Table IV. Data Collection Details for $NaEu(N(SiMe_3)_2)_3$ and $NaYb(N(SiMe_3)_2)_3$

Crystal Parameters[a]

	Eu	Yb
space group	$P2_1/n$	*Pbca*
a, Å	17.586 (6)	19.334 (6)
b, Å	19.170 (6)	18.534 (6)
c, Å	21.808 (6)	20.020 (6)
β, deg	107.90 (4)	
V, Å^3	6996	7174
Z	8	8
M_r	656.1	677.2
density (calcd), g/cm^3	1.246	1.254
μ(calcd, Mo Kα), cm^{-1}	20.2	28.2

Intensity Data Measurement

radiation	Mo Kα (λ = 0.710 73 Å)
monochromator	highly oriented graphite, $2\theta_m = 12.2°$
scan type	θ(crystal)–2θ(counter)
reflcns measd	$3° < 2\theta < 45°$; $+h,+k,\pm l$ for Eu; $+h,+k,+l$ for Yb
scan speed	variable from 0.63 to 6.7° (θ)/min
scan width	$\Delta\theta = 0.5 + 0.347 \tan\theta$
bkgd	an additional $\Delta(2\theta)/4$ at each end of the scan
scans collected	for Eu 7643 (including standards), yielding 7397 unique reflcns; for Yb 3199 (including standards), yielding 2904 unique reflcns
std reflctns	3 measd after every 250 scans; 5% decay in intensity obsd for both complexes

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections.

was refined by using anisotropic thermal parameters on the carbon atoms, the *R* factor went from 0.056 to 0.048 but several of the carbon anisotropic thermal parameters were unacceptably large. A careful study of the electron difference maps of the Yb complex after the isotropic refinement had converged showed many peaks near the carbon atom positions, which suggests large thermal motions or disorder, but no clear pattern of disorder could be recognized. In comparison to the Eu structure the Yb structure is reasonable, if not accurate. Because of the large number of parameters in the Eu structure and the limited size of the available memory in our computer, the parameters of one molecule were refined by least-squares techniques while those for the other molecules were included but not refined; the parameters of each molecule were alternately refined. After the final refinements the largest shift/esd was less than 0.20 (Eu) and 0.09 (Yb). The standard deviations of a reflection of unit weight were 1.17 (Eu) and 1.99 (Yb). The final electron density difference maps showed maximum and minimum peaks of 0.5 and −0.7 e/Å^3 (Eu) and 0.9 and −0.8 e/Å^3 (Yb). In the final difference maps of the Eu complex some of the largest peaks are near carbon atoms at distances that could be interpreted as hydrogen atom peaks, but they were poorly resolved. The majority of the peaks represented "noise". The carbon atom C(8) in the Eu structure has large thermal parameters, but no indication of disorder was evident in the difference maps. The final *R* factors[16] are as follows: for the Eu complex $R_F = 0.031$ for 6751 data ($F^2 > \sigma(F^2)$) and $R_{wF} = 0.041$; for the Yb complex $R_F = 0.056$ for 2546 data ($F^2 > 3\sigma(F^2)$) and $R_{wF} = 0.080$.

Acknowledgment. This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF0098. We thank Dr. F. J. Hollander, staff crystallographer of the U.C. Berkeley X-ray facility (CHEXRAY), for collecting the X-ray data.

Supplementary Material Available: Listings of thermal parameters, Si–C distances, selected angles, and observed and calculated structure factors (45 pages). Ordering information is given on any current masthead page.

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(16) $R_F = \sum||F_o| - |F_c||/\sum|F_o|$; $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

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Synthesis and Molecular Structure of Pentakis(triphenylphosphine)hexakis(4-chlorobenzenethiolato)hexasilver(I), Derived from a New $Ag_5(SR)_6$ Cage Structure

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The reaction of triphenylphosphine and (4-chlorobenzenethiolato)silver in toluene yields $Ag_6(SC_6H_4Cl)_6(PPh_3)_5(tol)_2$ (tol = toluene) as colorless crystals in which the toluene is lattice bound. The unprecedented $Ag_6(SR)_6(PPh_3)_5$ molecular aggregate, enclosed by 21 aryl substituents, contains an $Ag_5(SR)_6$ central cage, with phosphine ligands terminal at three of the silver atoms and an $Ag(PPh_3)_2$ appendage inserted between two bridging thiolates. The $Ag_5(SR)_6$ cage, when symmetrized, contains a basal unit comprised of an irregular hexagon of alternating silver and sulfur atoms ($\mathrm{Ag}_{\mathrm{basal}}^{\mathrm{peripheral}}$ and $\mathrm{S}_{\mathrm{basal}}$), centered by a silver atom ($\mathrm{Ag}_{\mathrm{basal}}^{\mathrm{central}}$) with trigonal-planar $(\mathrm{S}_{\mathrm{bas}})_3$ coordination. A trigonal-planar podal unit, $\mathrm{Ag}_{\mathrm{pod}}(\mathrm{S}_{\mathrm{pod}})_3$, is parallel to the basal plane and is attached to it by three $\mathrm{S}_{\mathrm{pod}}$–$\mathrm{Ag}_{\mathrm{bas}}^{\mathrm{per}}$ bonds. Tetrahedral coordination of each $\mathrm{Ag}_{\mathrm{bas}}^{\mathrm{per}}$ atom is completed by a terminal phosphine ligand. The additional $Ag(PPh_3)_2$ moiety ($\mathrm{Ag}_{\mathrm{bridge}}$) bridges two $\mathrm{S}_{\mathrm{pod}}$ atoms. A structural relationship between the cage polyhedra of the $Ag_5(SR)_6$ core and the established $[M_5(S\text{-}t\text{-}Bu)_6]^-$ (M = Cu, Ag) molecular cage is proposed. The basal thiolate ligands are triply bridging, but with an unusual stereochemistry in which the sulfur atom lies outside the polyhedron of four atoms to which it is bonded. The distances between silver atoms ($\mathrm{Ag}_{\mathrm{bas}}^{\mathrm{cen}}$–$\mathrm{Ag}_{\mathrm{bas}}^{\mathrm{per}}$, mean 2.95 Å; $\mathrm{Ag}_{\mathrm{bas}}^{\mathrm{cen}}$–$\mathrm{Ag}_{\mathrm{pod}}$ = 3.05 Å; and $\mathrm{Ag}_{\mathrm{br}}$–$\mathrm{Ag}_{\mathrm{pod}}$ = 3.19 Å) do not indicate metal–metal bonding, and the aggregate structure is maintained by doubly and triply bridging arenethiolate ligands. The complex undergoes phosphine-dissociative reactions in solution. Crystal data for $C_{140}H_{115}Ag_6S_6Cl_6P_5$: triclinic, $P\bar{1}$, $a = 15.024\ (5)$ Å, $b = 18.488\ (5)$ Å, $c = 26.506\ (10)$ Å, $\alpha = 82.14\ (2)°$, $\beta = 86.19\ (2)°$, $\gamma = 66.45\ (3)°$, $Z = 2$, 8093 observed (Mo Kα) reflections, R (R_w) 0.060 (0.074).

