Inorg. Chem. **1981**, *20*, 1487–1492

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Crystallization and Structure of Bis(tetramethylammonium) Octakis(benzenethiolato)hexaargentate(I), Extending the Series of Cages $[M_4(SPh)_6]^{2-}$, $[M_5(SPh)_7]^{2-}$, $[M_6(SPh)_8]^{2-}$, and $[M_{12}(SPh)_{16}]^{4-}$

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Received May 14, 1980

Nonaqueous solutions containing Ag^+, PhS^-, and Me_4N^+ crystallize pale yellow $(Me_4N)_2[Ag_6(SPh)_8]$, as well as yellow $(Me_4N)_2[Ag_5(SPh)_7]$ and colorless $(AgSPh)_n$. Crystalline $(Me_4N)_2[Ag_6(SPh)_8]$ contains one-dimensionally nonmolecular $[Ag_6(SPh)_8]_n{}^{2n-}$, in which there is a tubular framework of silver atoms and the sulfur atoms of bridging benzenethiolate ligands. There are two distinct lengths of Ag–S bonds, "normal" (2.52 ± 0.02 Å) and "long" (2.82 ± 0.04 Å). Molecular cages $[Ag_{12}(SPh)_{16}]^{4-}$, constituted by normal Ag–S bonds, are linked along the chain direction by long Ag–S bonds. Each $[Ag_{12}(SPh)_{16}]^{4-}$ cage is composed like an hourglass of two globular $[Ag_6(SPh)_8]^{2-}$ cages butt-jointed across a center of symmetry. Existence in solution of the monomeric $[Ag_6(SPh)_8]^{2-}$ and dimeric $[Ag_{12}(SPh)_{16}]^{4-}$ molecular cages is proposed. The $[Ag_6(SPh)_8]^{2-}$ cage, after angular idealization, extends the sequence $[M_4(SPh)_6]^{2-}$, $[M_5(SPh)_7]^{2-}$, and $[M_6(SPh)_8]^{2-}$, in which the *tetrahedro*-M_4-*octahedro*-$(\mu\text{-}SPh)_6$ polyhedron is expanded by insertion of $\{(\mu\text{-}SPh)M\}$ at $(\mu\text{-}SPh)$ vertices. Crystal data: $P\bar{1}$; $a = 12.252$ (1), $b = 13.371$ (2), $c = 18.831$ (3) Å; $\alpha = 92.15$ (1), $\beta = 96.18$ (1), $\gamma = 84.64$ (1)°; $Z = 2$ $(\times Ag_6S_8N_2C_{56}H_{64})$; 5787 observed reflections (Mo Kα); $R = 0.046$.

Introduction

Homoleptic silver thiolate complexes, $[Ag_x(SR)_y]^{x-y}$, are not well-known. They occur in the uncharged compounds AgSR $(x = y)^{1-7}$, which are frequently insoluble, and no doubt also exist in the solutions formed when AgSR compounds dissolve due to the presence of excess thiolate ions.[5,7,8] Only recently has some definitive X-ray diffraction information displaced speculation regarding the structures and formulations of these complexes. (Cyclohexanethiolato)silver, $AgSC_6H_{11}$, has a complicated one-dimensionally nonmolecular crystal structure which has been reinterpreted[4] as the association of cyclic molecules $(AgSC_6H_{11})_{12}$; such cycles may have general occurrence in crystalline and dissolved AgSR when R is a secondary alkyl group.

The anionic complexes $[Ag_5(SPh)_7]^{2-}$ and $[Ag_5(S\text{-}t\text{-}Bu)_6]^-$ occur, at least in crystals, as molecular cages with both two- and three-coordinate silver.[7,8]

Prospects for identification and structure determination of $[Ag_x(SR)_y]^{x-y}$ species *in solution* are not good, particularly when $x > 1$. Correlations of structure and physical properties (charge-transfer spectra, XPS spectra,[9] vibrational data[7]) are virtually nonexistent. Investigations aiming to crystallize species from solution and to determine crystal structures are more informative and provide the foundation for possible structure/spectra correlations. This paper describes (i) crystallizations from solutions containing Ag(I), PhS^-, and Me_4N^+, (ii) the crystal structure of $(Me_4N)_2[Ag_6(SPh)_8]$, and (iii) the structural pattern appearing for thiolate cages of copper(I) and silver(I).

Experimental Section

Synthesis. Reagent grade solvents were stored over molecular sieves but not specifically dried. All solutions containing thiols were deoxygenated with dinitrogen, and all solutions for crystallization were sealed under ca. 1 atm of dinitrogen.

Bis(tetramethylammonium) Octakis(benzenethiolato)hexaargentate(I), $(Me_4N)_2[Ag_6(SPh)_8]$. A. To a well-stirred solution of benzenethiol (6.0 g) and tri-*n*-butylamine (9.5 g) in acetonitrile (80 mL) was added a solution of tetramethylammonium chloride (4.5 g) in methanol (75 mL), followed by a solution of silver nitrate (2.7 g) in acetonitrile (45 mL), all at ca. 20 °C. Any precipitate which formed immediately redissolved. Absolute ethanol (155 mL) was added, and the mixture was sealed and stored at ca. 0 °C for 6 days. The well-formed pale yellow crystals which grew slowly were collected, washed with ethanol, and vacuum dried. A further crop of the same product was obtained in similar fashion from the mother liquor after removal of ca. 100 mL of solvent by low-temperature distillation.

The PhS^-/Ag^+ molar ratio in this solution was 3.4. Variations of this ratio up to 5.0 also result in crystallization of $(Me_4N)_2[Ag_6(SPh)_8]$, as from the following preparative solution where the ratio is 3.9.

B. To a solution containing benzenethiol (4.5 g), tri-*n*-butylamine (7.2 g), and tetramethylammonium chloride (3.4 g) in acetonitrile (50 mL) and methanol (50 mL) was added silver nitrate (1.8 g) dissolved in acetonitrile (25 mL), followed by absolute ethanol (120 mL), all at room temperature. When this solution was stored at ca. 0 °C, pale yellow crystals of the product began to grow after 12 h and continued to grow during 4 days.

Anal. Calcd for $(Me_4N)_2[Ag_6(SPh)_8]$: C, 40.30; H, 3.87; N, 1.68. Found: C, 40.57; H, 3.84; N, 1.60.

