

# An icosanuclear silver(I) cluster supported by bis(thiosemicarbazonato) ligands<sup>†</sup>

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## ABSTRACT

The synthesis and structural characterisation of an icosanuclear silver(I) cluster complex is reported here. The complex includes twenty silver(I) ions supported by eighteen bis(thiosemicarbazonato) ligands. The cluster of silver(I) ions involves several close Ag...Ag contacts suggesting some degree of argentophilic interactions and the bis(thiosemicarbazonato) ligands are present in three different conformations highlighting the ability of thiosemicarbazone ligands to coordinate to metal ions in different modes.

**Keywords:** argentophilic interactions, cluster of 20 silver ions, cluster, silver, sulfur ligands, thiosemicarbazone.

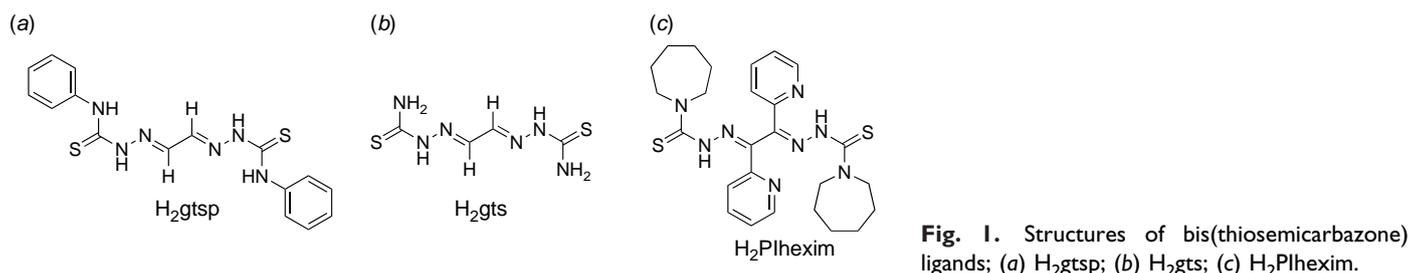
## Introduction

Thiosemicarbazones and bis(thiosemicarbazones) are versatile ligands containing both nitrogen and sulfur donor atoms that can coordinate to metal ions as either anionic or charge neutral mono- or multidentate ligands.<sup>[1]</sup> As part of an exploratory study on the synthesis of zinc(II) complexes with glyoxal-bis(4-phenyl-3-thiosemicarbazone) (H<sub>2</sub>gtsp, Fig. 1) we isolated a trinuclear [3 × Zn(II) + 3 × ligand] prism-like complex, and recrystallisation of this complex in the presence of either CO<sub>2</sub>, CS<sub>2</sub> or CH<sub>3</sub>CN led to the formation of tetranuclear [4 × Zn(II) + 4 × ligand] coordination nanotubes.<sup>[2]</sup> In a continuation of this work, we have investigated the coordination chemistry of H<sub>2</sub>gtsp with silver(I).

The closed d<sup>10</sup> valence shell of silver(I) tolerates a variety of different coordination geometries. Simple silver(I) complexes can be either 2-coordinate and approximately linear or 3- or 4-coordinate,<sup>[3]</sup> but the use of chelating ligands often leads to polymeric species or multinuclear clusters.<sup>[1b]</sup> The resonance delocalisation within thiosemicarbazones contributes to them acting as ‘masked thiolate’ donors that are less reducing than conventional thiols. This masked thiolate nature contributes to thiosemicarbazones forming a vast array of coordination complexes with thiophilic silver(I). The first structural characterisation by X-ray crystallography of a silver(I) salicylaldehyde thiosemicarbazone complex of silver(I) was reported in 2004 and revealed a hexameric complex with the Ag<sub>6</sub>S<sub>6</sub>N<sub>6</sub> core consisting of two six-membered Ag<sub>3</sub>S<sub>3</sub> rings in a chair configuration, stacked one above the other and linked by bridging ligands.<sup>[4]</sup> Each silver (I) cation is 3-coordinate, coordinated to two thiolate sulfur atoms and one hydrazinic nitrogen atom, while each sulfur bridges two silver(I) cations. Since this initial report, a range of different silver clusters<sup>[1b,5]</sup> and helicates<sup>[5b,6]</sup> supported by thiosemicarbazones have been reported as well as some discrete complexes featuring stabilising phosphine<sup>[5a,7]</sup> or 1,10-phenanthroline co-ligands.<sup>[8]</sup>

There are relatively few reports of silver(I) complexes with bis(thiosemicarbazone) ligands derived from 1,2-diones, such as H<sub>2</sub>gtsp (Fig. 1), although glyoxal-bis(thiosemicarbazone) (H<sub>2</sub>gts, Fig. 1) has previously been investigated as a

<sup>†</sup>Dedicated to Prof. Glen B. Deacon, on the occasion of his 85th birthday and in recognition of his many outstanding contributions to inorganic chemistry.