Introduction

There is very limited knowledge of the structures of the uncharged binary arenethiolates of copper and silver, $[MSAr]_n$, mainly due to difficulty in obtaining single crystals of diffraction quality. Copper compounds of this type, including CuSPh, are semiconducting,[1] while CuSPh electrochemically deposited on CdS electrodes in photoelectrochemical cells improves their stability and possibly performance.[2] It is generally assumed that these compounds are structurally

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0020-1669/84/1323-2276$01.50/0

nonmolecular in at least one dimension. Polycrystalline diffraction data from AgSAr (Ar = C_6H_5, C_6H_4Cl-4) suggest a layer structure in which aryl substituents protrude approximately normal to a central Ag,S slab.[3]

Information about structural principles applicable to $[MSAr]_n$ may be derived from the structures of molecules $[M_x(SAr)_xL_y]$ that contain a small proportion (y/x) of additional ligands L and that may be molecular fragments of the nonmolecular $[MSAr]_n$ structures. We have reported the formation and structures of the anionic molecular aggregates $[Cu_4(SPh)_6]^{2-}$,[6] $[M_5(SPh)_7]^{2-}$,[7] and $[Ag_6(SPh)_8]^{2-}$ [8] in which L is the same as SAr. When L is triphenylphosphine, the complexes $Cu_2(SAr)_2(PPh_3)_4$,[9] $Cu_3(SAr)_3(PPh_3)_4$,[10] and $Cu_4(SPh)_4(PPh_3)_4$[11] (Ar = C_6H_5, C_6H_4Cl-4) are formed. In these molecules the number (x) of metal thiolate units in the core increases, as expected, as the proportion (y/x) of phosphine ligands decreases from 2 to 1. We now report the formation and structure of $Ag_6(SC_6H_4Cl)_6(PPh_3)_5$ (**1**), which extends this series of structures by increasing x to 6 as y/x decreases below 1. As will be shown, this molecular aggregate can also be regarded as a $(Ph_3P)_2Ag^+$ derivative of $[(Ph_3P)_3Ag_5(SAr)_6]^-$ (**2**).

Experimental Section

All solutions were flushed with nitrogen gas. The precursor (4-chlorobenzenethiolato)silver was precipitated from dilute solution by reaction of silver nitrate with an equimolar amount of 4-chlorobenzenethiolate and triethylamine and was washed thoroughly before drying.

$Ag_6(SC_6H_4Cl)_6(PPh_3)_5(tol)_2$. A solution of triphenylphosphine (1.58 g, 6 mmol) in toluene (40 mL) was added to (4-chlorobenzenethiolato)silver (1.0 g, 4 mmol) and the mixture stirred first at room temperature for 30 min and then at 50 °C for 45 min. The solution was filtered to remove the small amount of unidentified high-melting white solid that was sometimes present at this stage. Warm propanol (25 mL) was added to the pale yellow filtrate, which was allowed to cool slowly in the dark, yielding the product (0.93 g, 47%) as colorless crystals that were collected and vacuum-dried. Higher yields, up to 90%, have been obtained by use of larger proportions of propanol.

Anal. Calcd for $C_{140}H_{115}Ag_6S_6Cl_6P_5$: C, 55.97; H, 3.86. Found: C, 56.38, 56.56; H, 3.74, 3.94.

Polycrystalline diffraction pattern [d (Å), relative intensity]: 16.83 vw, 15.00 vs. 13.60 m, 13.39 w, 13.15 ms, 12.68 w, 12.24 w, 11.50 vw, 11.02 vw, 10.03 vw, 8.98 mw, 8.67 mw, 8.28 vw, 7.90 mw, 7.73 vw, 7.50 s, 6.15 vw, 5.89 w, 5.56 w, 5.01 m, 4.72 w, 4.55 m, 4.09 m, 4.00 vw, 3.95 vw, 3.75 w, 3.67 vw, 3.64 w, 3.50 m, 3.40 w, 3.25 vw, 3.15 m, 2.99 mw, 2.94 mw, 2.61 mw, 2.39 w, 2.23 w.

