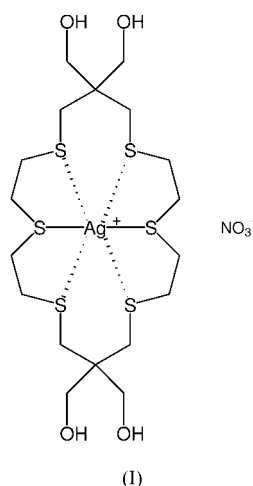
Single-crystal X-ray study  
T = 150 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$   
Disorder in solvent or counterion  
R factor = 0.050  
wR factor = 0.123  
Data-to-parameter ratio = 17.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the crystal structure of the title compound,  $[\text{Ag}(\text{C}_{18}\text{H}_{36}\text{S}_6\text{O}_4)] \cdot \text{NO}_3$ , the asymmetric unit comprises two structurally independent, but conformationally similar, complexes, both of which have crystallographic  $2/m$  symmetry. The nitrate counterions were modelled as rotationally disordered, with N atoms on  $2/m$  special positions.

## Comment

The title compound, (I), was of interest to us in the context of an investigation of structure–function relationships underlying metal-ion recognition by thioether donor ligands (Lee *et al.*, 2002).

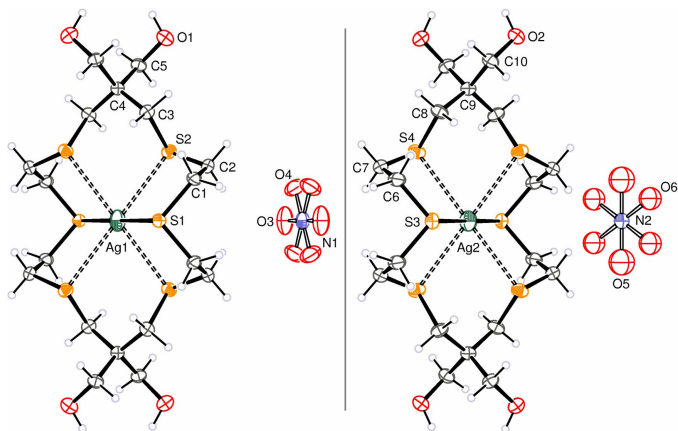


The crystal structure contains two structurally independent, but conformationally similar, silver complexes, both of which have crystallographic  $2/m$  symmetry (atoms Ag1 and Ag2 on  $2/m$  sites, S1 and S3 on special positions with symmetry  $m$ , C4 and C9 on twofold axes). The nitrate counterions were modelled as rotationally disordered, with N atoms N1 and N2 on  $2/m$  special positions. *ORTEP-3* (Farrugia, 1997) depictions of the molecular components of the crystal structure are given in Fig. 1.

The  $\text{Ag}^{\text{I}}$  coordination is linear, with  $\text{Ag1}-\text{S1}$  and  $\text{Ag2}-\text{S3}$  bond lengths of 2.650 (2) and 2.632 (2)  $\text{\AA}$ , respectively (shown as solid bonds in Fig. 1). The remaining four S atoms in each complex are organized around the silver centres, with  $\text{S2} \cdots \text{Ag1}$  and  $\text{S4} \cdots \text{Ag2}$  contact distances of 2.97 and 2.98  $\text{\AA}$ , respectively (shown as dashed lines in Fig. 1); the resulting arrangement of sulfur donors around the  $\text{Ag}^{\text{I}}$  atom is distorted octahedral (see Table 1 for geometric details).

A search of the Cambridge Structural Database (CSD, Version 5.24, Allen, 2002) showed that there is considerable

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**Figure 1**

ORTEP depictions of the crystallographically independent complexes in the crystal structure of (I). Both complexes display  $2/m$  crystallographic symmetry. Nitrate counterions are modelled as rotationally disordered on  $2/m$  special positions. The nitrate anion associated with atom N1 has two coplanar orientations. The nitrate anion associated with N2 was modelled with four orientations, two of which are shown. Displacement ellipsoids are drawn at the 50% probability level.

variation in reported  $\text{Ag}^{\text{I}}-\text{S}$  bond lengths (566 observations, range 2.40–3.00 Å, mean 2.63 Å, s.u. 0.13). The longer contact distances in this structure ( $\text{S}2 \cdots \text{Ag}1$  and  $\text{S}4 \cdots \text{Ag}2$ ) are at the upper limit of  $\text{Ag}-\text{S}$  bond lengths and, while possibly not true coordinate bonds, these contacts are almost certainly significant in the observed configurational organization of the relatively flexible ligands around the  $\text{Ag}^{\text{I}}$  centres.

The only significant intermolecular interactions are hydrogen bonds between the hydroxy groups and the nitrate counterions, details of which are presented in Table 2, together with normal ionic interactions.

