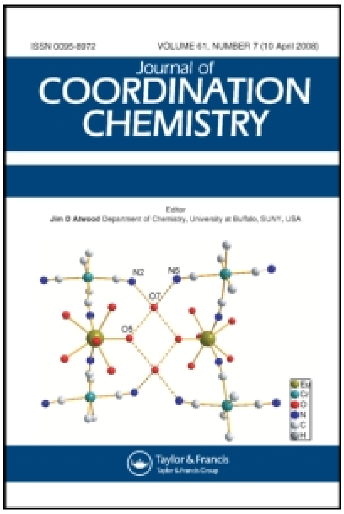

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Asymmetric <i>versus</i> symmetric silver-sulfur-nitrogen bonding in the solid-state structure of silver-1-phenyl- 1H-tetrazole-5-thiol: single crystal structure of {[(AgPMT)$_4$ · 0.5THF]}$_{<i>n</i>}$

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Asymmetric *versus* symmetric silver–sulfur–nitrogen bonding in the solid-state structure of silver-1-phenyl-1H-tetrazole-5-thiol: single crystal structure of $\{[(\mathrm{AgPMT})_4 \cdot 0.5\mathrm{THF}]\}_n$

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The solid-state structure of the highly insoluble silver complex 1-phenyl-1*H*-tetrazole-5-thiol (AgPMT), without solubilizing ligands, has been successfully resolved. The crystal structure of $\{[(\mathrm{AgPMT})_4 \cdot 0.5\mathrm{THF}]\}_n$ consists of polymeric repeating units of asymmetrically constructed AgPMT dimers. The asymmetric dimers are based on S–Ag–N and N–Ag–N links, and reveal the routes of connectivity possible with this multidentate ligand. This is one of the few linear, one-dimensional silver-based polymers.

Keywords: PMT; Tetrazole; Silver; Crystal; Structure; Polymer

1. Introduction

Despite the commercial importance of 1-phenyl-1*H*-tetrazole-5-thiol (PMT), figure 1, in photographic materials [1], such as its use as a stabilizer in photographic films [2, 3] and black-and-white photothermographic materials [4], and investigation of AgPMT as a silver source in high-speed photothermographic materials (see, for example, [5]), very little has been published on the nature of AgPMT [6–8]. PMT has also been studied in its role in changing the morphology of Ag^0 during electrocrystallization deposition [9], an important consideration in the optical properties of black-and-white photothermographic imaging materials [4, 10].

Considering the long history of photography and the ability to determine, in detail, the solid-state structure of silver complexes of photographic importance, it is somewhat surprising that more information regarding the nature of AgPMT or its derivatives has not been reported. Part of the reason is related to the difficulty in isolating well-formed single crystals for X-ray crystal structure determination. The extremely poor solubility

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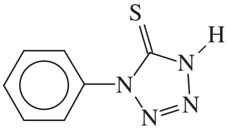


Figure 1. 1-Phenyl-1*H*-tetrazole-5-thiol.

of AgPMT, $pK_{sp} = 16.2$ [11], illustrates this difficulty and is also most likely a contributing factor to the ability of PMT to act as a photographic stabilizer. Consequently, the only closely related crystal structure of which we are aware is the triphenyphosphine complex of AgPMT, $\{AgPMT \cdot (Ph_3P)_2(CH_3OH)\}$ [12]. To our knowledge, the only structures of photographically important silver complexes published in the literature are for those complexes containing tetraazadindole [13], 5-methyl-mercaptobenzimidazole (5MBI) [14, 15], 2-(tribromomethylsulfonyl)-benzothiazole [16], and alkyl carboxylates [17–21].

We now report that the silver complex of another important photographic stabilizer, and a potential ligand for photothermographic silver sources, PMT [1–4], has been resolved. The structure is a polymer based on dimeric $[AgPMT]_4$ subunits, containing THF, $\{[(AgPMT)_4 \cdot 0.5THF]\}_n$, and is constructed from eight-membered rings, similar to the basic building block in silver carboxylate complexes [4]. The details of this structure are described below.