The crystalline compound is not affected by laboratory light or atmosphere during a 24-h exposure. On slow heating the solid becomes yellow at about 60 °C but has a well-defined melting point of 115–117 °C. The compound is soluble in chloroform and carbon tetrachloride, slightly soluble in ethanol, 2-propanol, acetone, acetonitrile, and toluene, and insoluble in methanol and ether and can be recrystallized from toluene/propanol. All solutions change color to yellow on heating and eventually deposit yellow solids.

Crystallography. An Enraf-Nonius CAD4 diffractometer with monochromatized Mo Kα radiation was used. The procedures for data collection, reduction, and correction for absorption have been described.[9] Corrections were made for the radiation damage sustained by the crystal. Numerical details of the crystallographic analysis, including the final least-squares refinement, are contained in Table I. The space group $P\bar{1}$ was confirmed by the successful refinement of the structure. Solution of the structure was by combination of direct methods (MULTAN80) and Patterson synthesis, and successive Fourier syntheses yielded the positions of all 163 non-hydrogen atoms. The least-squares refinement used the program RAELS,[12a] with **TL** or **TL**X models for rigid-body vibrations (T, translational tensor; **L**, librational tensor; X, coordinates of center of group libration[12b]). The phenyl rings of the PPh_3 ligands were treated as rigid groups, as were the C_6 rings of the 4-chlorobenzenethiolate ligands, and each group was allowed **TL** thermal motion. The S–C, C–Cl, and P–C distances were allowed independent variation. The two lattice-bound toluene molecules were treated as rigid groups (except that the C–CH_3 distance was variable) with **TL**X thermal motion.

Table I. Details of Diffraction Analysis of $Ag_6(SC_6H_4Cl)_6(PPh_3)_5(tol)_2$

formula, M_r	$C_{140}H_{115}Ag_6S_6Cl_6P_5$, 3004.63
cryst description	colorless blocks
space group	$P\bar{1}$
a, Å	15.024 (5)
b, Å	18.488 (5)
c, Å	26.506 (10)
α, deg	82.14 (2)
β, deg	86.19 (2)
γ, deg	66.45 (3)
V, Å^3	6685 (4)
temp, °C	21 (1)
Z	2
d_{calcd}, g cm^{-3}	1.49
d_{obsd}, g cm^{-3}	1.50 (1)
radiation; λ, Å	Mo Kα; 0.710 69
scan mode	$\theta/2\theta$
$2\theta_{max}$, deg	40
no. of intensity meas	12 781
std intensity decay	$1 \rightarrow 0.82$
cryst faces (dist from center, mm)	001 (0.100), $00\bar{1}$ 0.095), 011 (0.034), $0\bar{1}\bar{1}$ (0.034), $0\bar{1}1$ (0.098), 111 (0.083), $\bar{1}\bar{1}\bar{1}$ (0.077)
μ, cm^{-1}	11.71
max, mean, min transmission coeff	0.921, 0.883, 0.808
criterion for obsd reflcn	$I/\sigma(I) > 3$
no. of indep obsd reflcns	8093
no. of reflcns (m) and variables (n) in final refinement	7571, 530
$R = \Sigma^m\lvert\Delta F\rvert/\Sigma^m\lvert F_o\rvert$	0.060
$R_w = [\Sigma^m w\lvert\Delta F\rvert^2/\Sigma^m w\lvert F_o\rvert^2]^{1/2}$	0.074
$[\Sigma^m w\lvert\Delta F\rvert^2/(m-n)]^{1/2}$	2.19

The final stages of the refinement indicated that one of the chlorobenzenethiolate ligands was vibrating with much larger amplitude than the other five. The average rms displacements of the ligand chlorine atoms ranged from ~0.3 Å (ligand 2) through 0.45 Å (ligand 4) and 0.5 Å (ligand 6) to ~0.75 Å (ligand 1). Ligand 1 is also the least constrained, sterically, by the substituents of nearby ligands. The possibility that ligand 1 was disordered rather than librating extensively was assessed by examination of the refined dimensions of the ligand. If the large thermal amplitudes had arisen as an artifact of disorder some significant shortening of the S–Cl distance would have been expected. However, this distance in ligand 1, 6.27 Å, was no different from that of ligands 2–6 (6.25–6.30 Å). The final difference map contained peaks up to +2 e Å^{-3}, with the largest peak in the vicinity of the librating ligand 1, but not interpretable in terms of disorder. Most of the remaining large peaks were near either silver atoms or chlorobenzenethiolate ligands. There was no evidence of secondary extinction. Scattering factors, including real and imaginary anomalous scattering by Ag, Cl, S, and P, were from ref 13.

The atom labeling scheme of the core is shown in Figure 1. Thiolate ligand atoms are Sn, Cmn, and Cln, n = 1–6, m = 1–6; triphenyl-

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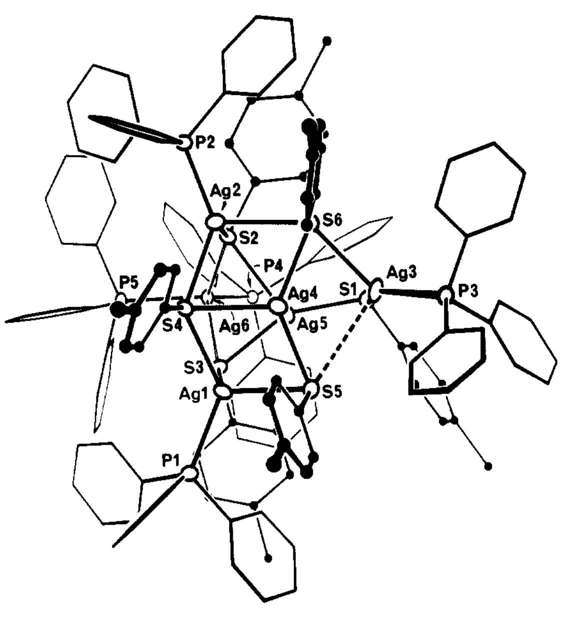

Figure 1. Complete $Ag_6(SC_6H_4Cl)_6(PPh_3)_5$ molecule (**1**) with the thiolate substituent atoms marked as closed circles.

