New Silver Cluster Compounds Containing Dithiobenzoate Ligands

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Abstract

Three new 4-atom silver cluster compounds have been synthesized using two different substituted dithiobenzoate ligands, and their crystal and molecular structures were determined by single crystal X-ray diffraction. Molecules of the complex $[Ag_4\{2,4,6\text{-}(CH_3)_3C_6H_2CS_2\}_4py_3]\cdot\frac{1}{2}py$ contain the four silver atoms in a roughly tetrahedral array, each forming three bonds to sulfur atoms, one-half of which bridge two Ag atoms and one-half of which attach to only one Ag atom. Pyridine nitrogens are attached to three of the four silvers. In the complex $[Ag_4(o\text{-}CH_3C_6H_4\text{-}CS_4)_4py_4]$ the four silver atoms are in a very distorted tetrahedral array, each forming three bonds to sulfur atoms, one-half of which bridge two Ag atoms and one-half of which attach to only one Ag atom. Each Ag atom is also coordinated to a pyridine nitrogen. In the third cluster complex, the anion $[Ag_4\{2,4,6\text{-}(CH_3)_3C_6H_2CS_2\}_6]^{2-}$ contains four silver atoms in a roughly square planar array, each forming four bonds to sulfur atoms, one-third of which bridge two Ag and two-thirds of which attach to only one Ag atom. Although there are Ag–Ag distances in these compounds which fall well within expected single bond distances it is uncertain whether there are (or even can be) substantial bonding interactions between the silver atoms.

Introduction

Compounds which contain discrete silver clusters are varied but quite limited in number. King [1] has defined a metal cluster as a network of metal atoms held together by metal–metal bonds to each metal atom, each metal atom being part of some ring of metal atoms. With one notable exception (*vide infra*) the well-known silver clusters involve anionic sulfur-donor ligands, and there are examples of 4-, 5-, 6-, 8- and 12-atom clusters which have been reported and substantiated by at least one single-crystal X-ray diffraction study. After our discovery of a 6-atom gold cluster with a unique, nearly-planar arrangement [2], using a dithiocarboxylate ligand, we hoped to be able to prepare the analogous silver (and copper) compounds. What we obtained instead, and what we report herein, are three quite different 4-atom silver clusters, one having the four metal atoms nearly square planar, and the other two having the four silver atoms in a distorted tetrahedral disposition. Their crystal and molecular structures are detailed.

Experimental

Reagent grade or better chemicals were used as received. Tetrapropylammonium 2,4,6-trimethyldithiobenzoate (TPAdtmes) and tetrapropylammonium *o*-methyldithiobenzoate (TPA*o*-dtt) were synthesized by a known procedure [3].

Preparation of $[Ag_4\{2,4,6\text{-}(CH_3)_3C_6H_2CS_2\}_4py_3]\cdot\frac{1}{2}py$ *(1)*

To a stirred solution of 0.0500 g of TPAdtmes (0.131 mmol) in 10 ml of DMF was added 0.0220 g of $AgNO_3$ (0.130 mmol) dissolved in 5 ml of DMF. The orange precipitate that resulted immediately upon mixing was collected by suction filtration after one hour, washed with DMF and air-dried. This orange precipitate was insoluble in most common organic solvents with the exception of pyridine. Yield: 88%, melting point (m.p.) 238–240 °C. *Anal.* Calc. for $Ag(S_2C_{10}H_{11})$: C, 39.61; H, 3.66; S, 21.15; Ag, 35.58. Found: C, 39.68; H, 3.67; S, 21.44; Ag (by difference), 35.21%. A recrystallization of this already pure product (containing no pyridine) from pyridine yielded reddish-orange crystals of **1** which were washed with pyridine and air-dried. Slow evaporation of pyridine yielded crystals of **1** which were suitable for X-ray analysis. Yield: 53%, m.p. 172 °C (decomp.).

Preparation of $[Ag_4(o\text{-}CH_3C_6H_4CS_2)_4py_4]$ *(2)*

To a stirred solution of 0.200 g of TPA*o*-dtt (0.566 mmol) in 40 ml of DMF was added 0.0955 g of $AgNO_3$ (0.562 mmol) dissolved in 20 ml of DMF. The yellowish-orange precipitate which formed immediately was collected by filtration the next day, washed with DMF and air-dried. This product was insoluble in most common organic solvents with the exception of pyridine. Yield: 0.1125 g (73%), m.p.

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180–182 °C. *Anal.* Calc. for $Ag_x(S_2C_8H_7)_x$: C, 34.92; H, 2.56; S, 23.31; Ag, 39.21. Found: C, 35.19; H, 2.58; S, 23.06; Ag (by difference), 39.17%. This pure product, of undetermined molecular complexity (unknown x) was dissolved in pyridine. Slow evaporation of the pyridine yielded orange crystals suitable for X-ray analysis. The crystal structure revealed x to be 4 with a pyridine attached to each silver. Of course it is not certain that x was 4 before the pyridines became attached.

Preparation of $[(C_3H_7)_4N]_2[Ag_4\{2,4,6\text{-}(CH_3)_3C_6H_2CS_2\}_6] \cdot \frac{1}{2}DMF \cdot H_2O$ *(3)*

To a stirred solution of 0.0500 g of TPAdtmes (0.131 mmol) in 10 ml of DMF was added 0.0110 g of $AgNO_3$ (0.0648 mmol) dissolved in 10 ml of DMF. The resulting orange solution was warmed for several hours. Upon cooling to room temperature, the solution yielded reddish-orange crystals which were collected by filtration, washed with DMF and air-dried. Slow evaporation of the DMF solvent yielded crystals suitable for X-ray analysis, m.p. 138 °C (decomp.).