Crystalline $(Me_4N)_2[Ag_6(SPh)_8]$ is oxidized only very slowly by air but is darkened by laboratory light over a period of several days. The crystals are not soluble in acetone or alcohols but are slightly soluble in acetonitrile. The resulting solution precipitates $(AgSPh)_n$ slowly at room temperature and rapidly on heating, indicating the occurrence of benzenethiolate dissociation: $[Ag_6(SPh)_8]^{2-} \rightleftharpoons (6/n)(AgSPh)_n + 2PhS^-$. For this reason recrystallization of isolated $(Me_4N)_2[Ag_6(SPh)_8]$ has not been attempted.

The compound dissolves in pyridine to give a bright yellow solution which is sensitive to dioxygen.

Complications in the Crystallization of $(Me_4N)_2[Ag_6(SPh)_8]$. Reaction mixtures similar to those in paragraphs A and B above have crystallized also as a related product, $(Me_4N)_2[Ag_5(SPh)_7]^8$. C. (The content of this preparative solution is almost identical with that of section A above.) A solution of benzenethiol (6.0 g) and tri-*n*-butylamine (9.6 g) in acetonitrile (80 mL) was treated with tetramethylammonium chloride (moist, 4.9 g) in methanol (75 mL), silver nitrate (2.7 g) in acetonitrile (45 mL), and absolute ethanol (150 mL). After the mixture was allowed to stand sealed at ca. 0 °C for 24 h, well-formed bright yellow crystals of $(Me_4N)_2[Ag_5(SPh)_7]$ were present. After a further 24 h at 0 °C, these crystals redissolved and pale yellow crystals of $(Me_4N)_2[Ag_6(SPh)_8]$ started to grow.

D. (This preparative solution differs from that in section B above by only 10 mL more of acetonitrile and 10 mL less of absolute ethanol.)

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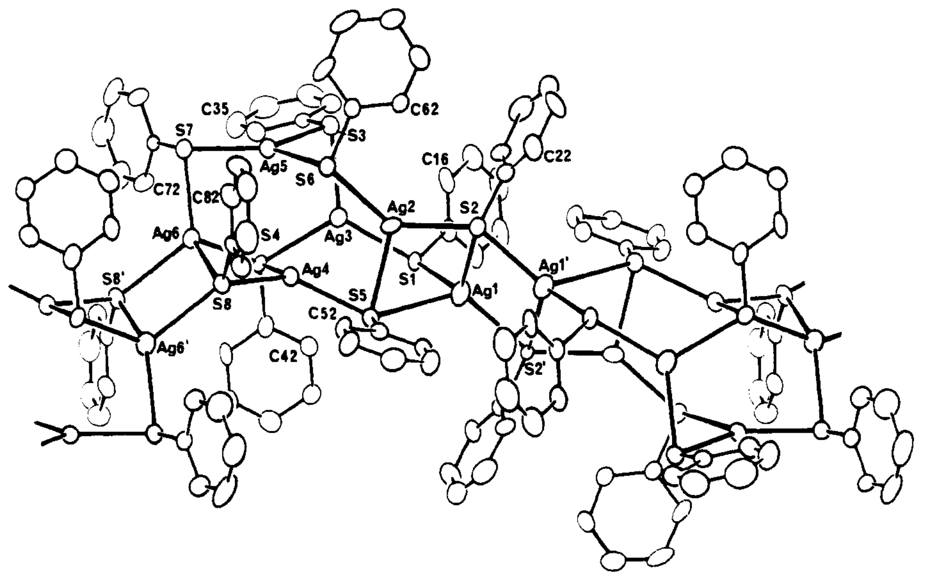

Figure 1. Approximately one repeat unit (two asymmetric units) of the extended crystal structure of $[Ag_6(SPh)_8]^{2-}$. Centers of symmetry which generate the primed atoms are located between Ag1 and Ag1′ and between Ag6 and Ag6′. The direction of the cyclic numbering of phenyl ring atoms C*mn* (*m* = 1–8, *n* = 1–6), with C*m*1 bonded to S*m*, is indicated.

A solution containing benzenethiol (4.5 g), tri-*n*-butylamine (7.2 g), tetramethylammonium chloride (3.3 g), silver nitrate (1.8 g), acetonitrile (85 mL), methanol (50 mL), and absolute ethanol (50 mL) did not precipitate any product after 2 days at 0 °C. A further 60 mL of absolute ethanol was added, causing slow crystallization of $(Me_4N)_2[Ag_5(SPh)_7]$ (identified by X-ray diffraction) at 0 °C.

E. Some attributes of the solution equilibria involving $(Me_4N)_2[Ag_6(SPh)_8]$ are revealed by the following experiment, in which the PhS^-/Ag^+ molar ratio was 5.0. Silver nitrate (1.7 g) in acetonitrile (12 mL) was added to a solution of benzenethiol (5.5 g), tri-*n*-butylamine (8.5 g), and tetramethylammonium chloride (3.4 g) in acetonitrile (50 mL) and methanol (50 mL). Addition of 1-propanol (150 mL) to the yellow solution and storage at 0 °C caused crystallization of pale yellow $(Me_4N)_2[Ag_6(SPh)_8]$ together with a single large well-developed crystal of $(Me_4N)_2[Ag_5(SPh)_7]$. When this mixture was heated to ca. 60 °C, much of the $(Me_4N)_2[Ag_6(SPh)_8]$ redissolved. After addition of more acetonitrile (ca. 30 mL) $(AgSPh)_n$ crystallized from this solution when it was heated to ca. 80 °C and redissolved when the temperature returned to ambient. The solution was then filtered warm to remove a small amount of residual precipitate and stored at ambient temperature for 4 weeks, during which period 1–3 mm crystals of $(Me_4N)_2[Ag_6(SPh)_8]$ slowly grew.

X-ray Crystallography. Numerical details of the structure determination are set out in Table I. Single crystals were selected from the final product of the reaction in paragraph C. The space group was determined photographically, the accurate unit-cell dimensions were obtained from ten high-angle reflections centered with a Siemens AED diffractometer using filtered Mo Kα radiation, and the density was measured by flotation. Intensity measurements with the same diffractometer used $\theta/2\theta$ scans and monitored a reference reflection at frequent intervals. The standard deviation of relative intensity ($I = N_p - N_b$) was calculated as $\sigma(I) = [N_p + N_b + (0.04N_p)^2]^{1/2}$, where N_p and N_b are the integrated peak and background counts, respectively. Absorption corrections calculated by numerical integration over a 5 × 5 × 5 point grid were applied.