Table II. Atomic Coordinates of Silver, Sulfur, and Phosphorus Atoms

atom	*x*	*y*	*z*	max rms displacement, Å
Ag1	0.884 95 (9)	0.321 21 (7)	0.178 21 (5)	0.272 (2)
Ag2	0.697 27 (8)	0.197 32 (7)	0.267 69 (5)	0.245 (2)
Ag3	1.002 49 (10)	0.153 70 (8)	0.354 86 (6)	0.327 (3)
Ag4	0.900 58 (9)	0.191 78 (8)	0.260 48 (5)	0.265 (2)
Ag5	0.798 27 (10)	0.349 05 (8)	0.304 67 (5)	0.319 (2)
Ag6	0.588 31 (8)	0.485 30 (6)	0.280 92 (4)	0.221 (2)
S1	0.901 40 (29)	0.290 15 (25)	0.377 56 (18)	0.292 (5)
S2	0.627 89 (27)	0.333 15 (21)	0.305 73 (15)	0.249 (5)
S3	0.752 46 (27)	0.438 82 (23)	0.224 80 (15)	0.235 (5)
S4	0.773 82 (27)	0.240 03 (22)	0.184 46 (15)	0.221 (5)
S5	1.039 37 (28)	0.231 20 (25)	0.238 75 (16)	0.259 (5)
S6	0.854 02 (27)	0.118 38 (24)	0.336 02 (15)	0.241 (5)
P1	0.943 96 (29)	0.376 69 (24)	0.099 90 (16)	0.226 (5)
P2	0.594 28 (28)	0.121 46 (23)	0.278 77 (16)	0.219 (5)
P3	1.153 01 (28)	0.062 24 (25)	0.393 13 (16)	0.232 (5)
P4	0.564 66 (28)	0.573 22 (23)	0.347 72 (16)	0.217 (5)
P5	0.461 08 (28)	0.545 49 (23)	0.212 44 (16)	0.219 (5)

phosphine carbon atoms are C*pqr*, $p = 1$–6 per phenyl ring, $q = 1$–3 on phosphorus P*r*, and $r = 1$–5. The toluene atoms are C1T–C7T and C8T–C14T. Atomic coordinates for the silver, sulfur and phosphorus atoms are contained in Table II. A complete tabulation of all atomic coordinates and thermal parameters, together with a listing of observed and calculated structure factors, comprises the supplementary material.[14]

Results

Formation and Solution Behavior. Although insoluble in noncoordinating solvents, $AgSC_6H_4Cl$ dissolves readily in the presence of triphenylphosphine. When the solvent system is toluene plus propanol, colorless crystals of **1**, as the toluene solvate $Ag_6(SC_6H_4Cl)_6(PPh_3)_5(tol)_2$, are readily formed. This compound has crystallized from solutions with $Ph_3P/AgSC_6H_4Cl$ ratios of 1, 1.5, 2, and 3, although the yield decreases in this order. Another colorless crystalline compound has also crystallized from these preparative solutions. This second product, not yet fully characterized, is identifiable by its polycrystalline diffraction pattern and higher melting point.

Solutions of **1** in chloroform or toluene change from colorless to yellow at temperatures above 45 °C, eventually depositing yellow solids which are not $AgSC_6H_4Cl$. Similarly, solid **1** changes to yellow when warmed with liquids which dissolve triphenylphosphine. Preliminary studies of the ^{31}P NMR of **1** in toluene reveal the occurrence of rapid phosphine-exchange processes. It is clear that phosphine-dissociation reactions are prevalent, but nevertheless it is possible to recrystallize **1** from toluene plus propanol at ambient temperature. We have observed also that **1** reacts with bromide ion in acetonitrile to produce a colorless crystalline compound. Characterization of the various products and solutions in the $AgSC_6H_4Cl/PPh_3$ system is continuing.

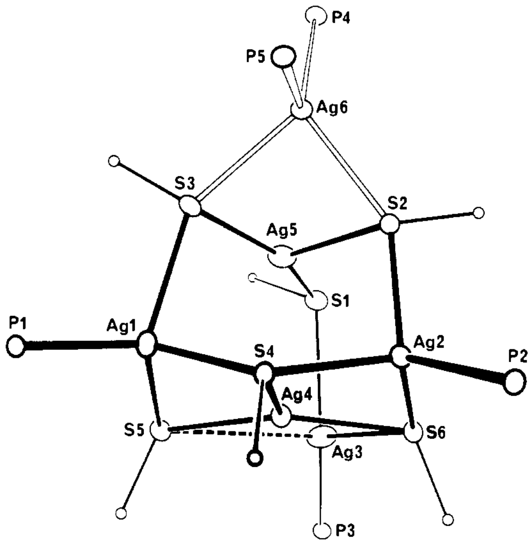

Figure 2. Central core of **1**, including the thiolate S–C bonds. In this figure and Figure 3 the $(Ph_3P)_2Ag$ addendum is marked with open bonds and the long peripheral bond in the basal segment is dotted.