## Experimental

The ligand 1,4,7,11,14,17-hexathia-9,9,19,19-tetrahydroxymethylcycloicosane was prepared according to the method of Setzer *et al.* (1998). The mass spectrum, ES  $m/z = 508.9$  ( $L + \text{H}$ )<sup>+</sup>, was in accord with the expected product; the melting point was 430–431 K. The title compound was prepared by the following procedure: A solution of silver(I) nitrate (3.7 mg, 0.022 mmol) in acetonitrile (0.20 ml) was added dropwise to a stirred suspension of the ligand (5.6 mg, 0.022 mmol) in ethanol (10 ml). Complexation was evident by the rapid dissolution of the ligand, resulting in a clear colourless reaction solution. Large colourless prismatic crystals suitable for X-ray structure determination were obtained by slow evaporation of the solvent in the absence of light.

### Crystal data

$[\text{Ag}(\text{C}_{18}\text{H}_{36}\text{O}_4\text{S}_6)] \cdot \text{NO}_3$   
 $M_r = 678.71$   
 Monoclinic,  $C2/m$   
 $a = 13.933$  (7) Å  
 $b = 19.401$  (10) Å  
 $c = 11.851$  (6) Å  
 $\beta = 125.907$  (7) $^\circ$   
 $V = 2595$  (2) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.737$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 943 reflections  
 $\theta = 3.0\text{--}28.1$  $^\circ$   
 $\mu = 1.30$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 Irregular, colourless  
 $0.43 \times 0.34 \times 0.25$  mm

### Data collection

Bruker SMART 1000 CCD diffractometer

$\omega$  scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1999)

$T_{\text{min}} = 0.585$ ,  $T_{\text{max}} = 0.723$

12 618 measured reflections

3180 independent reflections

3036 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\text{max}} = 28.3$  $^\circ$

$h = -18 \rightarrow 17$

$k = -25 \rightarrow 25$

$l = -15 \rightarrow 15$

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.123$

$S = 1.24$

3180 reflections

181 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0022P)^2 + 34.9089P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.85$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.95$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å,  $^\circ$ ).

S1—Ag1	2.6504 (18)	S3—Ag2	2.632 (2)
S2—Ag1	2.9730 (16)	S4—Ag2	2.9842 (16)
S1—Ag1—S1 <sup>i</sup>	180.00 (4)	S3—Ag2—S3 <sup>iii</sup>	180.00 (5)
S1—Ag1—S2	76.36 (4)	S3—Ag2—S4	76.50 (4)
S1—Ag1—S2 <sup>i</sup>	103.64 (4)	S4 <sup>iv</sup> —Ag2—S4	106.75 (6)
S2—Ag1—S2 <sup>i</sup>	180.00 (9)	S4—Ag2—S4 <sup>v</sup>	73.25 (6)
S2—Ag1—S2 <sup>ii</sup>	73.95 (6)	S3—Ag2—S4 <sup>iii</sup>	103.50 (4)
S2 <sup>i</sup> —Ag1—S2 <sup>ii</sup>	106.05 (6)	S4—Ag2—S4 <sup>iii</sup>	180.0

Symmetry codes: (i)  $1 - x, -y, -z$ ; (ii)  $1 - x, y, -z$ ; (iii)  $1 - x, -y, 1 - z$ ; (iv)  $x, -y, z$ ; (v)  $1 - x, y, 1 - z$ .

**Table 2**

Hydrogen-bonding geometry (Å,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1O $\cdots$ O4 <sup>vi</sup>	0.912 (19)	1.96 (3)	2.857 (9)	167 (6)
O1—H1O $\cdots$ O4 <sup>vii</sup>	0.912 (19)	2.09 (3)	2.963 (10)	160 (4)
O2—H2O $\cdots$ O5 <sup>viii</sup>	0.889 (19)	1.86 (3)	2.728 (13)	164 (4)
O2—H2O $\cdots$ O6 <sup>ix</sup>	0.889 (19)	2.02 (4)	2.862 (14)	157 (6)
O2—H2O $\cdots$ O8 <sup>viii</sup>	0.889 (19)	2.06 (4)	2.905 (19)	159 (6)
O2—H2O $\cdots$ O8 <sup>x</sup>	0.889 (19)	2.10 (3)	2.94 (2)	157 (3)

Symmetry codes: (vi)  $\frac{1}{2} - x, -\frac{1}{2} - y, -z$ ; (vii)  $\frac{1}{2} + x, -\frac{1}{2} - y, z$ ; (viii)  $\frac{1}{2} + x, y - \frac{1}{2}, 1 + z$ ; (ix)  $\frac{1}{2} + x, -\frac{1}{2} - y, 1 + z$ ; (x)  $\frac{1}{2} - x, y - \frac{1}{2}, -z$ .

CH H atoms were included in idealized positions and refined using a riding model. C—H bond lengths were fixed at 0.99 Å, and  $U_{\text{iso}}$  fixed at 1.2 times  $U_{\text{eq}}$  of the parent C atom. The OH H atoms were located in a Fourier difference map and refined with the following restraints: O—H 0.90 Å, C—O—H 109 $^\circ$  and  $U_{\text{iso}}$  fixed at 1.5 times  $U_{\text{eq}}$  of the parent O atom. The N—O bond lengths for the nitrate counterions were restrained to 1.23 Å.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT and XPREP (Siemens, 1995); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997) and WinGX-32 (Farrugia, 1999); software used to prepare material for publication: enCIFer (CCDC, 2003).

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