2. Experimental

Preparation of $\{[(AgPMT)_4 \cdot 0.5THF]\}_n$ was carried out following the procedure successfully used for obtaining X-ray-quality crystals of another poorly soluble silver complex [Ag(5-mercaptobenzimidazole)·THF]$_6$, $[Ag5MBI \cdot THF]_6$ [15]. To a dispersion of 0.20 g of silver stearate in 10 mL THF was added 91 mg of H-PMT. With stirring, a clear, colorless solution rapidly resulted. On standing a few minutes to hours (depending on the exact concentrations) fine, thin needle-shaped crystals of $\{[(AgPMT)_4 \cdot 0.5THF]\}_n$ slowly crystallized. The free stearic acid byproduct remained in solution. Alternately, including 20% water by volume improved the crystal size.

Attempts were made to isolate the soluble intermediate initially formed in the THF solution. Rapid precipitation with ether, for example, prior to $\{[(AgPMT)_4 \cdot 0.5THF]\}_n$ crystallization, provided a white powder that was characterized by elemental analysis. It was found to be predominantly $\{[(AgPMT)_4 \cdot 0.5THF]\}_n$ containing residual stearate. We were not able to obtain a better characterized intermediate.

Examination of the crystals under a microscope revealed they were of adequate size for single-crystal XRD analysis. However, these were weakly diffracting crystals, indicating that the quality of the crystals could impact the overall quality of the single-crystal data. All further attempts to grow better quality single crystals were unsuccessful. Nonetheless, the availability of these not-so-perfect single crystals allowed for successful single-crystal structure determination. A crystal of the title complex of approximate dimensions $0.01 \times 0.02 \times 0.10\,mm^3$ was chosen for data collection. Diffraction data were collected at 150 K using a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073\,Å$). A total of 295 frames were collected using phi plus omega scans to fill the asymmetric unit with

Table 1. Crystal data and structure refinement for $\{[(\mathrm{AgPMT})_4 \cdot 0.5\mathrm{THF}]\}_n$.

Empirical formula	$C_{30}H_{24}Ag_4N_{16}O_{0.50}S_4$
Formula weight	1176.37
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit-cell dimensions (Å, °)	$a = 15.6619(6)$, $\alpha = 90$ $b = 23.6142(8)$, $\beta = 105.2590(16)$ $c = 11.9926(4)$, $\gamma = 90$
Volume ($Å^3$)	4279.0(3)
Z	4
Density (calculated) ($Mg\,m^{-3}$)	1.826
Absorption coefficient (mm^{-1})	2.043
$F(000)$	2288
Crystal size (mm^3)	$0.01 \times 0.02 \times 0.10$
θ range for data collection (°)	2.58 to 21.47
Index ranges	$-16 \le h \le 16$, $-24 \le k \le 24$, $-12 \le l \le 12$
Reflections collected	9233
Independent reflections	4821 [$R(\mathrm{int}) = 0.0900$]
Completeness to $\theta = 21.47°$	98.3%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4821/0/349
Goodness of fit on F^2	1.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0592$, $wR_2 = 0.1426$
R indices (all data)	$R_1 = 0.1044$, $wR_2 = 0.1596$
Largest diff. peak and hole ($e\,Å^{-3}$)	1.215 and −0.626

a scan range of 1.4° and a counting time of 10 min per degree. The first ten frames were used for indexing reflections using the DENZO [22] package and refined to obtain final cell parameters. Data reductions were performed using DenzoSMN [22]. A total of 9233 reflections had their intensities integrated and scaled, of which 4821 were independent and 3182 were above $4\sigma(I)$. Details of cell data, data collection, and structure refinement are summarized in table 1.

The $P2_1/c$ space group was uniquely determined from space group absences. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-hydrogen atoms using Bruker SHELXTL [23]. An absorption correction was calculated but was found to be insignificant, hence omitted. The structure refined to a goodness-of-fit (GOF) of 1.032 and final residuals of $R_1 = 0.0592\%$ ($I > 2\sigma(I)$).