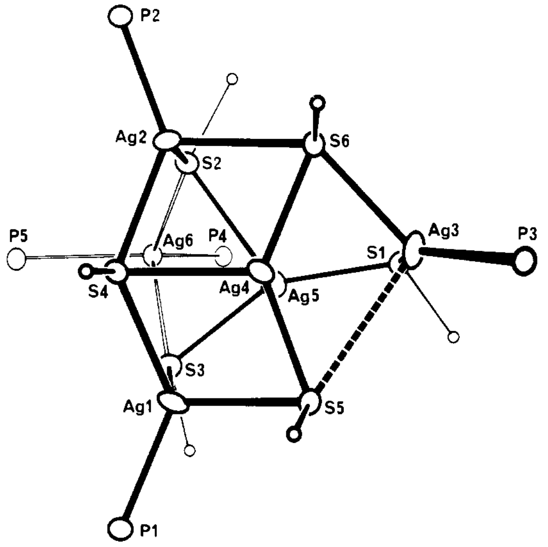

Figure 3. View of the $Ag_6S_6P_5$ core, with S–C bonds, from underneath the pseudohexagonal basal segment. Being approximately isotropic, the atoms are drawn with only the outlines of the vibrational ellipsoids.

Molecular Structure. The crystal contains molecules of $Ag_6(SC_6H_4Cl)_6(PPh_3)_5$ (**1**) together with two molecules of toluene per formula unit which are retained at ambient temperature and pressure. The 21 aryl substituents of **1** almost completely envelope[15] the molecule, as shown in Figure 1, and no intermolecular contacts penetrate its van der Waals surfaces. The unencumbered $Ag_6S_6P_5$ core of **1** is shown in

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(14) See paragraph at the end of this article regarding supplementary material.

(15) The least enclosed region of the surface of **1** is near the doubly bridging ligand at S1 (see Figure 1) which was found to have large vibrational amplitudes.

Table III. Selected Intramolecular Dimensions for $Ag_6(SC_6H_4Cl)_6(PPh_3)_5$

idealization[a]	distances, Å		angles, deg	
Ag^{cen}_{bas}-S_{bas}	Ag4-S4	2.673 (4)	S4-Ag4-S5	111.7 (1)
	Ag4-S5	2.480 (4)	S5-Ag4-S6	134.6 (1)
	Ag4-S6	2.484 (4)	S6-Ag4-S4	113.7 (1)
Ag^{cen}_{bas}-Ag^{per}_{bas}	Ag4-Ag1	2.954 (2)	Ag1-Ag4-Ag2	102.4 (1)
	Ag4-Ag2	3.009 (2)	Ag2-Ag4-Ag3	116.2 (1)
	Ag4-Ag3	2.875 (2)	Ag3-Ag4-Ag1	127.8 (1)
Ag^{per}_{bas}-S_{bas}	Ag1-S5	2.721 (4)	S5-Ag1-S4	105.4 (1)
	Ag1-S4	2.639 (4)	S4-Ag2-S6	105.3 (1)
	Ag2-S4	2.593 (4)	S6-Ag3-S5	99.4 (1)
	Ag2-S6	2.838 (4)		
	Ag3-S6	2.656 (4)	Ag4-S4-Ag1	67.6 (1)
	Ag3-S5	3.322 (5)	Ag4-S4-Ag2	69.7 (1)
			Ag4-S5-Ag1	69.0 (1)
			Ag4-S5-Ag3	57.2 (1)
			Ag4-S6-Ag2	68.5 (1)
			Ag4-S6-Ag3	67.9 (1)
Ag_{pod}-S_{pod}	Ag5-S1	2.407 (5)	S1-Ag5-S2	118.3 (1)
	Ag5-S2	2.689 (4)	S2-Ag5-S3	89.6 (1)
	Ag5-S3	2.456 (4)	S3-Ag5-S1	151.4 (2)
Ag^{per}_{bas}-S_{pod}	Ag1-S3	2.677 (4)	Ag1-S3-Ag5	87.2 (1)
	Ag2-S2	2.621 (4)	Ag2-S2-Ag5	95.6 (1)
	Ag3-S1	2.503 (4)	Ag3-S1-Ag5	102.2 (2)
S_{pod}-Ag^{per}_{bas}-S_{bas}			S1-Ag3-S5	89.9 (1)
			S1-Ag3-S6	95.8 (1)
			S2-Ag2-S4	98.7 (1)
			S2-Ag2-S6	96.7 (1)
			S3-Ag1-S4	92.9 (1)
			S3-Ag1-S5	112.1 (1)
Ag^{cen}_{bas}-Ag_{pod}	Ag4-Ag5	3.051 (2)		
Ag^{per}_{bas}-P	Ag1-P1	2.459 (4)	P1-Ag1-S3	109.9 (1)
	Ag2-P2	2.451 (4)	P1-Ag1-S4	126.8 (1)
	Ag3-P3	2.405 (4)	P1-Ag1-S5	108.7 (1)
			P2-Ag2-S2	115.8 (1)
			P2-Ag2-S4	128.6 (1)
			P2-Ag2-S6	107.0 (1)
			P3-Ag3-S1	126.6 (2)
			P3-Ag3-S6	125.7 (1)
			P3-Ag3-S5	111.2 (1)
Ag_{bridge}	Ag6-S2	2.628 (4)	S2-Ag6-S3	86.2 (1)
	Ag6-S3	2.684 (4)	P4-Ag6-P5	112.9 (1)
	Ag6-P4	2.479 (4)	S2-Ag6-P4	120.6 (1)
	Ag6-P5	2.529 (4)	S2-Ag6-P5	111.2 (1)
			S3-Ag6-P4	120.7 (1)
	Ag6-Ag5	3.189 (2)	S3-Ag6-P5	101.4 (1)
S-C	S1-C11	1.76 (1)		
	S2-C12	1.77 (1)		
	S3-C13	1.76 (1)		
	S4-C14	1.78 (1)		
	S5-C15	1.77 (1)		
	S6-C16	1.76 (1)		

[a] Key: bas, atom in the basal plane; pod, atom in the podal group; cen, central in the basal plane; per, peripheral in the basal plane.