Table I

compn, fw	$(Me_4N)_2Ag_6(SPh)_8$ $(Ag_6S_8N_2C_{56}H_{64})$, 1668.86
cryst description	pale yellow blocks; $\{100\}$, $\{010\}$, $\{001\}$
space group	$P\bar{1}$
a, Å	12.252 (1)
b, Å	13.371 (2)
c, Å	18.831 (3)
α, deg	92.15 (1)
β, deg	96.18 (1)
γ, deg	84.64 (1)
V, Å^3	3052.6
temp, °C	21.0
Z	2
$F(000)$	1647
d_{obsd}, g cm^{-3}	1.80 (2)
d_{calcd}, g cm^{-3}	1.82
radiation	Mo Kα, 0.71069 Å
μ, cm^{-1}	21.56
cryst dimens, mm	0.36 × 0.15 × 0.09
$2\theta_{max}$, deg	50
no. of intens measmts	10 830
criterion for obsd reflctn	$I/\sigma(I) > 2.58$
no. of independent obsd reflctns	5787
restrictions and no. (m) of reflctns in final refinement	obsd data, $(\sin\theta)/\lambda > 0.15$, 5633
no. of variables refined (n)	650
Larson extinction coeff (g)[10]	16 (1) × 10^{-6}
$R = \Sigma^m\lvert\Delta F\rvert/\Sigma^m\lvert F_o\rvert$	0.046
$R_w = [\Sigma^m w\lvert\Delta F\rvert^2/\Sigma^m w\lvert F_o\rvert^2]^{1/2}$	0.040
$[\Sigma^m w\lvert\Delta F\rvert^2/(m-n)]^{1/2}$	1.33

Silver atom location was achieved by direct methods (programs MULTAN and SHELX), and the remainder of the structure was revealed by standard Fourier methods. Least-squares refinement based on F, with $w = [\sigma(F)]^{-2}$, proceeded normally. At appropriate stages anisotropic temperature factors were assigned to all nonhydrogen atoms, phenyl ring hydrogen atoms were included and maintained at calculated positions (C–H = 0.95 Å), and Larson's isotropic extinction correction[10] was included. A difference Fourier in the final stages showed evidence of the methyl hydrogen atoms in staggered conformation, and thereafter these atoms were included at positions idealized for this conformation. An isotropic temperature factor for each hydrogen atom was maintained equal to the temperature factor of the atom bearing the hydrogen atom. In the final difference map the larger peaks were associated with the silver atom locations, the largest density being 1.0 e Å^{-3}. In the least-squares error cycle all nonhydrogen atom coordinates were blocked together, so that all positional parameter correlation is included in the quoted esd's of atom positions and derived quantities.

Scattering factors for neutral atoms, with real and imaginary dispersion corrections for silver and sulfur, were taken from standard sources.[11]

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Table II. Fractional Atomic Coordinates and Estimated Standard Deviations for $(Me_4N)_2[Ag_6(SPh)_8]$