Physical Measurements

Nuclear magnetic resonance spectra were obtained on an IBM NR/100 FTNMR spectrometer. For the proton studies in pyridine-d_5, TMS was used as the internal standard. All chemical shifts are reported on the δ scale. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator, using ω–2θ scans of variable speed designed to yield measurements of equal relative precision for all significant reflections. A maximum was placed on the scan time spent on any reflection. One quadrant of data was collected for each crystal. Angular limits and other specifics of data collection are given in Table 1. Data reduction included corrections for background, Lorentz, polarization and absorption. No intensity decay during data collection was noted. Absorption corrections were based on ψ scans of reflections near $\chi = 90°$. Equivalent data were merged, and data having $I > 3\sigma(I)$ were considered observed and used in the refinements. All structures were solved by heavy atom methods and refined by full matrix least-squares based on F with weights $w = \sigma^{-2}(F_o)$, using the Enraf-Nonius SDP programs. With some exceptions, detailed below, nonhydrogen atoms were refined anisotropically, whereas hydrogen atoms

TABLE 1. X-ray diffraction data for the three new reported silver compounds

Compound	1	2	3
Formula	$Ag_4S_8C_{55}H_{59}N_3 \cdot \frac{1}{2}C_5H_5N$	$Ag_4S_8C_{56}H_{48}N_4$	$[N(C_3H_7)_4]_2[Ag_4S_{12}C_{60}H_{66}] \cdot \frac{1}{2}C_3H_7NO \cdot H_2O$
Formula weight	1489.6	1417.0	1010.9
Space group	monoclinic, $P2_1/c$	monoclinic, $P2/c$	monoclinic, $P2_1/n$
a (Å)	12.853(2)	15.1601(13)	20.454(2)
b (Å)	22.013(5)	12.211(3)	24.133(11)
c (Å)	21.659(4)	20.934(2)	20.734(3)
β (°)	96.281(14)	135.237(8)	95.51(1)
V (Å^3)	6091(4)	2729.0(9)	10187(7)
Z	4	2	4
D (g cm^{-3})	1.624	1.724	1.318
T (°C)	24	22	21
μ (cm^{-1})	15.6	17.3	10.3
Crystal size (mm)	0.16 × 0.32 × 0.36	0.06 × 0.40 × 0.44	0.08 × 0.28 × 0.32
Color	orange	red–orange	red–orange
Min. relative transmission (%)	89.66	55.14	81.40
2θ limits (°)	2–50	2–50	2–36
Scan rates (° min^{-1})	1.8–10.0	0.91–4.0	1.8–4.0
Max. scan time (s)	30	60	30
Unique data	10701	5650	6996
Observed data	5357	3700	4163
B for H atoms (Å^2)	1.3 × B for C	1.3 × B for C	H ignored
R	0.038	0.038	0.059
R_w	0.038	0.043	0.064
GOF	1.25	1.74	3.30
Variables	643	308	517
Max. residence (e Å^{-3})	0.47	1.05	0.61
Notes	disordered solvent capillary mounted	Me hydrogens ignored	disordered solvent

were included as fixed contributions, in calculated positions where possible. In **1** a pyridine solvent molecule lies on a center of symmetry. This disorder was modelled by treating all atoms as carbon and ignoring hydrogen. In **3**, due to poor quality of the crystals and limited resolution of the data, only Ag and S were refined anisotropically, light atoms were refined isotropically, and H atoms were ignored. Disordered solvent in this structure was modelled as a site shared by a DMF molecule in 50% occupancy, and two water molecules in 50% occupancy. Final R factors and residual electron densities are given in Table 1.

Discussion

The reported silver cluster compounds are listed in Table 2 where the second column records the approximate geometric arrangements defined by the

TABLE 2. Silver cluster compounds[a]

No.	Compound	Geometric arrangement of silver atoms	Geometry around silver atoms	Ag–Ag distances	Reference
1	$[Ag\{\overbrace{S(CH_2)_3CH_2}\}I]_4$	distorted tetrahedron	distorted tetrahedral	2.961–3.189 3.10 ave.	4
2	$[Ag_4\{cpFecpCH_2N(CH_3)_2\}_4]$	square plane	square planar (2 Ags + 2 cp-Cs)	2.740	5
3	$[Ag_4(\alpha\text{-}C_{10}H_7CS_2)_4(py)_4]\cdot 2py$	distorted tetrahedron	distorted tetrahedral	2.875–2.975 2.924 ave.	6
4	$[Ag_4\{S_2CC_6H_2(CH_3)_3\}_4(py)_3]\cdot\frac{1}{2}py$	distorted tetrahedron	distorted tetrahedral (3) + distorted trigonal planar (1)	2.814, 2.951, 3.007, 3.062, 3.101, 3.423	this work
5	$(n\text{-}Pr_4N)_2[Ag_4\{S_2CC_6H_2(CH_3)_3\}_6]$	square plane	distorted tetrahedral	2.821, 2.880, 2.882, 2.935	this work
6	$[Ag_4(o\text{-}CH_3C_6H_4CS_2)_4(py_4)]$	distorted tetrahedron	v. distorted tetrahedral	2.8693, 3.0215, 3.1966, 3.984	this work
7	$(Me_4N)_2Ag_5(SPh)_7$	tetrahedron plus extra Ag on an edge	distorted trigonal planar (4) + almost linear (1)	2.936–3.278 3.169 ave.	7
8	$[(C_3H_7)_2NCS_2Ag]_6$	distorted octahedron	distorted trigonal planar	2.905–3.199 3.023 ave.	8
9	$[(C_3H_7)_2NCOSAg]_6$	octahedron	distorted trigonal planar	2.943–3.281 3.107 ave.	9
10	$[(C_2H_5)_2NCSAg]_6$	hexameric doubly bent chain	distorted tetrahedral (2) + distorted trigonal planar (4)	2.841, 2.974 2.904 ave.	10, 11
11	$(Me_4N)_2[Ag_6(SPh)_8]$	polymeric	distorted tetrahedral (2) trigonal planar (4)	2,959–3.203 3.071 ave.	12
12	$(PhCH_2Et_3N)_6[Ag_6\{S_2C{=}C(CN)_2\}_6]$	octahedron	trigonal pyramidal	2.939–3.085 3.008 ave.	13
13	$Ag_6(SC_6H_4Cl)_6(PPh_3)_5$	unusual cage	trigonal planar (2) distorted tetrahedral (4)	2.875–3.189 3.016 ave.	14
14	$(n\text{-}Bu_4N)_4[Ag_8\{S_2C{=}C(CN)_2\}_6]$	cube	trigonal planar	2.957–3.085 3.017 ave.	15
15	$(Me_4N)_4[Ag_{12}(SPh)_{16}]$	polymeric cage results from hourglass linkage of two $[Ag_6(SPh)_8]^{2-}$ cages			12
16	$[Ag(SC_6H_{11})]_{12}$	cyclic polymer	distorted trigonal planar (8) distorted linear (4)	2.91–3.29 3.061 ave.	16, 17

[a]Containing only silver metal atoms in the cluster and well characterized by X-ray structure, but not including several polymeric compounds.