**Fig. 1.** Structures of bis(thiosemicarbazone) ligands; (a) H<sub>2</sub>gtsp; (b) H<sub>2</sub>gts; (c) H<sub>2</sub>Plhexim.

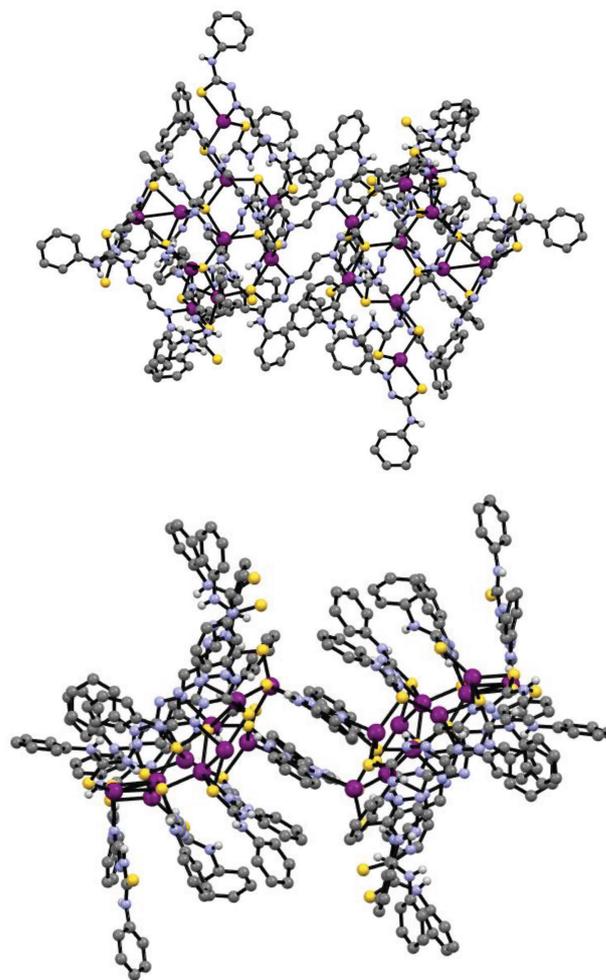
spectrophotometric reagent with silver(I), but the product was not structurally characterised.<sup>[9]</sup> Reaction of pyridyl-bis(3-hexamethyleneiminyl thiosemicarbazone) (H<sub>2</sub>Plhexim, Fig. 1) with various silver(I) salts and different metal-ligand ratios allowed isolation of mono-, di- and tetranuclear complexes.<sup>[10]</sup> In this work, we report the synthesis and structural characterisation of a complex comprising 20 silver(I) ions supported by 18 bis(thiosemicarbazone) ligands.

## Results and discussion

Addition of one equivalent of silver tetrafluoroborate (AgBF<sub>4</sub>) to a solution of H<sub>2</sub>gtsp in deoxygenated DMF in the presence of triethylamine resulted in the formation of a bright yellow/orange solution. Diffusion of diethyl ether to this mixture allowed isolation of yellow/orange crystals suitable for analysis by X-ray crystallography. The crystals were light stable but rapidly lost crystallinity when removed from the solvent, presumably due to desolvation. Plunging the crystals directly into Parobar low temperature oil followed by flash-cooling to 130 K allowed for suitable data for the crystals to be obtained. The X-ray analysis revealed the complex to be Ag<sub>20</sub>(Hgtsp)<sub>16</sub>(gtsp)<sub>2</sub> (x.DMF, y.diethylether) (Fig. 2, Table 1). The large volume of solvent accessible voids (7310.1 Å<sup>3</sup>) that account for just over 50% of the total volume of Ag<sub>20</sub>(Hgtsp)<sub>16</sub>(gtsp)<sub>2</sub>(x.DMF, y.diethylether), consisted of 2058 electrons that were modelled by the procedure SQUEEZE as implemented within the PLATON suite of programs.<sup>[11]</sup> Presumably, this solvent accessible void is occupied by a mixture of DMF and diethyl ether molecules, but the composition could not be determined.