atom	*x*	*y*	*z*
Ag1	0.10223 (7)	0.50929 (6)	0.94739 (4)
Ag2	−0.02662 (6)	0.63338 (5)	0.83536 (4)
Ag3	0.18895 (6)	0.68213 (6)	0.77940 (4)
Ag4	0.03348 (6)	0.53399 (5)	0.68794 (4)
Ag5	0.06505 (6)	0.81116 (5)	0.66564 (4)
Ag6	0.05385 (7)	0.61929 (6)	0.54387 (4)
S1	0.2448 (2)	0.5969 (2)	0.8943 (1)
S2	−0.1088 (2)	0.6157 (2)	0.9561 (1)
S3	0.1801 (2)	0.8754 (2)	0.7712 (1)
S4	0.2205 (2)	0.5892 (2)	0.6604 (1)
S5	0.0299 (2)	0.4482 (2)	0.8032 (1)
S6	−0.0816 (2)	0.7493 (2)	0.7389 (1)
S7	0.0392 (2)	0.8061 (2)	0.5362 (1)
S8	−0.0896 (2)	0.5024 (2)	0.5710 (1)
C11	0.3229 (7)	0.6737 (7)	0.9540 (4)
C12	0.4061 (7)	0.6313 (8)	1.0015 (5)
C13	0.4720 (9)	0.6867 (12)	1.0460 (6)
C14	0.4549 (11)	0.7905 (12)	1.0456 (6)
C15	0.3730 (11)	0.8345 (9)	0.9994 (6)
C16	0.3060 (8)	0.7757 (8)	0.9536 (5)
C21	−0.1055 (8)	0.7322 (7)	1.0021 (5)
C22	−0.1948 (9)	0.7708 (9)	1.0372 (5)
C23	−0.1925 (15)	0.8626 (12)	1.0734 (7)
C24	−0.1040 (22)	0.9156 (10)	1.0735 (7)
C25	−0.0138 (15)	0.8813 (11)	1.0393 (8)
C26	−0.0173 (9)	0.7872 (7)	1.0050 (5)
C31	0.3060 (7)	0.9050 (6)	0.7435 (5)
C32	0.3791 (8)	0.9517 (7)	0.7933 (5)
C33	0.4760 (9)	0.9812 (9)	0.7731 (7)
C34	0.5053 (9)	0.9647 (9)	0.7071 (8)
C35	0.4342 (9)	0.9164 (9)	0.6572 (6)
C36	0.3357 (8)	0.8865 (7)	0.6752 (5)
C41	0.2967 (6)	0.4695 (6)	0.6713 (4)
C42	0.3288 (7)	0.4304 (7)	0.7378 (5)
C43	0.3909 (9)	0.3390 (8)	0.7453 (5)
C44	0.4227 (8)	0.2866 (8)	0.6853 (6)
C45	0.3908 (9)	0.3248 (8)	0.6203 (6)
C46	0.3263 (8)	0.4145 (8)	0.6126 (5)
C51	−0.0999 (6)	0.3971 (6)	0.8026 (4)
C52	−0.1730 (7)	0.3927 (7)	0.7421 (5)
C53	−0.2703 (8)	0.3473 (8)	0.7409 (5)
C54	−0.2951 (7)	0.3093 (7)	0.8037 (5)
C55	−0.2239 (8)	0.3128 (7)	0.8646 (5)
C56	−0.1282 (8)	0.3585 (6)	0.8635 (4)
C61	−0.1390 (6)	0.8645 (6)	0.7747 (4)
C62	−0.1617 (8)	0.8727 (7)	0.8447 (5)
C63	−0.2098 (9)	0.9610 (8)	0.8718 (5)
C64	−0.2381 (9)	1.0410 (8)	0.8311 (7)
C65	−0.2180 (8)	1.0353 (8)	0.7617 (7)
C66	−0.1690 (8)	0.9455 (8)	0.7322 (5)
C71	0.1616 (7)	0.8392 (6)	0.5032 (4)
C72	0.2490 (9)	0.7667 (7)	0.4939 (5)
C73	0.3393 (10)	0.7947 (11)	0.4657 (7)
C74	0.3493 (10)	0.8900 (12)	0.4466 (6)
C75	0.2637 (11)	0.9612 (10)	0.4560 (6)
C76	0.1700 (9)	0.9364 (7)	0.4844 (5)
C81	−0.2234 (7)	0.5629 (6)	0.5763 (4)
C82	−0.2431 (8)	0.6656 (8)	0.5779 (5)
C83	−0.3490 (10)	0.7117 (9)	0.5815 (6)
C84	−0.4352 (9)	0.6572 (11)	0.5835 (6)
C85	−0.4173 (8)	0.5537 (10)	0.5824 (5)
C86	−0.3115 (7)	0.5060 (7)	0.5796 (5)
N1	−0.4164 (5)	0.6501 (6)	0.8150 (4)
C1N1	−0.4050 (10)	0.7310 (11)	0.8698 (7)
C2N1	−0.5200 (9)	0.6699 (10)	0.7711 (6)
C3N1	−0.3241 (9)	0.6440 (11)	0.7718 (6)
C4N1	−0.4170 (12)	0.5579 (9)	0.8531 (7)
N2	0.0953 (7)	0.1729 (5)	0.6796 (4)
C1N2	0.0816 (15)	0.2715 (9)	0.6485 (6)
C2N2	0.1381 (18)	0.0969 (11)	0.6319 (7)
C3N2	0.1591 (14)	0.1737 (11)	0.7481 (8)
C4N2	−0.0103 (15)	0.1481 (16)	0.6912 (14)
HC12	0.4173	0.5604	1.0026
HC13	0.5290	0.6545	1.0784
HC14	0.5028	0.8281	1.0768
HC15	0.3618	0.9064	0.9996
HC16	0.2481	0.8083	0.9226
HC22	−0.2580	0.7333	1.0366
HC23	−0.2556	0.8882	1.0973
HC24	−0.1060	0.9771	1.0980
HC25	0.0485	0.9202	1.0409
HC26	0.0453	0.7611	0.9827
HC32	0.3613	0.9641	0.8413
HC33	0.5227	1.0152	0.8079
HC34	0.5720	0.9852	0.6939
HC35	0.4537	0.9035	0.6099
HC36	0.2883	0.8537	0.6406
HC42	0.3075	0.4664	0.7791
HC43	0.4122	0.3131	0.7914
HC44	0.4669	0.2242	0.6902
HC45	0.4128	0.2894	0.5789
HC46	0.3015	0.4383	0.5662
HC52	−0.1570	0.4219	0.6997
HC53	−0.3182	0.3422	0.6982
HC54	−0.3629	0.2799	0.8045
HC55	−0.2398	0.2836	0.9074
HC56	−0.0805	0.3637	0.9065
HC62	−0.1438	0.8166	0.8749
HC63	−0.2228	0.9645	0.9208
HC64	−0.2724	1.1008	0.8501
HC65	−0.2369	1.0915	0.7321
HC66	−0.1570	0.9424	0.6829
HC72	0.2454	0.6996	0.5072
HC73	0.3982	0.7447	0.4590
HC74	0.4134	0.9069	0.4278
HC75	0.2684	1.0286	0.4424
HC76	0.1125	0.9868	0.4911
HC82	−0.1833	0.7059	0.5767
HC83	−0.3604	0.7828	0.5828
HC84	−0.5074	0.6872	0.5854
HC85	−0.4773	0.5133	0.5831
HC86	−0.2992	0.4343	0.5805
H1C1N1	−0.3370	0.7229	0.9012
H2C1N1	−0.4645	0.7386	0.9003
H3C1N1	−0.4045	0.7973	0.8489
H1C2N1	−0.5318	0.6180	0.7339
H2C2N1	−0.5834	0.6741	0.7979
H3C2N1	−0.5236	0.7313	0.7447
H1C3N1	−0.3297	0.5917	0.7348
H2C3N1	−0.2542	0.6318	0.7991
H3C3N1	−0.3229	0.7057	0.7456
H1C4N1	−0.4239	0.4999	0.8203
H2C4N1	−0.3486	0.5419	0.8831
H3C4N1	−0.4765	0.5589	0.8824
H1C1N2	0.0537	0.3232	0.6782
H2C1N2	0.0414	0.2721	0.6019
H3C1N2	0.1561	0.2914	0.6386
H1C2N2	0.1509	0.0318	0.6497
H2C2N2	0.0998	0.0969	0.5848
H3C2N2	0.2156	0.1130	0.6213
H1C3N2	0.1685	0.1089	0.7704
H2C3N2	0.1306	0.2224	0.7816
H3C3N2	0.2353	0.1902	0.7442
H1C4N2	−0.0105	0.0824	0.7129
H2C4N2	−0.0478	0.1949	0.7240
H3C4N2	−0.0617	0.1454	0.6479

The labeling of metal and sulfur atoms in the asymmetric unit $(Me_4N)_2[Ag_6(SPh)_8]$ is shown in Figure 1. The carbon and hydrogen atoms of the phenyl ring bonded to S*m* (m = 1–8) are labeled C*mn* and HC*mn* (n = 1–6), and the Me_4N^+ atoms are N*p*, C*q*N*p*, and H*r*C*q*N*p* (p = 1, 2, q = 1–4, and r = 1–3). Atomic coordinates are presented in Table II.