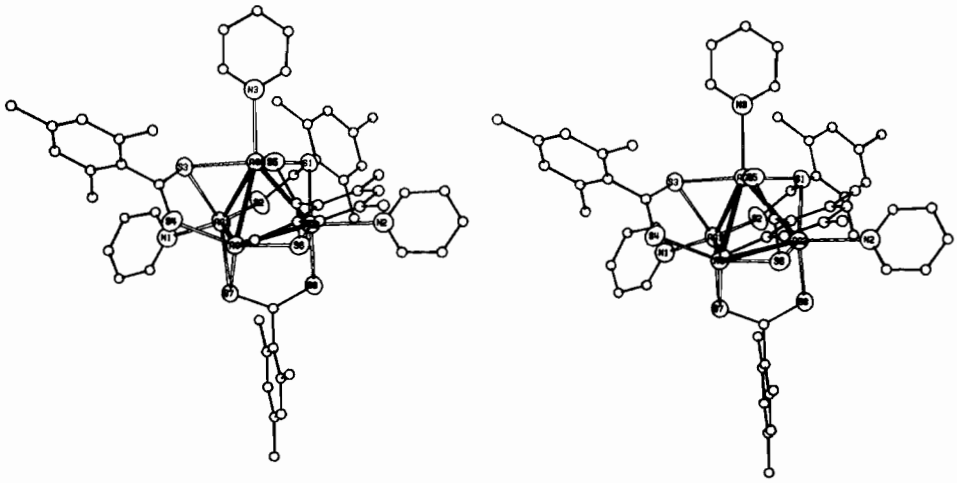


Fig. 1. The molecular structure of **1**, in stereopair. Ag, S and N atoms are represented by ellipses enclosing 40% probability, while C atoms are drawn as circles of arbitrary radius.

TABLE 3. Atomic coordinates for **1**

Atom	*x*	*y*	*z*	*B* (Å^2)
Ag1	0.68251(5)	0.25883(3)	0.82667(3)	4.11(1)
Ag2	0.89564(4)	0.17431(3)	0.88258(3)	3.88(1)
Ag3	0.90965(4)	0.28264(3)	0.80379(3)	3.61(1)
Ag4	0.82061(5)	0.29275(3)	0.93069(3)	3.84(1)
S1	0.9033(1)	0.17145(9)	0.76660(9)	3.57(4)
S2	0.6663(2)	0.1707(1)	0.7552(1)	4.85(5)
S3	0.7587(2)	0.35820(9)	0.78122(9)	3.75(5)
S4	0.7990(2)	0.4033(1)	0.9130(1)	5.10(6)
S5	1.0673(2)	0.3178(1)	0.87545(9)	4.21(5)
S6	0.9847(2)	0.23988(9)	0.97376(9)	3.94(5)
S7	0.6530(2)	0.23544(9)	0.94454(9)	3.90(5)
S8	0.7629(2)	0.11492(9)	0.9325(1)	4.47(5)
N1	0.5048(5)	0.2935(3)	0.8035(3)	4.5(2)
N2	1.0265(5)	0.0888(3)	0.9001(3)	4.4(2)
N3	0.9966(5)	0.3157(3)	0.7108(3)	4.7(2)
C1	0.7814(5)	0.1483(3)	0.7367(3)	3.2(2)
C2	0.7796(6)	0.0993(3)	0.6894(3)	3.6(2)
C3	0.7708(6)	0.0390(3)	0.7067(4)	4.8(2)
C4	0.7637(8)	−0.0052(4)	0.6610(4)	7.1(3)
C5	0.770(1)	0.0093(4)	0.5993(5)	8.9(3)
C6	0.785(1)	0.0694(5)	0.5848(4)	9.3(4)
C7	0.7885(7)	0.1147(4)	0.6280(4)	5.5(2)
C8	0.7638(8)	0.0199(4)	0.7722(4)	7.3(3)
C9	0.767(2)	−0.0404(6)	0.5501(6)	17.1(7)
C10	0.7992(9)	0.1796(4)	0.6081(4)	7.3(3)
C11	0.7706(5)	0.4132(3)	0.8371(3)	3.8(2)
C12	0.7543(6)	0.4770(3)	0.8142(3)	3.7(2)
C13	0.6555(6)	0.4972(4)	0.7948(4)	5.1(2)
C14	0.6429(7)	0.5576(4)	0.7736(4)	5.8(2)
C15	0.7258(8)	0.5954(4)	0.7715(4)	6.2(3)
C16	0.8233(7)	0.5748(4)	0.7908(4)	5.8(2)
C17	0.8415(6)	0.5148(4)	0.8114(3)	4.3(2)
C18	0.5591(7)	0.4581(4)	0.7955(5)	7.5(3)

(continued)