There are a total of 18 ligands and 20 silver atoms in the complex with two centrosymmetric charge neutral Ag<sub>10</sub>(Hgtsp)<sub>8</sub>(gtsp) clusters that are situated on a crystallographic centre of inversion. The two Ag<sub>10</sub>(Hgtsp)<sub>8</sub>(gtsp) clusters are linked to each other by two gtsp<sup>2-</sup> ligands that are related by the inversion centre and coordinate as a bidentate N,S donor to both Ag1 and Ag2 (Fig. 2).

The silver atoms are coordinated to three sulfur atoms and an azomethinic nitrogen atom except for Ag9, which is coordinated to two sulfur atoms and an azomethinic nitrogen atom in a distorted T-shaped trigonal coordination geometry (Fig. 3). The coordination environment of the other nine Ag(I) ions is tending toward a distorted



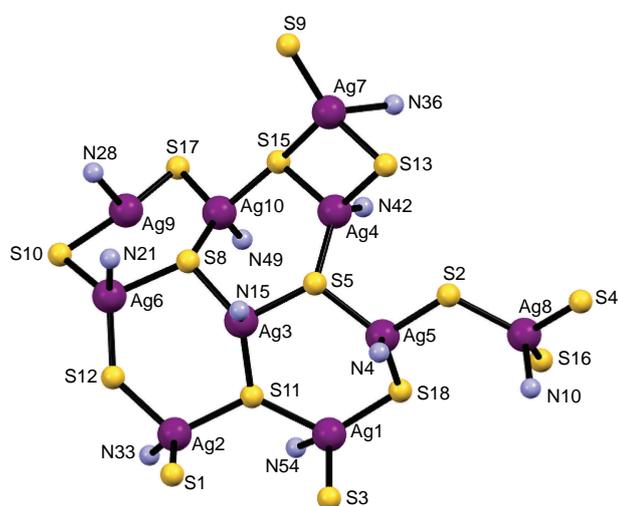
**Fig. 2.** Two different orientations of the crystal structure of Ag<sub>20</sub>(Hgtsp)<sub>16</sub>(gtsp)<sub>2</sub>. Hydrogen atoms are omitted for clarity (except hydrogen atoms bound to nitrogen). Atom colours: carbon = grey; hydrogen = white; nitrogen = blue; silver = purple; sulfur = yellow.

trigonal-pyramidal geometry. The shortest Ag...Ag distances, Ag9–Ag10 (2.8577(18) Å) and Ag4–Ag7 (3.0551(12) Å), are less than twice the van der Waals radius for silver (3.44 Å) consistent with some degree of argentophilic Ag–Ag interactions.<sup>[4,5]</sup> The Ag–Ag distance in metallic silver is 2.889 Å.<sup>[7a]</sup>

The Ag–S bond distances range from 2.395(4) Å (Ag9–S17) to 2.769(3) Å (Ag7–S15). There are four sulfur

**Table 1.** Crystallographic data for  $\text{Ag}_{20}(\text{Hgtsp})_{16}(\text{gtsp})_2$ .

Crystal identification	$\text{Ag}_{20}(\text{Hgtsp})_{16}(\text{gtsp})_2$
Chemical formula	$\text{C}_{288}\text{H}_{266}\text{Ag}_{20}\text{N}_{108}\text{S}_{36}$
$M_w/\text{Da}$	8551.63
Crystal system	Triclinic
$T/\text{K}$	130(2)
Space group	$P\bar{1}$
$a/\text{\AA}$	21.5547(6)
$b/\text{\AA}$	24.8420(9)
$c/\text{\AA}$	30.1603(9)
$\alpha/^\circ$	103.352(3)
$\beta/^\circ$	101.724(2)
$\gamma/^\circ$	107.658(3)
$V/\text{\AA}^3$	14 307(3)(6)
Z	1
Independent reflections	42 997 $[R(\text{int}) = 0.0768]$
$R (I > 2\sigma(I))$	0.0737
wR (all data)	0.2025

**Fig. 3.** A representation of the asymmetric unit,  $\text{Ag}_{10}(\text{Hgtsp})_8(\text{gtsp})$ , showing the nitrogen and sulfur atoms coordinated to the silver atoms.

atoms acting as  $\mu_3$ -bridges (S5, S8, S11, and S15) and six sulfur atoms acting as  $\mu_2$ -donors between silver atoms (S2, S10, S12, S13, S17, and S18). The Ag–N bond distances range from 2.176(9) Å (Ag10–N49) to 2.444(10) Å (Ag9–N28) and are fairly typical for Ag(I) thiosemicarbazone complexes.<sup>[4]</sup>