The asymmetric unit consists of four molecules of AgPMT and a THF molecule of half occupancy. There was considerable disorder in the structure, two of the phenyl rings C9–C14 and C23–C28 were disordered. It was not possible to model accurately the electron density in terms of alternative atom positions; hence, disorder was left untreated. All carbon atoms were left isotropic because of low observable data-to-parameter ratio (3182 > $4\sigma(I)$ for 349 parameters). Selected bond distances and angles are shown in table 2.

3. Results and discussion

There are multiple coordination sites available on the PMT ligand, including an argentophilic sulfur, a deprotonatable nitrogen, and an azine group. The latter is the

Table 2. Selected bond distances for $\{[(AgPMT)_4 \cdot 0.5THF]\}_n$.

Ag(1)–Ag(2)	3.2296(15)
Ag(1)–Ag(3)	3.0525(14)
Ag(1)–Ag(4)#1	3.3219(15)
Ag(2)–Ag(3)#2	3.2845(15)
Ag(2)–Ag(4)	2.9484(14)
Ag(3)–Ag(4)	3.3382(15)
Ag(1)–S(2)	2.736(4)
Ag(1)–S(3)#1	2.712(4)
Ag(2)–S(1)	2.722(4)
Ag(2)–S(2)	2.443(3)
Ag(3)–S(1)#1	2.409(3)
Ag(3)–S(4)	2.408(3)
Ag(4)–S(3)	2.454(3)
Ag(4)–S(4)	2.686(4)
Ag(1)–N(4)#1	2.265(9)
Ag(1)–N(12)	2.270(9)
Ag(2)–N(5)	2.212(9)
Ag(4)–N(13)	2.244(9)

#1: $x, -y+1/2, z-1/2$; #2: $x, -y+1/2, z+1/2$.

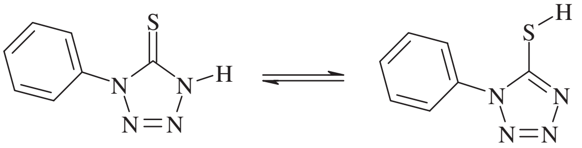


Figure 2. PMT tautomeric isomers.

same bonding group as in phthalazine, which is known to be a good complexing agent for silver carboxylates [19, 21].

The N–H position ortho to the thione provides the possibility of tautomeric isomers in which the sulfur can coordinate either as a neutral donor or an anionic ligand, figure 2.

From the literature, both the thiol and thioamide structures have been reported as the primary isomer [2, 3, 7, 11]. The similar 5MBI ligand reacts in both forms, with AgBr to yield $[\{AgBr \cdot 5MBI \cdot acetone\}_4]$ and with silver stearate to yield $[Ag5MBI \cdot THF]_6$ [14, 15]. This is a function of the nature of the counterion initially associated with the silver source. With a weak acid anion, the starting silver carboxylate readily lost HO_2CR to form yellow $[Ag5MBI \cdot THF]_6$, but with a strong acid anion, such as would form from AgBr deprotonation of H–5MBI, white $[AgBr \cdot 5MBI]_4$ results instead. Despite the similarity in reaction chemistry of these two types of ligands with silver carboxylates, the solid-state structures diverge dramatically.

3.1. *Description of the* $\{[(AgPMT)_4 \cdot 0.5THF]\}_n$ *structure*

Some time ago, based on IR and elemental analysis, the solid-state structure of AgPMT was proposed to consist of Ag–N–C–S four-membered rings polymerized by a coordinated link to adjacent AgPMT units *via* a Ag–N bond [7]. While consistent with the