TABLE 3. *(continued)*

Atom	*x*	*y*	*z*	*B* (Å^2)
C19	0.710(1)	0.6611(4)	0.7491(5)	9.5(4)
C20	0.9514(7)	0.4951(4)	0.8319(4)	6.2(2)
C21	1.0762(5)	0.2835(3)	0.9438(3)	3.6(2)
C22	1.1780(5)	0.2899(3)	0.9862(3)	3.7(2)
C23	1.1864(6)	0.3344(4)	1.0323(4)	4.7(2)
C24	1.2826(6)	0.3396(5)	1.0686(4)	6.4(3)
C25	1.3637(6)	0.3008(5)	1.0615(4)	6.9(3)
C26	1.3511(6)	0.2570(5)	1.0155(4)	6.3(2)
C27	1.2596(6)	0.2498(4)	0.9782(4)	5.0(2)
C28	1.0945(7)	0.3744(5)	1.0436(4)	6.9(3)
C29	1.4692(8)	0.3084(7)	1.1019(5)	12.0(4)
C30	1.2485(7)	0.2011(4)	0.9299(5)	6.8(3)
C31	0.6739(5)	0.1602(3)	0.9585(3)	3.5(2)
C32	0.5992(5)	0.1311(3)	0.9975(3)	3.3(2)
C33	0.6218(6)	0.1300(3)	1.0619(3)	4.0(2)
C34	0.5508(6)	0.1021(4)	1.0972(4)	4.9(2)
C35	0.4605(6)	0.0756(4)	1.0684(4)	5.1(2)
C36	0.4404(6)	0.0769(4)	1.0057(4)	5.0(2)
C37	0.5083(6)	0.1036(4)	0.9678(4)	4.2(2)
C38	0.7204(7)	0.1584(4)	1.0933(4)	6.1(2)
C39	0.3833(7)	0.0468(5)	1.1081(5)	8.0(3)
C40	0.4815(6)	0.1046(4)	0.8993(4)	5.8(2)
C41	0.4408(6)	0.3052(4)	0.8456(4)	5.3(2)
C42	0.3386(6)	0.3255(4)	0.8312(5)	6.5(3)
C43	0.3047(7)	0.3328(4)	0.7691(5)	6.7(3)
C44	0.3687(7)	0.3217(4)	0.7251(4)	6.6(3)
C45	0.4699(6)	0.3018(4)	0.7449(4)	5.7(2)
C46	1.0521(6)	0.0688(4)	0.9571(4)	5.4(2)
C47	1.1297(7)	0.0266(4)	0.9725(4)	6.0(2)
C48	1.1845(6)	0.0039(4)	0.9284(4)	5.7(2)
C49	1.1597(7)	0.0238(4)	0.8691(4)	5.8(2)
C50	1.0801(6)	0.0654(4)	0.8561(4)	5.3(2)
C51	1.0524(7)	0.2764(4)	0.6823(4)	5.6(2)

(continued)

TABLE 3. *(continued)*

Atom	x	y	z	B (Å^2)
C52	1.1093(6)	0.2914(4)	0.6337(4)	5.8(2)
C53	1.1084(7)	0.3483(4)	0.6144(4)	6.1(2)
C54	1.0487(8)	0.3905(4)	0.6422(4)	7.0(3)
C55	0.9937(7)	0.3720(4)	0.6898(4)	5.4(2)
C1S	0.529(2)	0.032(1)	0.450(1)	25(1)*
C2S	0.529(2)	0.068(1)	0.506(1)	29(1)*
C3S	0.497(2)	−0.031(1)	0.442(1)	29(1)*

Starred atoms were refined isotropically. The equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation:

$$\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + abB_{12}\cos\gamma + acB_{13}\cos\beta + bcB_{23}\cos\alpha].$$

TABLE 4. Selected bond distances for **1**

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ag1	Ag2	3.4234(8)	Ag3	Ag4	3.1008(8)
Ag1	Ag3	3.0618(8)	Ag3	S1	2.576(2)
Ag1	Ag4	2.8138(8)	Ag3	S3	2.564(2)
Ag1	S2	2.478(2)	Ag3	S5	2.536(2)
Ag1	S3	2.633(2)	Ag3	N3	2.517(6)
Ag1	S7	2.673(2)			
Ag1	N1	2.410(6)	Ag4	S4	2.477(2)
			Ag4	S6	2.500(2)
Ag2	Ag3	2.9508(8)	Ag4	S7	2.544(2)
Ag2	Ag4	3.0072(8)			
Ag2	S1	2.527(2)			
Ag2	S6	2.609(2)			
Ag2	S8	2.490(2)			
Ag2	N2	2.526(6)			

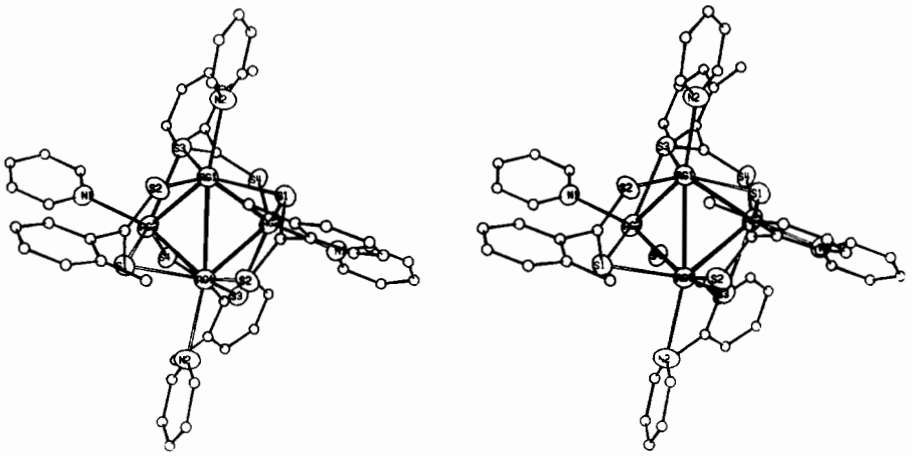


Fig. 2. The molecular structure of **2**, in stereopair, viewed approximately down the crystallographic twofold axis. Atoms are represented as in Fig. 1.

ligand atoms attached to the silvers, and the fourth column records pertinent Ag–Ag distances. The compounds numbered 4, 5 and 6 are our present contributions to this relatively short list of silver clusters. From Table 2 it is seen that clusters of 4, 5, 6, 8 and 12 silver atoms have been reported, and that our three new compounds, **1**, **2** and **3** (compounds 4, 5, and 6 in Table 2), double the number of reported 4-atom silver clusters.