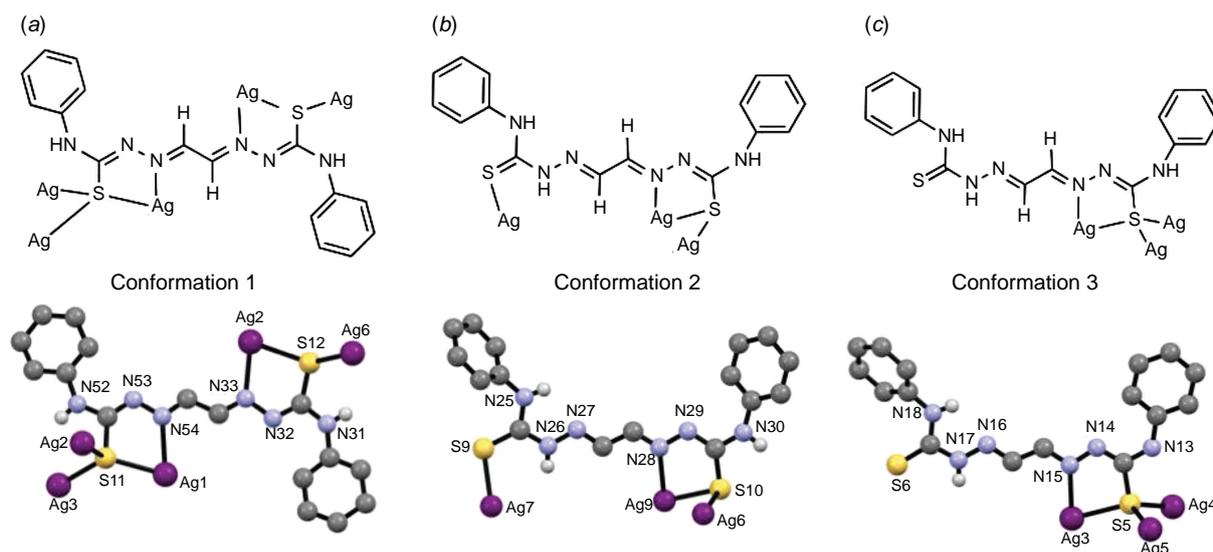
The ligand adopts three different conformations within the  $\text{Ag}_{20}(\text{Hgtsp})_{16}(\text{gtsp})_2$  complex highlighting the flexibility and versatility of bis(thiosemicarbazone) ligands. In each conformation the ligand adopts a *s-trans* conformation about the C–C

backbone of the ligand. Two of the ligands are doubly deprotonated ( $\text{gtsp}^{2-}$ ) whilst sixteen ligands are singly deprotonated ( $\text{Hgtsp}^-$ ) to give an overall charge neutral cluster. One ligand in the asymmetric unit has ‘conformation 1’ (Fig. 4a), which involves a *Z* configuration about the two C–N<sub>hydrazinic</sub> bonds (C145–N53, C88–N32) and is doubly deprotonated with the loss of two protons from the hydrazinic nitrogen atoms (N53, N32). The ligand coordinates to both Ag1 and Ag2 through the azomethinic nitrogen (N54 and N33) and thiolate sulfur atoms resulting in two 5-membered chelate rings. The thiolate-like sulfur atoms also have the ability to act as a bridge between silver atoms. The deprotonation and change in resonance structure of the ligand is supported by an increase in the C–S bond distances which average 1.74 Å when compared to the structure of the charge neutral free ligand,  $\text{H}_2\text{gtsp}\cdot 0.5\text{Et}_2\text{O}$ , where the C=S bond distances average 1.68 Å (Supplementary material) consistent with a shift toward thiolate-like rather than thione-like in nature. The deprotonation also results in a reduction in the length of the C–N<sub>hydrazinic</sub> (e.g. C145–N53) bonds to an average value of 1.31 Å compared to an average 1.36 Å in  $\text{H}_2\text{gtsp}$  consistent with the thiolate resonance form predominating.