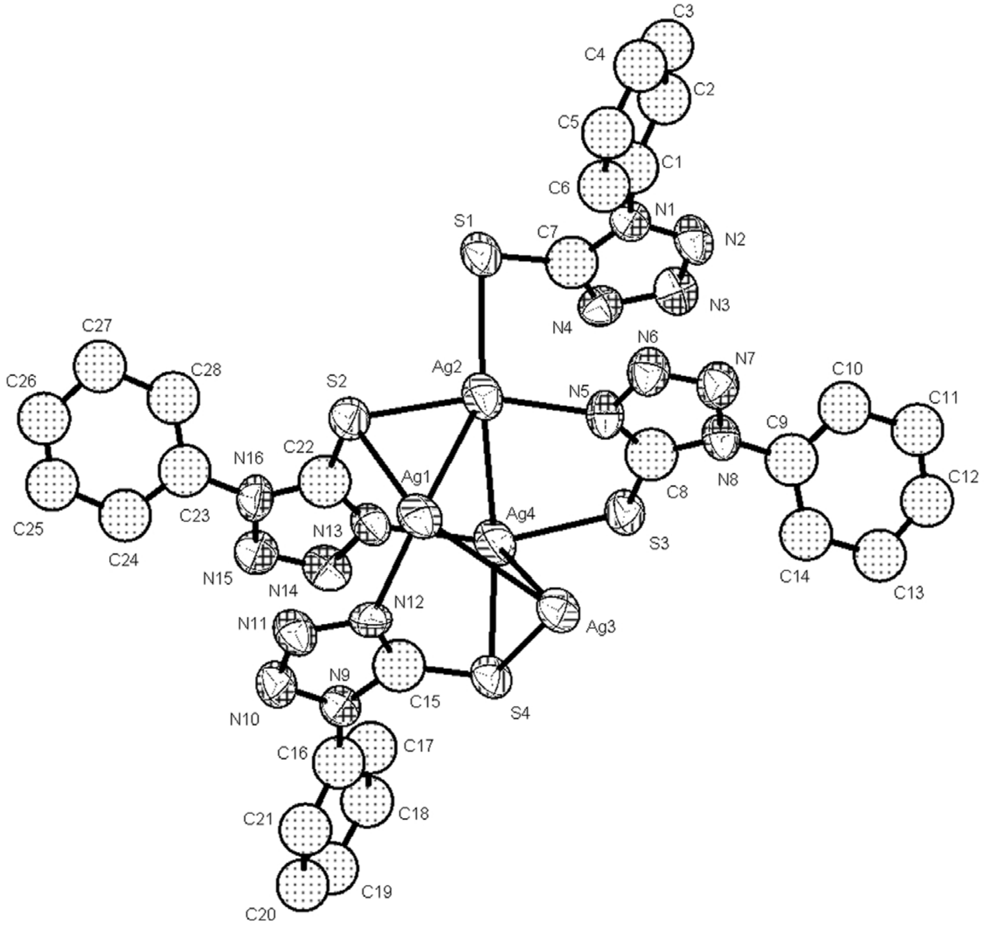
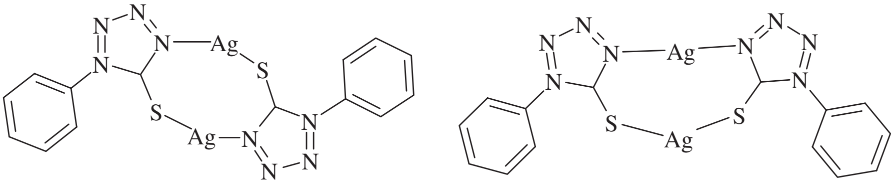


Figure 3. Molecular plot of $\{[(AgPMT)_4 \cdot 0.5THF]\}_n$, showing the labeling of the non-hydrogen atoms and their displacement ellipsoids at the 50% probability level. Hydrogen atoms and the THF molecule are omitted for clarity.

analytical data, the highly strained four-membered ring would be unusual, and as can be seen from the structure details below, this is not accurate. The solid-state structure of AgPMT consists of repeating octamers, constructed from eight-membered ring dimers, $[AgPMT]_2$. A molecular view of the AgPMT crystal structure with the atom-labeling scheme is given in figure 3.