The 'tetrahedral' cluster compound **1**, pictured in Fig. 1, contains four silver atoms roughly in a tetrahedral array, each forming three bonds to sulfur atoms, one-half of which (S1, S3, S6, S7) bridge two Ag atoms (with Ag–S bond lengths 2.500–2.673, ave. 2.578 Å) and one-half of which (S2, S4, S5, S8) attach to only one Ag atom (with Ag–S bond lengths 2.477–2.536, ave. 2.495 Å). Three of the four Ag atoms (Ag1, Ag2, Ag3) form a fourth coordinate bond to pyridine nitrogens (with Ag–N distances 2.410–2.526, ave. 2.484 Å), whereas the Ag4 atom forms only three coordinate bonds to sulfurs.

Three sulfur atoms are bonded to each silver atom in a trigonal arrangement that is approximately planar. The S–Ag–S angles range from 103.11–134.85° and average 119.52°. The deviation of the silver atoms from the appropriate S_3 planes in the Ag_4S_8 fragment ranges from 0.074–0.290 Å and averages 0.154 Å.

Each silver atom has three neighboring silver atoms with Ag–Ag distances ranging from 2.814–3.101, ave. 2.987 Å, except for one longer distance of 3.423 Å, between Ag1 and Ag2. Atomic coordinates for **1** are given in Table 3. Selected bond distances for **1** are given in Table 4 and selected bond angles are listed in Table 5.

The distorted 'tetrahedral' cluster compound **2**, pictured in Fig. 2, contains four silver atoms in a very distorted tetrahedral array, each forming three

TABLE 5. Selected bond angles for **1**

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Ag2	Ag1	Ag3	53.78(2)	Ag1	Ag2	Ag4	51.40(2)
Ag2	Ag1	Ag4	56.64(2)	Ag3	Ag2	Ag4	62.72(2)
Ag3	Ag1	Ag4	63.54(2)	Ag3	Ag2	S1	55.46(4)
Ag3	Ag1	S2	92.83(5)	Ag3	Ag2	S6	86.62(5)
Ag3	Ag1	S3	52.86(4)	Ag3	Ag2	S8	139.85(5)
Ag3	Ag1	S7	115.19(4)	Ag4	Ag2	S1	114.55(5)
Ag3	Ag1	N1	144.3(2)	Ag4	Ag2	S6	52.29(4)
Ag4	Ag1	S2	135.33(5)	Ag4	Ag2	S8	92.50(5)
Ag4	Ag1	S3	81.43(4)	S1	Ag2	S6	134.85(6)
Ag4	Ag1	S7	55.17(4)	S1	Ag2	S8	121.50(7)
Ag4	Ag1	N1	125.7(2)	S1	Ag2	N2	91.9(2)
S2	Ag1	S3	115.26(7)	S6	Ag2	S8	103.11(7)
S2	Ag1	S7	115.80(7)	S8	Ag2	N2	91.2(1)
S2	Ag1	N1	96.1(2)	Ag1	Ag3	Ag2	69.38(2)
S3	Ag1	S7	127.97(6)	Ag1	Ag3	Ag4	54.33(2)
S3	Ag1	N1	92.4(2)	Ag2	Ag3	Ag4	59.53(2)
S7	Ag1	N1	91.7(2)	Ag1	Ag3	S1	83.69(4)
Ag1	Ag2	Ag3	56.83(2)				
Ag1	Ag3	S3	54.95(4)	Ag1	Ag4	Ag3	62.13(2)
Ag1	Ag3	S5	131.78(5)	Ag2	Ag4	Ag3	57.75(2)
Ag2	Ag3	Ag4	59.53(2)	Ag1	Ag4	S4	94.98(5)
Ag2	Ag3	S1	53.90(4)	Ag1	Ag4	S6	127.48(5)
Ag2	Ag3	S3	122.83(5)	Ag1	Ag4	S7	59.61(5)
Ag2	Ag3	S5	89.30(5)	Ag2	Ag4	Ag3	57.75(2)
Ag4	Ag3	S1	110.10(4)	Ag2	Ag4	S4	146.54(5)
Ag4	Ag3	S3	77.11(4)	Ag2	Ag4	S6	55.64(5)
Ag4	Ag3	S5	77.48(5)	Ag2	Ag4	S7	83.35(5)
S1	Ag3	S3	24.06(6)	Ag3	Ag4	S4	88.83(5)
S1	Ag3	S5	118.50(6)	Ag3	Ag4	S6	85.34(5)
S1	Ag3	N3	91.5(2)	Ag3	Ag4	S7	117.98(5)
S3	Ag3	S5	117.20(7)	S4	Ag4	S6	126.28(7)
S3	Ag3	N3	93.1(2)	S4	Ag4	S7	115.08(7)
S5	Ag3	N3	90.3(1)	S6	Ag4	S7	114.62(7)
Ag1	Ag4	Ag2	71.96(2)				
Ag1	Ag4	Ag3	62.13(2)				
Ag2	Ag4	Ag3	57.75(2)				

TABLE 6. Atomic coordinates for **2**

Atom	*x*	*y*	*z*	*B* (Å^2)
Ag1	0.85644(3)	0.41950(4)	0.65451(2)	3.55(1)
Ag2	1.04018(3)	0.29888(4)	0.67787(2)	3.82(1)
S1	0.9612(1)	0.4842(1)	0.59906(7)	3.52(3)
S2	1.1592(1)	0.5855(1)	0.78418(7)	4.24(4)
S3	0.76343(9)	0.2399(1)	0.64257(7)	3.32(3)
S4	0.91992(9)	0.1250(1)	0.62316(7)	3.63(3)
N1	1.1756(3)	0.2584(4)	0.6590(2)	3.9(1)
N2	0.6501(4)	0.4702(5)	0.4946(3)	4.9(2)
C1	1.0669(3)	0.5821(4)	0.6738(2)	3.1(1)
C2	1.0762(4)	0.6771(4)	0.6331(2)	3.3(1)
C3	1.1482(4)	0.6658(5)	0.6155(3)	4.1(1)
C4	1.1654(4)	0.7525(6)	0.5835(3)	5.3(2)
C5	1.1094(5)	0.8526(6)	0.5681(3)	5.2(2)
C6	1.0372(5)	0.8634(5)	0.5838(3)	4.9(2)

(continued)