Table IV. Molecular Planes

	atom displacements, Å				
atom[a]	plane A (basal)	plane B (podal)	plane C (at S2)	plane D (at S3)	plane E (pseudo-mirror)
Ag1	+0.86			+0.01P	
Ag2	+0.60		−0.02P		
Ag3	+0.44				+0.23P
Ag4	0.00P				−0.08P
Ag5		−0.08P	+2.51	+2.16	−0.37P
Ag6			−0.02P	+0.01P	+0.11P
S1		+0.03P			−0.05P
S2		+0.01P	+0.06P		
S3		+0.03P		−0.03P	
S4	0.00P				−0.03P
S5	0.00P				
S6	0.00P				
P3					+0.04P
P4					+0.02P
P5					+0.10P
C12			−0.02P		
C13				+0.01P	
C14					+0.03P

[a] P signifies inclusion in the least-squares plane calculation.

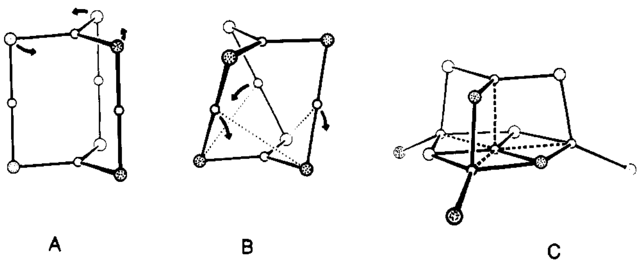

Figure 4. Relationships between $M_5(SR)_6$ cage polyhedra: dotted circles are thiolate sulfur atoms. A, trigonal-bipyramido-M_5-trigonal-prismo-S_6, twisting to B (structure **5**) with octahedro-S_6 twisting to C (structure **2**) with base-centered-trigonal-pyramido-M_5 and added terminal phosphines.

Figures 2 and 3, and pertinent intramolecular dimensions and planes are reported in Tables III and IV. At first examination the molecular core does not appear to possess the high symmetry often present in metal thiolate cages.[5,8,16] Two silver atoms (Ag4, Ag5) have trigonal AgS_3 coordination; two (Ag1, Ag2) have tetrahedral AgS_3P coordination; Ag6 has tetrahedral AgS_2P_2 coordination, while Ag3 has distorted AgS_3P coordination with one very long Ag–S bond, marked as a broken line on the figures. Five of the thiolate ligands are triply bridging, while that at S1 is doubly bridging. The Ag–S distances (Table III) range from 2.40 to 2.84 Å, except for Ag3–S5, which is 3.32 Å. There is an approximate mirror plane applicable to the $Ag_6S_6P_5$ core, passing through atoms P4, P5, Ag6, Ag5, S1, Ag3, P3, Ag4, and S4 (see Table IV).

Despite the apparent molecular dissymmetry and the variation of connectivity and bond distances, the structure of the core can be interpreted in terms of a higher symmetry polyhedron of metal and ligand atoms. Experience with many other metal thiolate cage and aggregate structures has revealed that the array of metal and sulfur atoms approaches a high-symmetry polyhedron and that recognition of this idealization allows fuller interpretation of the structure and of the relationships between different structures. In these symmetrized core structures the metal and sulfur atoms often constitute sets of interpenetrating regular (or at least semiregular) polyhedra. In most of these cases it is impossible for the thiolate substituents to maintain the high symmetry of the metal–sulfur core, and the observed distortions of the core from the high potential symmetry correlate with the dissymmetry of the substituent array.

Our symmetrization and idealization of **1** incorporate the long bond Ag3–S5 into the core but separate the unique $Ag(PPh_3)_2$ group (Ag6) as an addendum to the primary silver thiolate polyhedron. Bonds of the core polyhedron are drawn as filled lines in the figures. The atoms Ag1, S4, Ag2, S6, Ag3, and S5 constitute a hexagon, which contains a fourth silver atom (Ag4) at its center (Figure 3) and is approximately planar (Figure 2). This centered hexagonal unit is termed the basal plane. The trigonal-coordination plane of the fifth silver atom, Ag5, is parallel to the basal plane and linked to it in podant mode by three S–Ag bonds to the peripheral silver atoms Ag1, Ag2, and Ag3. Therefore the Ag5, S1, S2, S3 plane is labeled the podal plane. Terminal phosphine ligands complete the tetrahedral coordination at Ag1, Ag2, and Ag3

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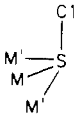
Table V. Stereochemistry at Triply Bridging Thiolate Ligands S4, S5, and S6[a]



S	M	M'	M-S-M'	M'-S-M'	M-S-C1	M'-S-C1	S dist from MM'_2 plane
S4	Ag4	Ag1, Ag2	67.5, 69.8	125.4	105.0	109.7, 113.0	1.05
S5	Ag4	Ag1, Ag3	69.1, 57.2	119.7	106.3	99.8, 118.8	1.26
S6	Ag4	Ag2, Ag3	68.5, 68.0	130.8	112.3	105.0, 111.8	0.83

[a] All angles in degrees; distances in angstroms.

as appendages to the idealized Ag_5S_6 polyhedron, which is shown in Figure 4C. Figure 3 is an underneath view of the cage polyhedron, close to the threefold axis common to the basal and podal planes. The Ag_5 polyhedron is a base-centered triangular pyramid, and the S_6 polyhedron is an octahedron. As a polycyclic cage, Ag_5S_6 is composed of three fused Ag_2S_2 cycles in the basal plane and three Ag_3S_3 cycles, each in pseudochair conformation.