A listing of F_o and F_c, a tabulation of all atomic thermal parameters, and a tabulation of the powder diffraction pattern of $(Me_4N)_2[Ag_6(SPh)_8]$ comprise the supplementary material.

Results

Description of the Structure. At first view (Figure 1) the anion appears to be a continuous, bent multiple chain with alternating silver and sulfur atoms and with phenyl rings protruding like flippers, one from each sulfur atom. The phenyl rings generate nonbonding boundaries around the chain, which is thus one-dimensionally nonmolecular. Centers of symmetry occur along the chain, and the asymmetric unit of the chain (unprimed atom symbols in Figure 1) between such centers has the formulation $[Ag_6(SPh)_8]^{2-}$.

The Ag–S bonds drawn in Figure 1 show that the two silver atoms (Ag1, Ag6) near the centers of symmetry are four-coordinate, while the other four possess trigonal-planar coordination. Four benzenethiolate ligands (S2, S4, S5, S8) are triply bridging, and the other four doubly bridge silver atoms.

Selected interatomic distances and angles are presented in Table III. The Ag–S distances, which vary from 2.42 to 2.88 Å, fall into two groups. The shorter group ranges from 2.42 to 2.61 Å, and the longer group, from 2.71 to 2.88 Å. Statistical results are as follows:[12] "short" Ag–S, 16, 2.520 Å, 0.061 Å, 0.015 Å; "long" Ag–S, 4, 2.820 Å, 0.077 Å, 0.039 Å.

Examination of the positions of short and long Ag–S bonds in the structure suggests subdivision of the crystal structure into molecular units which may represent the structures of species in solution in equilibrium with the crystal. Similar interpretations were made for the crystal structure of (cyclohexanethiolato)silver:[4] in both silver thiolates the one-dimensionally nonmolecular structure of the crystals could not exist as such in solution.

Each of the four-coordinate silver atoms engages two "short" Ag–S bonds and two "long" Ag–S bonds, whereas all trigonal-planar silver atoms are involved only with "short" bonds. If the long bonds are assumed to be the result of association of species with independent existence in solution and are disregarded, Ag1 and Ag6 become two-coordinate and the structure appears as shown in Figure 2. The structurally molecular unit is centrosymmetric $[Ag_{12}(SPh)_{16}]^{4-}$. Figure 2 also shows that this $[Ag_{12}(SPh)_{16}]^{4-}$ unit is composed of two globular polyhedral cages linked only by two bonds (Ag1-S2′, Ag1′-S2) across the center of symmetry. In terms of molecular structure the basic unit for this compound is $[Ag_6(SPh)_8]^{2-}$, the crystallographic asymmetric unit.

The trigonally coordinated silver atoms Ag2, Ag3, Ag4, and Ag5 are displaced 0.45, 0.34, 0.38, and 0.09 Å, respectively, from their S_3 donor atom planes, all toward the center of the cluster. This raises the question of possible bonding interactions between silver atoms within the cluster. The shorter Ag--Ag distances are 2.96 Å (Ag1--Ag2), 2.99 Å (Ag3--Ag5), 3.03 Å (Ag4--Ag6), and 3.08 Å (Ag2--Ag3), which are similar in length and their unsymmetrical distribution to the shorter Ag--Ag distances of 2.94 and 3.03 Å in $(Me_4N)_2[Ag_5(SPh)_7]$[8] and are greater than the Ag--Ag distance of 2.88 Å in cubic close-packed silver metal. The conclusion elaborated previously for $[Ag_5(SPh)_7]^{2-}$, namely, that any attractive interactions between silver atoms are minor influences in the existence and structure of the cage, applies also to $[Ag_6(SPh)_8]^{2-}$. This cage is maintained by the bridging benzenethiolate ligands.

Additional geometrical results, presented as a statistical summary, are as follows:[12] trigonal coordination S–Ag–S angles, 12, 118.2°, 12.8°, 3.7°; S–C, 8, 1.772 Å, 0.012 Å, 0.004 Å; C–C (ring), 48, 1.37 Å, 0.17 Å, 0.02 Å; C–N (cation), 8, 1.444 Å, 0.020 Å, 0.007 Å.

Table III. Selected Interatomic Distances (Å) and Angles (Deg) in $(Me_4N)_4[Ag_{12}(SPh)_{16}]$[a]