Surprisingly, the dimers are not identical; two different bonding modes are observed. In addition, the crystal structure can be seen to contain a complicated network of alternating rings, comprising two different types of eight-membered rings, arranged in spatially oriented alternating pairs. That is, the two different types of rings comprise a pair of N–Ag–S/N–Ag–S connections in the ring structure, figure 4(a), compared to a pair of N–Ag–N/S–Ag–S connections in the neighboring ring structures, figure 4(b).

The pair of N–Ag–N/S–Ag–S eight-membered rings are arranged such that the N–Ag–N linkages are opposite each other, with the rings separated by the ''normal'' N–Ag–S/N–Ag–S ring structure. The latter are twisted relative to each other, as needed, which is due to the flip-flop in the N–Ag–N/S–Ag–S structure. One view



(a) N–Ag–S/N–Ag–S dimers (b) N–Ag–N/S–Ag–S dimers.

Figure 4. (a) N–Ag–N/S–Ag–S dimers; (b) N–Ag–N/S–Ag–S dimers.

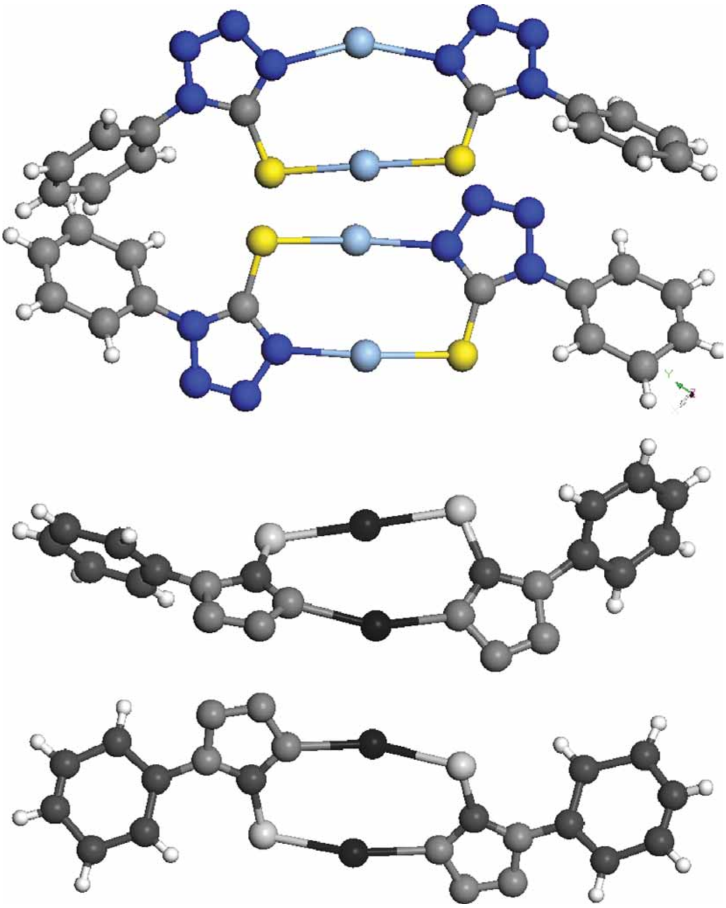


Figure 5. Two dimers comprising the tetramer in $\{[(\text{AgPMT})_4 \cdot 0.5\text{THF}]\}_n$.

of one pair of this dimer set, half the octamer, is shown in figure 5. Figure 6 demonstrates the connectivity relationship of N–Ag–N and S–Ag–S *versus* N–Ag–S bonding.