There are five ligands in the asymmetric unit which adopt ‘conformation 2’ (Fig. 4b) with one thiosemicarbazone moiety in a *Z* configuration about the C–N<sub>hydrazinic</sub> bond (e.g. C75–N29). The hydrazinic nitrogen of this moiety has lost a proton giving the ligand a 1<sup>−</sup> charge. Both the azomethinic nitrogen (e.g. N28) and thiolate sulfur atoms coordinate to a silver atom resulting in a five-membered chelate ring. Some of the thiolate sulfur atoms of this conformation also act as  $\mu_2$  and  $\mu_3$  bridges between silver atoms. The second moiety has the sulfur atom *s-trans* to the azomethinic nitrogen similar to the structure of  $\text{H}_2\text{gtsp}\cdot 0.5\text{Et}_2\text{O}$  (Supplementary material). In this moiety, the hydrazinic nitrogen (e.g. N26) is not deprotonated. Whilst the sulfur atom in this moiety coordinates a silver atom, the azomethinic nitrogen atom (e.g. N27) does not participate in silver coordination. This charge neutral moiety has an average C–S bond length of 1.68 Å, which is more thione than thiolate-like, and an average C–N<sub>hydrazinic</sub> bond length of 1.33 Å.

There are three ligands in the asymmetric unit with ‘conformation 3’ (Fig. 4c). This conformation has one thiosemicarbazone moiety deprotonated and adopting the *Z* configuration giving the ligand a 1<sup>−</sup> charge. The second thiosemicarbazone moiety is not deprotonated with the sulfur atom *s-trans* to the azomethinic nitrogen atom (N16) and not participating in silver coordination. The average C–S and C–N<sub>hydrazinic</sub> bond lengths in the ligand are 1.79 Å and 1.31 Å for the 1<sup>−</sup> moiety and 1.65 Å and 1.34 Å for the neutral moiety, respectively.

The isolation of this cluster was repeatable from several separate synthetic preparations using the same procedure, but also when a different silver salt,  $\text{Ag}(\text{CF}_3\text{SO}_3)$  was used as the starting material. The <sup>1</sup>H NMR spectrum of crystals of  $\text{Ag}_{20}(\text{Hgtsp})_{16}(\text{gtsp})_2$  dissolved in  $d_6$ -DMSO was broad and



**Fig. 4.** Representations of the different ligand conformations in  $\text{Ag}_{20}^{\text{I}}(\text{Hgtsp})_{16}(\text{gtsp})_2$ . (a) Ligand is doubly deprotonated; (b) loss of proton from hydrazinic nitrogen gives a ligand with a  $\text{I}^-$  charge and both sulfur atoms coordinated to  $\text{Ag}(\text{I})$ ; (c) loss of proton from hydrazinic nitrogen gives a ligand with a  $\text{I}^-$  charge, one sulfur donor is involved in close contacts to three  $\text{Ag}(\text{I})$  ions. Hydrogen atoms are omitted for clarity (except hydrogen atoms bound to nitrogen).

unresolved, which is consistent with the ligands being present in both coordinated and non-coordinated forms as well as charge neutral and deprotonated forms. An attempt at obtaining ESI-MS spectra failed to provide any characterisation data consistent with the  $\text{Ag}_{20}^{\text{I}}$  cluster, which may indicate that the complex is unstable in the solution and gas phases.

## Conclusions

A complex with a cluster of 20 silver(I) ions supported by eighteen bis(thiosemicarbazato) ligands is reported. The formation of this high nuclearity cluster involves the ligand adopting three different conformations highlighting the versatility of bis(thiosemicarbazone) ligands that are capable of coordinating to metal ions in a variety of different modes. The reproducible self-assembly of this cluster of twenty silver(I) ions is presumably supported by several close  $\text{Ag}\cdots\text{Ag}$  contacts and the resulting argentophilic interactions as well as the flexible coordination geometries of closed shell silver(I).

## Experimental

### Glyoxal bis(4-phenylthiosemicarbazone), $\text{H}_2\text{gtsp}$

This compound was synthesised utilising a similar published procedure for the synthesis of glyoxal bis(thiosemicarbazone).<sup>[13]</sup> To a solution of 4-phenyl-3-thiosemicarbazide (2.02 g, 12.1 mmol) in a mixture of boiling water (7.5 mL), ethanol (10 mL) and acetic acid (0.76 mL), a mixture of