Silver Coordination			
Ag1-S1	2.503 (3)	Ag4-S4	2.582 (2)
Ag1-S2	2.850 (3)	Ag4-S5	2.499 (2)
Ag1-S5	2.878 (2)	Ag4-S8	2.576 (2)
Ag1-S2[b]	2.505 (2)	Ag5-S3	2.485 (2)
Ag2-S2	2.610 (2)	Ag5-S6	2.431 (3)
Ag2-S5	2.576 (2)	Ag5-S7	2.424 (2)
Ag2-S6	2.431 (3)	Ag6-S4	2.845 (2)
Ag3-S1	2.484 (3)	Ag6-S7	2.497 (3)
Ag3-S3	2.587 (3)	Ag6-S8	2.561 (2)
Ag3-S4	2.569 (2)	Ag6-S8[c]	2.706 (4)
S1-Ag1-S2[b]	134.21 (9)	S4-Ag4-S5	117.13 (7)
S1-Ag1-S2	117.79 (8)	S5-Ag4-S8	125.99 (8)
S1-Ag1-S5	86.16 (7)	S8-Ag4-S4	110.31 (7)
S2-Ag1-S2[b]	101.78 (7)	S3-Ag5-S6	95.03 (8)
S2-Ag1-S5	88.76 (7)	S6-Ag5-S7	120.60 (8)
S5-Ag1-S2[b]	118.41 (7)	S7-Ag5-S3	143.89 (8)
S2-Ag2-S5	101.15 (8)	S7-Ag6-S8	130.14 (8)
S5-Ag2-S6	118.49 (8)	S7-Ag6-S4	100 87 (7)
S6-Ag2-S2	130.60 (8)	S7-Ag6-S8[c]	121.61 (8)
S1-Ag3-S3	121.49 (8)	S8-Ag6-S4	102.92 (7)
S3-Ag3-S4	113.14 (8)	S8-Ag6-S8[c]	87.16 (7)
S4-Ag3-S1	120.19 (8)	S4-Ag6-S8[c]	113.37 (7)
Angles at Sulfur			
Ag1-S1-Ag3	117.65 (10)	Ag2-S5-Ag4	77.06 (7)
Ag1-S1-C11	115.61 (28)	Ag4-S5-Ag1	130.55 (9)
Ag3-S1-C11	110.58 (31)	Ag1-S5-Ag2	65.43 (5)
Ag1-S2-Ag2	65.44 (6)	Ag2-S5-C51	100.05 (25)
Ag1-S2-Ag1[b]	78.22 (7)	Ag4-S5-C51	108.67 (27)
Ag2-S2-Ag1[b]	139.04 (10)	Ag1-S5-C51	108.61 (26)
Ag1-S2-C21	114.36 (31)	Ag2-S6-Ag5	120.25 (11)
Ag2-S2-C21	107.39 (31)	Ag2-S6-C61	109.16 (29)
Ag1[b]-S2-C21	104.30 (30)	Ag5-S6-C61	101.14 (28)
Ag3-S3-Ag5	72.31 (7)	Ag5-S7-Ag6	86.72 (8)
Ag3-S3-C31	107.57 (28)	Ag5-S7-C71	108.86 (26)
Ag5-S3-C31	108.49 (29)	Ag6-S7-C71	107.50 (28)
Ag3-S4-Ag4	76.91 (6)	Ag4-S8-Ag6	72.18 (6)
Ag4-S4-Ag6	67.57 (6)	Ag6-S8-Ag6[c]	92.84 (7)
Ag6-S4-Ag3	117.82 (9)	Ag6[c]-S8-Ag4	131.16 (9)
Ag3-S4-C41	113.32 (27)	Ag4-S8-C81	109.96 (26)
Ag4-S4-C41	96.68 (25)	Ag6-S8-C81	114.39 (30)
Ag6-S4-C41	119.90 (25)	Ag6[c]-S8-C81	118.44 (26)
Ag--Ag Distances			
Ag1--Ag1[b]	3.389 (2)	Ag3--Ag4	3.203 (1)
Ag1--Ag2	2.959 (1)	Ag3--Ag5	2.993 (1)
Ag1--Ag3	4.267 (1)	Ag4--Ag5	3.805 (1)
Ag2--Ag3	3.080 (1)	Ag4--Ag6	3.026 (1)
Ag2--Ag4	3.162 (1)	Ag5--Ag6	3.379 (1)
Ag2--Ag5	4.355 (1)	Ag6--Ag6[c]	3.817 (2)

[a] Estimated standard deviations (in parentheses) refer to the least significant digit(s) quoted. [b] $-x, 1-y, 2-z$. [c] $-x, 1-y, 1-z$.

There are no unusual interion distances in the structure.

Crystallization Equilibria. Very well-formed, pale yellow blocks of $(Me_4N)_2[Ag_6(SPh)_8]$ have crystallized from solutions containing $AgNO_3$, PhSH, *n*-Bu_3N (deprotonating agent), Me_4NCl, acetonitrile, and the lower alcohols. The presence of chloride ion at Cl^-/Ag^+ molar ratios up to 3.1 has not interfered with this crystallization: silver chloride is soluble in solutions containing benzenethiolate ion. The PhS^-/Ag^+ molar ratios in solutions precipitating $(Me_4N)_2[Ag_6(SPh)_8]$ were very different from the value of 1.33 in the product: solutions with PhS^-/Ag^+ ratios 3.4, 3.98 and 5.0 have yielded $(Me_4N)_2[Ag_6(SPh)_8]$ crystals in fair yield. Recrystallization of isolated $(Me_4N)_2[Ag_6(SPh)_8]$ from a noncoordinating solvent such as acetonitrile is not possible, as ligand dissociation and precipitation of $(AgSPh)_n$ occur.

These observations, together with the fact that a related compound $(Me_4N)_2[Ag_5(SPh)_7]$ has also crystallized from solutions almost identical in composition with those yielding

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[12] All statistical results in this paper are presented as follows: number of values in sample, sample mean, esd of sample, esd of mean.

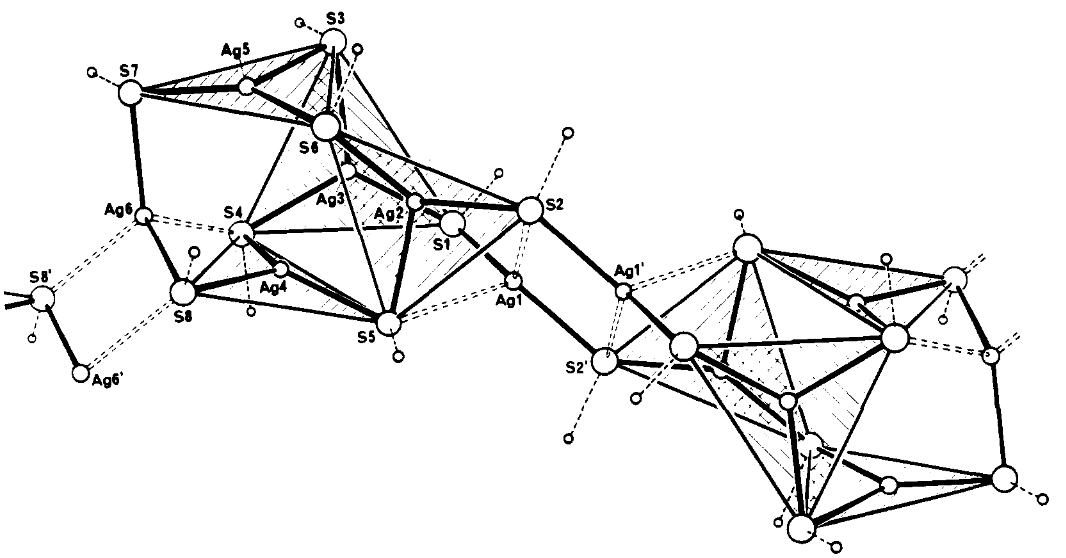

Figure 2. Distribution of normal Ag–S bonds (dark solid lines) and coordination triangles (cross-hatched) in the centrosymmetric molecule $[Ag_{12}(SPh)_{16}]^{4-}$, which appears when the "long" Ag–S bonds (double dashed lines) are disregarded. The small circles are the α-carbon atoms of the omitted phenyl rings.