All the AgPMT units are arranged into eight-membered rings, which are connected in a polymeric lattice by Ag–S bonds. Thus, because of the asymmetric nature of the

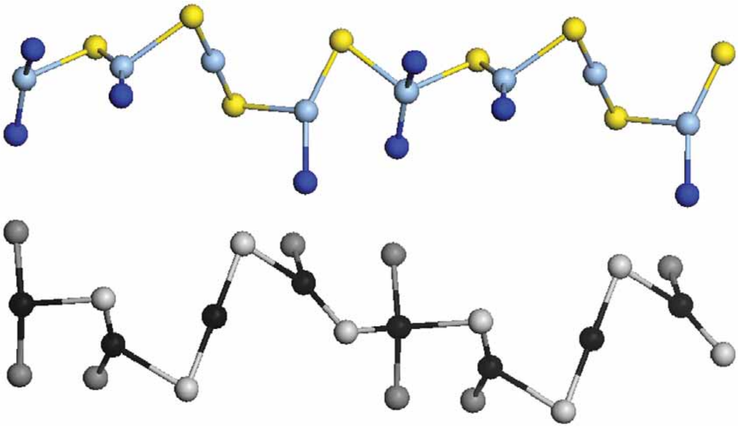


Figure 6. Connectivity relationship of N–Ag–N and S–Ag–S vs. N–Ag–S bonding. Light Blue – Ag, Blue – N, Yellow – S.

eight-membered rings, the molecule contains two-, three-, and four-coordinate silver atoms. The Ag–Ag distances range from 2.9–3.3 Å, the shorter of which are within the normal range for Ag–Ag bonds in metallic silver, thus, all of the silvers contain a silver–silver bond and then become three-, four-, and five-coordinate, as is common for silver. Those distances indicate the existence of additional weak metal–metal interactions. This is precisely the same range noted for the Ag–Ag bonding distances in the hexameric silver cluster, $[Ag_6(\mu_3\text{-}SC_5H_4N)_4(\mu_4\text{-}SC_5H_4N)_2]_n$ [24–26], as well as for the silvers in the 5MBI complex, $[AgBr \cdot 5MBI]_4$ (Ag–Ag(1) = 3.0983(8), Ag–Ag(2) = 3.1425(8)) [14].

Each S-atom in the AgPMT complex bridges two Ag atoms. Interestingly, one Ag–S bond length is 2.41 Å and the other Ag–S bond length is around 2.74 Å. In these same complexes the Ag–S bond lengths vary from 2.46 to 2.70 Å. The Ag–S in the triphenylphosphine derivative of AgPMT is 2.4909(10) [12]. The average Ag–N bond distance of 2.25 Å compares with 2.31 to 2.37 Å in the pyridine–thione complexes [24–26]. The structure of AgPMT·$(PPh_3)_2$ [12] is similar to other phosphine silver complexes, such as $((C_6H_5)_3P)_2Ag(O_2C(CH_2)_{16}CH_3)$ [27], in that it is a monomeric, not polymeric, species. In this case, the silver is three-coordinate, bonded by the two phosphines and the deprotonated thiol. The aromatic nitrogen of the thiourea-based structure that is available for coordination to the silver is not involved with any silver bonding.

It should be noted that the solid state of $\{[(AgPMT)_4 \cdot 0.5THF]\}_n$ also contains uncoordinated THF as a solvate, similar to the Ag5MBI complex reported previously [15]. In addition, it is interesting to observe that while both 5MBI and PMT ligands are deprotonated and form similar silver complex structures, the Ag5MBI complex is yellow, but the linearly coordinated $\{[(AgPMT)_4 \cdot THF]\}_n$ is colorless.

4. Conclusions

The solid-state structure of the highly insoluble silver 1-Phenyl-1*H*-tetrazole-5-thiol (AgPMT) complex, without solubilizing ligands, has been successfully resolved.

The crystal structure of $\{[(AgPMT)_4 \cdot 0.5THF]\}_n$ consists of polymeric repeating units of asymmetrically constructed AgPMT dimers. The asymmetric dimers are based on S–Ag–N and N–Ag–N links, and reveal the routes of connectivity possible with this multidentate ligand. This is one of few linear, one-dimensional silver-based polymers. The polymeric structure is consistent with the extremely low solubility.

Supplementary material

Crystallographic data for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary data no. 273650. Copies of the data may be obtained free of charge upon request from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk; WEB: http://www.csdc.cam.ac.uk.

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