aqueous glyoxal (40 wt%, 0.35 g, 6.05 mmol) in water (14 mL) was added. A precipitate formed instantly, which was stirred for 5 min. The solid was collected by hot filtration and washed with water, ethanol and diethyl ether, then dried under vacuum at room temperature (1.72 g, 80%). (Found: C, 54.09; H, 4.64; N, 23.70; calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_6\text{S}_2$ : C, 53.91; H, 4.52; N, 23.58).  $^1\text{H}$  NMR ( $d_6$ -DMSO, 500 MHz):  $\delta = 7.19$ , 2H, m, Ar- $\text{H}^4$ ; 7.35, 4H, m, Ar- $\text{H}^3$ ; 7.56, 4H, m, Ar- $\text{H}^2$ ; 7.90, 2H, s, H-C=N; 10.18, 2H, s, NH-Ar; 12.14, 2H, s, NH-N.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz):  $\delta = 125.3$ , ArC $^4$ ; 125.5, ArC $^2$ ; 128.1, ArC $^3$ ; 138.9, ArC $^1$ ; 140.7, C=N; 176.0, C=S. MS: (+ve ion)  $m/z$  100%  $[\text{M} + \text{H}^+]$  356.09 (experimental), 356.09 (calculated). Crystals suitable for single crystal X-ray crystallography were grown from vapour diffusion diethyl ether into a mixture of  $\text{H}_2\text{gtsp}$  dissolved in DMF (Supplementary material).

### $\text{Ag}_{20}^{\text{I}}(\text{Hgtsp})_{16}(\text{gtsp})_2 \cdot (x.\text{DMF}, y.\text{diethylether})$

To a degassed solution of  $\text{H}_2\text{gtsp}$  (0.10 g, 0.28 mmol) and triethylamine (40  $\mu\text{L}$ , 0.28 mmol) in DMF (2 mL) was added  $\text{AgBF}_4$  (0.05 g, 0.28 mmol). Vapour diffusion of diethyl ether into the yellow/orange solution resulted in yellow crystals of  $\text{Ag}_{20}^{\text{I}}(\text{Hgtsp})_{16}(\text{gtsp})_2 \cdot \text{solvent}$  (0.08 g) after 12 h that were suitable for analysis by X-ray crystallography. The crystals were collected by filtration and dried before they were dissolved in  $d_6$ DMSO for analysis by  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR ( $d_6$ -DMSO, 500 MHz):  $\delta = 2.73$ ,  $\text{CH}_3$ , DMF; 2.89,  $\text{CH}_3$ , DMF; 6.68, m, Ar-H; 6.85, m, Ar-H; 7.19, Ar-H; 7.35, m, Ar-H; 7.55, m, Ar-H; 7.65, m, Ar-H; 7.84, s, H-C=N; 7.89, s, H-C=N; 7.95, DMF; 9.66, s, NH; 10.16, s, NH.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.7 MHz):  $\delta = 30.5$ ,  $\text{CH}_3$ , DMF; 35.6,  $\text{CH}_3$ , DMF; 120.6,

Ar–C; 125.4, Ar–C; 125.5, Ar–C; 128.1, Ar–C; 138.8, C=N; 140.8, C=N; 162.3, DMF, CH; 176.0, C=S.

## X-ray crystallography

Crystals were mounted in a low temperature oil then flash cooled to 130 K using an Oxford low temperature device. Intensity data were collected at 130 K with an Oxford XCalibur X-ray diffractometer with Sapphire CCD detector using Cu-K $\alpha$  radiation (graphite crystal monochromator  $\lambda = 1.54184 \text{ \AA}$ ) or a Bruker SMART Apex CCD detector using Mo-K $\alpha$  radiation (graphite crystal monochromator  $\lambda = 0.71073 \text{ \AA}$ ). Data were reduced and corrected for absorption. The structure was solved by direct methods and difference Fourier synthesis using the SHELX suite of programs<sup>[14]</sup> as implemented within the WINGX software.<sup>[15]</sup> The solvent was extensively disordered to the extent that modelling the disorder was not practical given the number of restraints that would be required and given that the identity of the solvent was questionable. The large (7310.1  $\text{\AA}^3$ ) amount of solvent accounts for just over 50% of the total volume  $\text{Ag}_{20}(\text{Hgtsp})_{16}(\text{gtsp})_2$  consisted of 2058 electrons and is presumably occupied by a combination of DMF and diethylether molecules.<sup>[11]</sup>

## Supplementary material

The details of the crystal structure of  $\text{H}_2\text{gtsp}\cdot\text{Et}_2\text{O}$  are available in Supplementary material [online](#).

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**Data availability.** The data that support this study are available from the Cambridge Crystallographic Data Centre CCDC 2128093 and CCDC 2128318.

**Conflicts of interest.** Jonathan M. White is an Associate Editor for the *Australian Journal of Chemistry* but was blinded from the peer review of this manuscript.

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