$(Me_4N)_2[Ag_6(SPh)_8]$, clearly indicate the occurrence of the equilibria in eq 1. Other species, more soluble under the

$$(AgSPh)_n(s) \xrightleftharpoons{PhS^-} [Ag_6(SPh)_8]^{2-} \xrightleftharpoons{PhS^-} [Ag_5(SPh)_7]^{2-} \quad (1)$$

conditions investigated, probably exist.

Equilibria between the species shown in (1) can be controlled via the solvent composition and the temperature. In the Experimental Section is described an experiment in which $(Me_4N)_2[Ag_6(SPh)_8]$ and $(Me_4N)_2[Ag_5(SPh)_7]$ first crystallized together and then were redissolved by addition of acetonitrile and heating, which caused crystallization of $(AgSPh)_n$. Cooling caused redissolution of the $(AgSPh)_n$, and it was possible to find an intermediate temperature at which the anionic complexes and $(AgSPh)_n$ could be kept in solution; further temperature reduction effected slow, good crystallization of $(Me_4N)_2[Ag_6(SPh)_8]$. In other similar experiments the slow crystallization of $(AgSPh)_n$ has been controlled by slow temperature increase from 20 to 30 °C: PhS^- dissociation from anionic $[Ag_x(SPh)_y]^{x-y}$ species is endothermic.

An informative method for identifying the $[Ag_x(SPh)_y]^{x-y}$ species *in solution* and monitoring their relative concentrations is not available. Compounds which crystallize from solution are not necessarily representative of its composition, and observations recorded in the Experimental Section confirm the vagarious influence of nucleation (in addition to solubility differences) on the identity of anionic cage complexes which crystallize from solution. However, small variations do occur in the intensity of the pale yellow colors of the preparative solutions. An increase in the alcohol content of an alcohol/acetonitrile solution increases its yellow color, while temperature reduction decreases the yellow intensity. The intensity of yellow color in the crystalline compounds increases in the order $(AgSPh)_n$ < $(Me_4N)_2[Ag_6(SPh)_8]$ < $(Me_4N)_2[Ag_5(SPh)_7]$.

The $[Ag_6(SPh)_8]^{2-}$ Cage Polyhedron. It has already been shown that the one-dimensionally nonmolecular crystal structure of $(Me_4N)_2[Ag_6(SPh)_8]$ is easily interpretable as an association of $[Ag_{12}(SPh)_{16}]^{4-}$ cages and that each $[Ag_{12}(SPh)_{16}]^{4-}$ cage is the result of hourglass linkage of two $[Ag_6(SPh)_8]^{2-}$ cages. Independent existence for both $[Ag_{12}(SPh)_{16}]^{4-}$ and $[Ag_6(SPh)_8]^{2-}$ in solution is probable. The Ag_6S_8 core of the $\{Ag_6(SPh)_8\}$ unit is quite irregular, but it is related to the structures of other known benzenethiolate cages of copper(I) and silver(I). This relationship is clearly apparent after the following idealization of the Ag_6S_8 polyhedron.

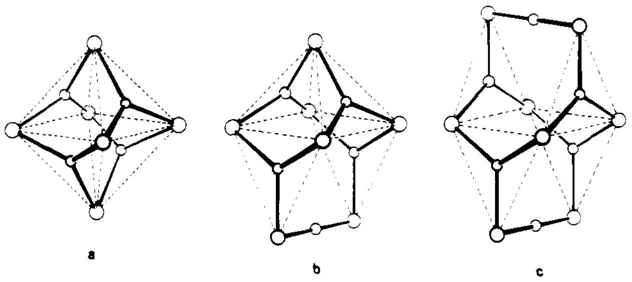

Figure 3. Idealized cage polyhedra: (a) M_4S_6; (b) M_5S_7; (c) M_6S_8.

In Figure 2 the four triangles of the three-coordinate silver atoms Ag2, Ag3, Ag4, and Ag5 are cross-hatched and are seen to share vertices at a distorted square of sulfur atoms S3, S4, S5, and S6. The four triangles are arrayed around this square in the same fashion as the four coordination triangles in the M_4S_6 cage polyhedron, which is shown in Figure 3a. This cage polyhedron, with an M_4 tetrahedron occupying faces of an S_6 octahedron, occurs in $[Cu_4(SPh)_6]^{2-}$[13] and $[Cu_4(SCH_3)_6]^{2-}$.[14] It is also the parent polyhedron for the idealization of $Ag_6(SPh)_8$.

Figure 3b shows the idealized M_5S_7 polyhedron which is derived from M_4S_6 through expansion of one S vertex by opening out two coordination trigonal planes and replacing the sulfur atom which linked then with a linear S–M–S group. If this polyhedron expansion process is repeated at the trans vertex of the original octahedron, the M_6S_8 polyhedron of Figure 3c is obtained. There are then two linearly coordinated metal atoms and four trigonal-planar metal atoms.

Imposition of the M_6S_8 idealization of Figure 3c on the $\{Ag_6(SPh)_8\}$ unit of Figure 2 requires twisting the trigonal planes to make S3, S4, S5, and S6 square, straightening the coordination of Ag6 between S7 and S8, and coordinating Ag1 linearly between S1 and S2. This idealization is in fact supported by the occurrence of the two "short" Ag–S bonds at Ag6, but at Ag1 the two short Ag–S bonds constitute an *inter*-$\{Ag_6(SPh)_8\}$-cage Ag1–S2′ linkage rather than the *intra*cage link of the idealization. The $[Ag_{12}(SPh)_{16}]^{4-}$ cage

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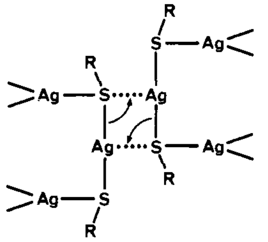

Figure 4. Geometry of the butt-joining of $[Ag_6(SPh)_8]^{2-}$ cages at two-coordinate silver. Arrows indicate original and new positions of short Ag–S bonds.

structure is therefore two $[Ag_6(SPh)_8]^{2-}$ cage units which are butt-joined at two-coordinate silver atoms, as shown diagramatically in Figure 4. The arrows show the change from short Ag–S bonds in the $[Ag_6(SPh)_8]^{2-}$ cages to short Ag–S bonds joining the cages; there is concomitant movement of Ag1 and S2 toward S2′.