TABLE 6. *(continued)*

Atom	*x*	*y*	*z*	*B* (Å^2)
C7	1.0165(4)	0.7765(5)	0.6166(3)	3.8(1)
C8	0.9335(4)	0.7931(6)	0.6307(3)	5.2(2)
C9	0.8077(3)	0.1320(4)	0.6196(2)	2.8(1)
C10	0.7337(3)	0.0299(4)	0.5931(3)	3.0(1)
C11	0.7650(4)	−0.0336(5)	0.6627(3)	4.0(1)
C12	0.7003(4)	−0.1296(5)	0.6433(3)	5.1(2)
C13	0.6004(4)	−0.1603(5)	0.5530(3)	5.2(2)
C14	0.5716(4)	−0.0992(5)	0.4854(3)	4.7(2)
C15	0.6355(4)	−0.0026(5)	0.5013(3)	4.0(1)
C16	0.5989(5)	0.0638(6)	0.4250(3)	5.3(2)
C17	1.1802(4)	0.3243(5)	0.6103(3)	4.1(1)
C18	1.2554(4)	0.3040(6)	0.5974(3)	5.5(2)
C19	1.3258(5)	0.2121(7)	0.6321(3)	7.3(2)
C20	1.3207(5)	0.1429(7)	0.6812(4)	6.7(2)

(continued)

TABLE 6. *(continued)*

Atom	x	y	z	B (Å^2)
C21	1.2451(4)	0.1682(6)	0.6934(3)	5.1(2)
C22	0.5932(6)	0.5624(7)	0.4725(4)	6.8(2)
C23	0.4803(6)	0.5884(7)	0.3871(4)	7.5(3)
C24	0.4263(8)	0.5163(9)	0.3234(5)	10.3(4)
C25	0.483(1)	0.4177(9)	0.3438(5)	12.8(5)
C26	0.5938(7)	0.3987(7)	0.4305(4)	8.2(3)

The equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation:

$$\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + abB_{12}\cos\gamma + acB_{13}\cos\beta + bcB_{23}\cos\alpha].$$

TABLE 7. Selected bond distances for **2**

Atom 1	Atom 2	Distance
Ag1	Ag1′	3.1966(7)
Ag1	Ag2	2.8693(5)
Ag1	Ag2′	3.0215(5)
Ag2	Ag2′	3.9784(7)
Ag1	S1	2.667(1)
Ag1	S2	2.499(1)
Ag1	S3	2.522(1)
Ag1	N2	2.550(4)
Ag2	S1	2.544(1)
Ag2	S3	2.760(1)
Ag2	S4	2.486(1)
Ag2	N1	2.403(4)

TABLE 8. Selected bond angles for **2**

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Ag1	Ag1	Ag2	59.46(1)	S2	Ag1	S3	120.41(4)
Ag1	Ag1	Ag2	54.87(1)	S2	Ag1	N2	90.1(1)
Ag2	Ag1	Ag2	84.92(1)	S3	Ag1	N2	90.2(1)
Ag1	Ag2	Ag1	65.67(1)	S1	Ag2	S3	132.15(4)
Ag1	Ag2	Ag2	49.16(1)	S1	Ag2	S4	127.41(4)
Ag1	Ag2	Ag2	45.92(1)	S1	Ag2	N1	98.0(1)
S1	Ag1	S2	106.63(4)	S3	Ag2	S4	97.69(4)
S1	Ag1	S3	132.71(4)	S3	Ag2	N1	87.1(1)
S1	Ag1	N2	84.9(1)	S4	Ag2	N1	100.5(1)

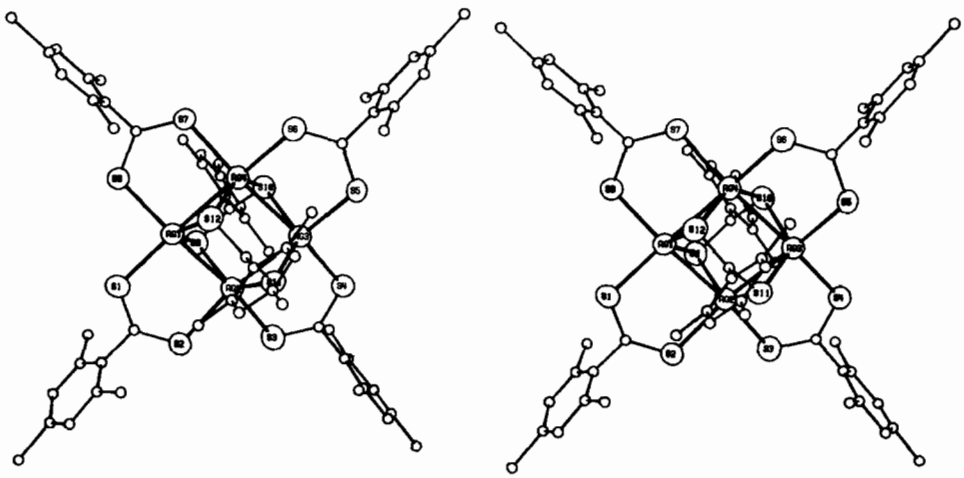


Fig. 3. The molecular structure of **3**, in stereopair, illustrated as in Fig. 1.

bonds to sulfur atoms. One-half of these sulfur atoms (S1, S3, S1′, S3′) bridge two silver atoms (with Ag–S lengths of 2.522–2.760, ave. 2.623 Å) and the other half of the sulfur atoms (S2, S4, S2′, S4′) attach to only one silver atom (with Ag–S lengths 2.486–2.499, ave. 2.4925 Å). All four silver atoms form a fourth coordinate bond to pyridine nitrogen atoms (with Ag–N distances 2.403–2.550, ave. 2.476 Å).

Because the molecule lies on a crystallographic two-fold rotation axis, there are only two unique silver atoms in this cluster. Each of these silver atoms is surrounded by a triangle of sulfur atoms in a nearly trigonal-planar array. The S–Ag–S angles average 119.50° and range from 97.69–132.71°. The distances of the silver atoms from these triangular planes of sulfur atoms are 0.073 and 0.242 Å.