Intermolecular bond distances and angles in Table III are categorized according to the atom types in this polyhedron, namely Ag_{bas}^{cen}, Ag_{bas}^{per}, Ag_{pod}, S_{bas}, S_{pod}. Table IV confirms the close planarity of the AgS_3 coordination in the basal and podal planes, which are within 5.4° of being parallel. The Ag_{bas}^{per} atoms Ag1, Ag2, and Ag3 are raised above the Ag_{bas}^{cen}–$(S_{bas})_3$ plane by 0.86, 0.60, and 0.44 Å, respectively. This permits the three Ag_3S_3 cycles each to elongate toward the chair conformation and the Ag_{bas}^{per} atoms to approach tetrahedral stereochemistry. As shown in Figures 2 and 3, the aryl substituents at the podal sulfur atoms are approximately equatorial, relative to the polyhedron pseudo-3-fold axis: the angles of the bonds Sn–Cln to plane B (Table IV) are 25.2, 20.0, and 30.5° for $n = 1$, 2, and 3, respectively. The S–C bonds at the basal sulfur atoms are close to axial; the angles of Sn–$C1n$ to plane A (Table IV) are 74.9, 67.9, and 67.1° for $n = 4$, 5, and 6, respectively. The terminal phosphine ligands are arrayed approximately equatorial to the basal plane, being inclined at 11.7, 16.1, and 25.0° (P1, P2, and P3, respectively) to the $(Ag_{bas}^{per})_3$ plane.

The symmetrized basal hexagon is not regular: the Ag_{bas}^{cen}–S_{bas} distances average 2.55 (0.11[17]) Å while the radial Ag_{bas}^{cen}–Ag_{bas}^{per} distances average 2.95 (0.07) Å. The Ag–Ag distance between the basal and podal planes, Ag4–Ag5 = 3.05 Å, is approximately the same as the radial Ag–Ag distances within the basal plane, and the distance to the added silver atom, Ag5–Ag6 = 3.19 Å, is only slightly longer. None of these Ag–Ag distances can be construed as a symptom of direct Ag–Ag bonding.

The S_6 polyhedron approximates an octahedron, S–S = 4.19 (0.32[17]) Å. In the basal plane S–S distances are slightly longer than the average, whereas the podal face of the octahedron is distorted by the shortening of S2–S3 caused by the addition of Ag6.

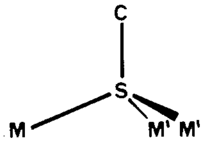
Examination of Figure 1 shows that the aryl substituents are closely and regularly packed over the surface of the cage. Six aryl rings are approximately normal to the basal plane, three from the basal thiolates and one from each of the basal triphenylphosphine ligands. There are no abnormally short interligand contacts, the shortest C–C distance being 3.31 Å, and only seven intramolecular C–C contacts (excluding intra-PPh_3 distances) are less than 3.5 Å.

There are close similarities between the detailed stereochemistries of Ag1 and Ag2: in both cases the S4–Agn–Pn (n = 1, 2) angle is large. This, like the fact that Ag1 and Ag2 lie above the basal plane, is presumably to relieve interactions between thiolate 4 and phosphines 1 and 2. At Ag3 the coordination to S1, S6, and P3 is partially flattened (Ag3 is 0.49 Å from the S1, S6, P3 plane; sum of three angles at Ag3 = 348.1°), in concert with the elongation of Ag3–S5 to 3.32 Å. This long bond is not near the most crowded section of the molecular surface. Ligand configurations, or ligand substituent interactions, provide no reason for the elongation of only one of the six peripheral Ag–S bonds in the basal plane.

At both of the planar silver atoms (Ag4 and Ag5) with approximate trigonal coordination there is inverse correlation of Ag–S distance with opposite S–Ag–S angle, as observed in other silver thiolates.[8,18]

Stereochemistry at Triply Bridging Thiolate. Five of the thiolate ligands bridge three silver atoms but with the stereochemistry of the four atoms bonded to sulfur being far from tetrahedral. At S2 and S3 two of the S–Ag bonds (to Ag6 and Ag2 or Ag1) and the S–C bond are virtually coplanar (planes C and D, Table IV), while the third S–Ag bond (to Ag5) is inclined to this plane at 67 or 63°. There is no correlation with different bond lengths to Ag5. Figure 1 shows that it is possible that potential interference of the thiolate substituent with phenyl groups at phosphine 5 causes the S–C bonds at S2 and S3 to be bent away from the axis of their SAg_3 tripods.

At S4, S5, and S6 there occurs a different stereochemistry, which is related to the regular tetrahedron **3** by reflection of two metal atoms (M′) through the plane normal to the M–S–C plane and containing S–C, as in **4**. In this unusual stereochemistry the sulfur atom lies well outside its coordination polyhedron and yet all angles at sulfur except the two M–S–M′ are approximately tetrahedral. Table V records details for S4, S5, and S6: the Ag–S–Ag′ angles range from 57 to 70° and the Ag′–S–Ag′ angles from 120 to 131°, and the sulfur atoms are 0.83–1.26 Å from the Ag_3 plane.