The M_6S_8 cage unit has not been observed previously. This crystal structure reveals the mode of closing the two-coordinate ends of this cage and also shows the geometry of the polymerization mechanism at two-coordinate silver.

Low Rigidity of $[Ag_6(SPh)_8]^{2-}$. The $\{Ag_6(SPh)_8\}$ unit is substantially distorted from the idealized polyhedral geometry of Figure 3c. For instance, the angles between the planes of trigonal coordination are as follows (ideal values in parentheses): Ag2/Ag3, 22.4° (0°); Ag4/Ag5, 16.6° (0°), Ag2/Ag4, 89.5° (90°); Ag2/Ag5, 81.6° (90°); Ag3/Ag4, 107.5° (90°); Ag3/Ag5, 67.8° (90°). Within the trigonal coordination planes there is wide variation of the S–Ag–S angles (sample esd 12.8°) and no correlation (negative) between the Ag–S distance and the opposite S–Ag–S angle; such correlation does occur in the crystal structure of $(AgSC_6H_{11})_{12}$.[4] Evidence of the distortion of the polyhedron appears also in the Ag–S–Ag angles: ideally the angles Ag6–S7–Ag5, Ag6–S8–Ag4, Ag1–S1–Ag3, and Ag1–S2–Ag2 would be 104.5°, but they are 72.3, 120.3, 76.9, and 77.1° respectively.[15]

These distortions from ideality are generally larger than those observed for $[Ag_5(SPh)_7]^{2-}$.[8] This is consistent with the larger size of the empty Ag_6S_8 polyhedron, which would be expected to be more responsive to nonspecific lattice forces in the crystal.

The two additional "long" interactions, Ag6–S4 and Ag1–S5, presumably exist to confer sufficient rigidity at the two-coordinate silver atoms, which would constitute the weakest structural component of the Ag_6S_8 polyhedron.

Discussion

The $Ag^+/^-SPh$ system manifests the homoleptic molecular cages $[Ag_5(SPh)_7]^{2-}$, $[Ag_6(SPh)_8]^{2-}$, and $[Ag_{12}(SPh)_{16}]^{4-}$, in equilibrium with $(AgSPh)_n$ for which the structural molecularity is not known. An expected member of this sequence, $[Ag_4(SPh)_6]^{2-}$, has not yet been crystallized, but in view of the structural correspondence between copper(I) and silver(I) with benzenethiolate[8] and the crystallization of $[Cu_4(SPh)_6]^{2-}$[13] there is no reason to doubt the existence of $[Ag_4(SPh)_6]^{2-}$ in solution.

The structures of these cages comprise a sequence (Figure 3) of expanding closo polyhedra with bridging benzenethiolate ligands only. Polyhedral expansion occurs by insertion of AgSPh at an SPh vertex.

As a consequence of the low coordination numbers (2, 3) for silver in these cages the proportion of PhS^- bridges is low, and the rigidity of the cage polyhedra decreases appreciably with expansion. This decreasing rigidity is evident in the crystals as angular distortion, which is substantial in $[Ag_5(SPh)_7]^{2-}$ and marked in $[Ag_6(SPh)_8]^{2-}$. Two extra weak Ag–S interactions occur within $[Ag_6(SPh)_8]^{2-}$ to impart structural stability to the cage. It is expected that $[Ag_6(SPh)_8]^{2-}$ would be angularly floppy in solution.

For the same reasons, further polyhedral expansion beyond Ag_6S_8 appears unlikely in the $Ag^+/^-SPh$ system.[16] However, the crystal structure of $(Me_4N)_2[Ag_6(SPh)_8]$ shows that further increase in cage size, without polyhedral expansion, can occur by the joining of smaller cages. Thus centrosymmetric $[Ag_{12}(SPh)_{16}]^{4-}$ is the result of joining two $[Ag_6(SPh)_8]^{2-}$ cages at their two-coordinate silver atoms. It is proposed that this mechanism of increasing molecular size, namely, limited polyhedral expansion followed by filamentous joining of polyhedra, will occur generally in Ag/SR and Cu/SR systems. This mechanism is known in other inorganic cage systems where coordination numbers are low, for instance, the borane anions and carboranes.

Triply bridging benzenethiolate ligands (numbers 2, 4, 5, 8) occur in this crystal structure. In each instance the sulfur atom is involved in two "short" Ag–S bonds (2.52 ± 0.02 Å) and one "long" Ag–S bond (2.82 ± 0.04 Å), in addition to the S–C bond. This is the first reported example of an arenethiolate ligand bridging three metal atoms. Monothiolate ligands RS^- are usually found as terminal or doubly bridging, but some instances of triply bridging *alkane*thiolate ligands are known: methanethiolate in $[(CO)_3ReSCH_3]_4$;[17] propane-2-thiolate in $[CH_3ZnSCH(CH_3)_2]_8$;[18] 2-methylpropane-2-thiolate in $[CH_3ZnSC(CH_3)_3]_5$;[19] 2-hydroxyethanethiolate in $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$.[20]

Acknowledgment. This research is supported by the Australian Research Grants Committee. D. C. Craig is thanked for assistance with the collection of diffraction data.

Registry No. $(Me_4N)_2[Ag_6(SPh)_8]$, 76402-94-3; $(Me_4N)_2[Ag_5(SPh)_7]$, 68628-02-4; $(Me_4N)_4[Ag_{12}(SPh)_{16}]$, 76402-96-5.

Supplementary Material Available: A listing of structure factor amplitudes, a tabulation of atom thermal parameters, and a listing of the powder diffraction lines of $(Me_4N)_2[Ag_6(SPh)_8]$ (23 pages). Ordering information is given on any current masthead page.

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(15) The geometry of benzenethiolate bridging is such that the Ag–S–C angles are all close to the tetrahedral value: 20 angles, mean 109.2°, esd of sample 5.9°, esd of mean 1.3°.

(16) Stabilization of larger polyhedra can be achieved with additional structural components, such as encapsulation of a central spherical ligand or use of chelate ligands to span the edges of the polyhedron.[13]

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