TABLE 9. Atomic coordinates for 3

Atom	x	y	z	Atom	x	y	z
Ag1	0.42854(8)	0.72209(7)	0.95963(8)	C23	0.0706(11)	0.9024(9)	0.9910(10)
Ag2	0.42426(8)	0.79147(7)	0.84978(7)	C24	0.0036(12)	0.9158(11)	1.0043(12)
Ag3	0.28986(8)	0.82689(7)	0.85023(7)	C25	−0.0452(13)	0.8852(11)	0.9750(13)
Ag4	0.29320(8)	0.75387(7)	0.96369(8)	C26	−0.0379(12)	0.8436(11)	0.9295(12)
S1	0.5545(3)	0.7185(3)	0.9797(3)	C27	0.0299(11)	0.8285(10)	0.9190(11)
S2	0.5501(3)	0.7839(3)	0.8563(3)	C28	0.1233(11)	0.9364(10)	1.0269(11)
S3	0.4300(3)	0.8287(3)	0.7355(3)	C29	−0.1209(15)	0.8980(14)	0.9867(15)
S4	0.2915(3)	0.8681(3)	0.7360(3)	C30	0.0417(12)	0.7805(11)	0.8729(12)
S5	0.1835(3)	0.8728(2)	0.8792(3)	C31	0.3495(9)	0.6395(8)	1.0702(9)
S6	0.1850(3)	0.7968(3)	0.9929(3)	C32	0.3520(10)	0.6083(9)	1.1342(10)
S7	0.2809(3)	0.6730(3)	1.0450(3)	C33	0.3733(12)	0.6343(10)	1.1904(12)
S8	0.4200(3)	0.6387(3)	1.0339(3)	C34	0.3775(13)	0.6010(12)	1.2506(13)
S9	0.3928(3)	0.6854(2)	0.8400(3)	C35	0.3577(12)	0.5489(11)	1.2413(12)
S10	0.2526(3)	0.7234(2)	0.8464(3)	C36	0.3349(12)	0.5197(11)	1.1907(12)
S11	0.3903(3)	0.8781(2)	0.9121(3)	C37	0.3309(11)	0.5508(9)	1.1275(11)
S12	0.3900(3)	0.8050(2)	1.0306(3)	C38	0.3928(12)	0.6932(10)	1.1933(12)
C1	0.5866(9)	0.7465(8)	0.9158(9)	C39	0.3625(18)	0.5108(16)	1.3085(18)
C2	0.6597(9)	0.7331(8)	0.9092(9)	C40	0.3068(12)	0.5241(10)	1.0673(12)
C3	0.6774(10)	0.6859(9)	0.8816(10)	C41	0.3106(8)	0.6820(8)	0.8228(8)
C4	0.7452(11)	0.6753(10)	0.8710(11)	C42	0.2865(9)	0.6343(8)	0.7788(9)
C5	0.7882(11)	0.7168(10)	0.8938(11)	C43	0.2832(10)	0.6422(9)	0.7124(10)
C6	0.7728(12)	0.7642(11)	0.9251(12)	C44	0.2591(10)	0.5976(9)	0.6718(10)
C7	0.7053(11)	0.7728(10)	0.9346(11)	C45	0.2414(10)	0.5494(9)	0.6982(10)
C8	0.6275(12)	0.6437(11)	0.8541(12)	C46	0.2443(10)	0.5417(9)	0.7657(10)
C9	0.8653(13)	0.7056(12)	0.8812(13)	C47	0.2673(9)	0.5841(8)	0.8076(9)
C10	0.6868(13)	0.8256(12)	0.9680(13)	C48	0.2982(11)	0.6979(10)	0.6815(11)
C11	0.3657(9)	0.8623(8)	0.7051(9)	C49	0.2128(12)	0.5004(11)	0.6522(12)
C12	0.3718(10)	0.8945(9)	0.6419(10)	C50	0.2693(10)	0.5773(9)	0.8801(10)
C13	0.3945(11)	0.9490(10)	0.6445(11)	C51	0.3992(9)	0.8645(8)	0.9908(9)
C14	0.4015(12)	0.9789(11)	0.5839(12)	C52	0.4168(9)	0.9140(8)	1.0350(9)
C15	0.3802(12)	0.9515(10)	0.5293(12)	C53	0.4833(10)	0.9280(9)	1.0511(10)
C16	0.3633(12)	0.8979(11)	0.5223(12)	C54	0.4985(10)	0.9773(9)	1.0882(10)
C17	0.3565(12)	0.8658(11)	0.5836(12)	C55	0.4472(10)	1.0071(9)	1.1085(10)
C18	0.4146(12)	0.9781(11)	0.7081(12)	C56	0.3810(10)	0.9940(9)	1.0957(10)
C19	0.3887(14)	0.9814(13)	0.4603(14)	C57	0.3649(10)	0.9473(9)	1.0545(10)
C20	0.3334(14)	0.8070(12)	0.5809(14)	C58	0.5394(11)	0.8935(10)	1.0282(11)
C21	0.1494(9)	0.8413(8)	0.9406(9)	C59	0.4628(12)	1.0596(10)	1.1535(12)
C22	0.0812(10)	0.8576(9)	0.9517(10)	C60	0.2933(11)	0.9340(9)	1.0366(11)

Every silver atom has three neighboring silver atoms, with Ag–Ag distances ranging from 2.869–3.197 Å and averaging 2.996 Å, except for one much longer distance of 3.978 Å, between Ag2 and Ag2′. The atomic coordinates for **2** are tabulated in Table 6. Selected bond distances for **2** are given in Table 7 and selected bond angles are listed in Table 8.

The 'planar' cluster compound **3**, pictured in Fig. 3, contains four approximately octahedrally-coordinated silver atoms which are located in a square planar array to each other, coplanar to within 0.008 Å. Each of the silver atoms forms four bonds to sulfur atoms, one-third of which (S9–S12) bridge two silver atoms (with bond lengths 2.588–2.669, ave. 2.624 Å) and two-thirds of which (S1–S8) attach to only one Ag (with bond lengths 2.546–2.607, ave. 2.569 Å). In addition, each silver atom has two neighboring silver atoms (with distances 2.821–2.935, ave. 2.880 Å, and making Ag–Ag–Ag angles 82.85–97.42, ave. 90.00°), which may or may not be actually bonded to each other even though their internuclear separations are very close to the cubic close-packed metallic Ag–Ag distance of 2.883 Å. Atomic coordinates for **3** are listed in Table 9. Selected bond distances for **3** are given in Table 10 and selected bond angles are given in Table 11.