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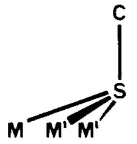

4

Discussion

There is no precedent for the molecular structure of **1**, or of its subunit $(Ph_3P)_3Ag_5(SC_6H_4Cl)_6$ (**2**) either as observed or as the base-centered-trigonal-pyramido-Ag_5-octahedro-$(SR)_6$ idealization. Known clusters containing six silver atoms and (chelating) anionic thiolate ligands usually possess a regular octahedral array of silver atoms: instances are $[Ag_6(S_2CC(CN)_2)_6]^{6-}$[19] and $Ag_6(S_2CNR_2)_6$[20,21] except when

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(17) The value in parentheses is the standard deviation of the sample, $(\sum\Delta^2/(n-1))^{1/2}$.

(18) Dance, I. G. *Inorg. Chim. Acta* **1977**, *25*, L17.

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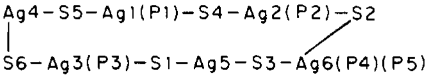
Inorg. Chem. **1984**, *23*, 2281–2286 **2281**

R = Et where a chain structure occurs.[20] The structure of 1 is not obviously related to the established $Ag_4X_4(PR_3)_4$ cubane structure,[22–24] to heterometallic sulfide–silver–phosphine cages such as $(MoS_4)_2(AgPPh_3)_4$,[25] or to the distorted $[Ag_6(SPh)_8]^{2-}$ cage.[8]

The unique component of the structure of 1 is the centered hexagonal $Ag(SR)_3Ag_3$ basal section. It is the basal-$Ag(SR)_3Ag_3$ plus podal-$(SR)_3Ag$ idealization of the $Ag_5(SR)_6$ core, with octahedro-$(SR)_6$, that allows this structure to be related to another known thiolate cage structure, namely the trigonal-bipyramido-M_5-octahedro-$(SR)_6$ structure, **5**, of $[M_5(S\text{-}t\text{-}Bu)_6]^-$, M = Cu, Ag.[16,26] The relationship is shown in Figure 4. The trigonal-bipyramido-M_5-trigonal-prismo-$(SR)_6$ structure (Figure 4A) is partially twisted about the threefold axis to generate structure **5** (Figure 4B), and then this twisting is continued by the three digonal metal atoms which drop into the lower trigonal plane as shown by the arrows in Figure 4B, thus creating the basal-centered hexagonal unit. The equatorial metal atoms of **5** become the peripheral basal metal atoms, and the upper trigonal plane of Figure 4A becomes the podal trigonal unit. Figure 4C shows the final structure with new silver–silver approaches marked as broken lines and with the terminal phosphine ligands added to peripheral metal atoms in the basal unit.

This type of interpretation of the structure of **1**, involving symmetrizations of the array of Ag, S, and P core atoms, must be tempered by the observed variability of dimensions. One peripheral Ag–S distance in the basal unit is ca. 0.6 Å longer than the remainder. The geometry of the core must also be subject to the requirements of the bulky phosphine ligands that cover its surface, and it will be pertinent to determine whether the structure **2** recurs with smaller phosphines, by investigations in progress.

In silver–thiolate structures, some Ag–S distances are long and may be relegated to secondary bonding, possibly nonexistent in other conformations of the molecule in solution.[8,18] This type of structure analysis led to recognition of the monocyclic structure of (cyclohexanethiolato)silver.[18] If only the two shortest Ag–SR bonds at each silver atom in the polycyclic molecule **1** are connected, the following 12-membered monocyclic molecule results:



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Registry No. 1·2tol, 90195-56-5.

Supplementary Material Available: A tabulation of all atomic coordinates and thermal parameters and selected bond lengths and angles and a listing of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

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Hexacarbonyl(fulvalene)ditungsten(*W*–*W*). A Stretched Tungsten–Tungsten Single Bond

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The title compound, $(\eta^5{:}\eta^5\text{-}C_5H_4C_5H_4)W_2(CO)_6$, is found as a byproduct of the synthesis of $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ via the thermolysis of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2C_6H_5$. The molecule possesses one of the longest W–W distances (3.347 (1) Å) recorded for which a bonding interaction can be established and is accompanied by a bending deformation of the fulvalene ligand toward the metal centers with a 16.1 (5)° dihedral angle. The structure was solved in the triclinic space group $P\bar{1}$ to an R factor of 0.049. Unit cell parameters are a = 6.708 (2) Å, b = 9.626 (2) Å, c = 12.450 (2) Å, α = 76.16 (1)°, β = 84.37 (2)°, γ = 74.95 (2)°, V = 753 (4) Å^3, and Z = 2. The molecule displays noncrystallographic 2-fold symmetry about an axis passing through the W–W bond and through the bridgehead C–C bond of the fulvalene ligand. The compound is more reactive toward iodine than the related unbridged $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ but is substantially less photoreactive than the unbridged dimer.

The thermal reactions[1] and photochemical behavior[2] of metal–metal-bonded compounds are areas of vigorous investigation at present. Many of the most intensively studied compounds are metal carbonyl dimers. A complex like $[CpW(CO)_3]_2$,[3] with a tungsten–tungsten single bond, is useful because of the relative inertness to thermal substitution of its carbonyl ligands and the reasonable reactivity toward cleavage of the metal–metal bond.[4,5] Modifications in the reactivity of this compound are to be anticipated if the two fragments are still connected after metal–metal bond cleavage.

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