TABLE 10. Selected bond distances for **3**

Atom 1	Atom 2	Distance
Ag1	Ag2	2.821(1)
Ag1	Ag4	2.882(1)
Ag1	S1	2.571(2)
Ag1	S8	2.550(2)
Ag1	S9	2.669(2)
Ag1	S12	2.647(2)
Ag2	Ag3	2.880(1)
Ag2	S2	2.572(2)
Ag2	S3	2.546(2)
Ag2	S9	2.641(2)
Ag2	S11	2.588(2)
Ag3	Ag4	2.935(1)
Ag3	S4	2.572(2)
Ag3	S5	2.563(2)
Ag3	S10	2.610(2)
Ag3	S11	2.624(2)
Ag4	S6	2.568(2)
Ag4	S7	2.607(2)
Ag4	S10	2.598(2)
Ag4	S12	2.615(2)

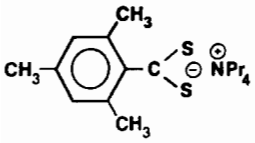
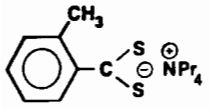
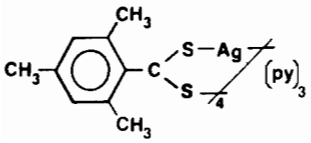
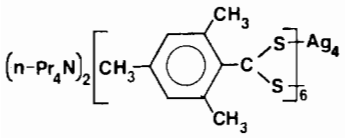
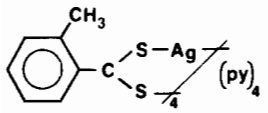
TABLE 11. Selected bond angles for **3**

Atom 1	Atom 2	Atom 3	Angle (°)
Ag2	Ag1	Ag4	84.85(2)
Ag2	Ag1	S1	95.96(5)
Ag2	Ag1	S8	163.14(6)
Ag2	Ag1	S9	57.43(5)
Ag2	Ag1	S12	90.71(5)
Ag4	Ag1	S1	162.69(7)
Ag4	Ag1	S8	94.04(5)
Ag4	Ag1	S9	86.40(5)
Ag4	Ag1	S12	56.26(5)
S1	Ag1	S8	90.08(7)
S1	Ag1	S9	108.66(7)
S1	Ag1	S12	106.43(8)
S8	Ag1	S9	105.72(8)
S8	Ag1	S12	102.69(7)
S9	Ag1	S12	134.21(6)
Ag1	Ag2	Ag3	97.42(2)
Ag1	Ag2	S2	87.83(5)
Ag1	Ag2	S3	163.64(6)
Ag1	Ag2	S9	58.39(5)
Ag1	Ag2	S11	93.74(5)
Ag3	Ag2	S2	166.46(6)
Ag3	Ag2	S3	91.58(5)
Ag3	Ag2	S9	93.56(5)
Ag3	Ag2	S11	57.06(5)
S2	Ag2	S3	86.48(7)
S2	Ag2	S9	99.80(7)
S2	Ag2	S11	110.31(7)
S3	Ag2	S9	107.60(8)
S3	Ag2	S11	102.62(7)
S9	Ag2	S11	138.32(6)
Ag2	Ag3	Ag4	82.85(2)
Ag2	Ag3	S4	90.85(5)
Ag2	Ag3	S5	163.92(5)
Ag2	Ag3	S10	89.51(5)
Ag2	Ag3	S11	55.86(5)
Ag4	Ag3	S4	165.67(6)
Ag4	Ag3	S5	91.53(5)
Ag4	Ag3	S10	55.51(5)
Ag4	Ag3	S11	86.21(5)
S4	Ag3	S5	97.77(7)
S4	Ag3	S10	111.81(7)
S4	Ag3	S11	100.93(7)
S5	Ag3	S10	99.73(7)
S5	Ag3	S11	108.90(7)
S10	Ag3	S11	132.66(6)
Ag1	Ag4	Ag3	94.87(2)
Ag1	Ag4	S6	165.08(6)
Ag1	Ag4	S7	88.42(5)
Ag1	Ag4	S10	96.81(5)
Ag1	Ag4	S12	57.34(5)
Ag3	Ag4	S6	89.58(5)
Ag3	Ag4	S7	166.29(6)
Ag3	Ag4	S10	55.89(5)
Ag3	Ag4	S12	95.74(5)
S6	Ag4	S7	90.61(7)
S6	Ag4	S10	97.47(7)
S6	Ag4	S12	108.08(8)
S7	Ag4	S10	110.53(7)
S7	Ag4	S12	97.23(7)
S10	Ag4	S12	141.91(6)

The 100 MHz ^{1}H NMR data for the three new silver cluster compounds and their corresponding tetrapropylammonium salts are listed in Table 12.

In the absence of evidence to the contrary, it is likely that any bonding interactions between silver atoms, in these or in analogous silver clusters, are at best weak and of only minor importance in the formation of the particular cluster structures.

TABLE 12. 100 MHz ^{1}H NMR data

Compound	Aromatic H	*o*-CH_3	*p*-CH_3	NCH_2–	–CH_2–	–CH_3	Solvent
	6.69 6.86	2.38 2.88	2.19 2.24	3.0–3.3 3.2–3.6	1.45–1.85 1.5–2.1	0.90–1.15 0.8–1.2	$CDCl_3$ py-d_5
	6.8–7.1, 7.1–7.2			3.1–3.4	1.5–1.95	0.85–1.2	$CDCl_3$
	6.87	2.65	2.22				py-d_5
	6.81	2.76	2.19	3.17–3.34	1.5–1.9	0.84–0.98	py-d_5
	7.45–7.95	2.68					py-d_5

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