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Structural isomers of octahedral M_6S_{12} clusters formed from dithiolates. An octahedral hexasilver(I) cluster containing dialkyl dithiophosphate ligands, $\{Ag[S_2P(OC_3H_7)_2]\}_6$, with a different geometrical arrangement from that of $\{Cu[S_2P(OC_2H_5)_2]\}_6$

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Abstract—The single crystal structure of $\{Ag[S_2P(OC_3H_7)_2]\}_6$, Ag_6DDP_6, **1**, is reported. The silver atoms, each of which is trigonally coordinated to three sulfur atoms of the diisopropyl-dithiophosphate ligands, are located at the vertices of a distorted octahedron. The Ag_6DDP_6 molecular arrangement is different from the structure of Cu_6DDP_6 which has a molecular S_6 symmetry. The displacements of the silver atoms from the plane through the sulfur atoms range from 0.328(1) to 0.392(8) Å. The Ag—S distances range from 2.485(2) to 2.572(2) Å. The ligands occupy six of the eight faces of the Ag_6 octahedron with bridging μ_2-S and terminal μ_1-S coordination in an idealized D_{3d} symmetry. The bridging S atoms in **1** occupy the six edges of two triangular faces on opposite sides of the octahedron while in $Cu_6[S_2P(OC_2H_5)_2]_6$ only terminal S atoms are on these faces. All plausible arrangements for these M_6DDP_6 complexes have been considered and a catalog of the surprisingly large number of distinct structures with MS_3 coordinations with cis and trans uncapped faces is presented. © 1997 Elsevier Science Ltd

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Zinc(II) and copper(I) phosphorodithiolates, MDDP, are widely used [1] as anti-oxidants in lubricating oils. Both materials are known to form clusters with Zn^{II} producing a basic oxide [2] in which the O^{2-} is encapsulated, $Zn_4O[S_2P(OR)_2]_6$. With R = I-propyl, the CuDDP is tetranuclear [3], but with R = ethyl, a hexanuclear cluster $Cu_6(DDP)_6$ also has been found [4]. Copper(I) also forms an encapsulating [4] product $\{Cu_8(S_2P(OR)_2]_6S\}$. With Au^I, dinuclear species having DDP ligands, R = *i*-propyl, [5] bridging the Au^I atoms are formed. This molecule has a chain structure with a short aurophilic intermolecular Au—Au distance, 3.050(2) Å.

We describe here the synthesis and structure of a AgDPP complex, R = *i*-propyl. It appears to be the first structural report, although Drew *et al.* [6,7] described the crystal structures of $\{Ag[S_2P(OEt)_2](PPh_3)\}_2$ and $[Me_4N]_2[Ag\{S_2P(OEt)_2\}_2]_2$ obtained from the reactions of $Ag[S_2P(OEt)_2]$ with PPh_3 and $[Me_4N][S_2P(OEt)_2]$, respectively. Apparently attempts to obtain suitable crystals of $Ag[S_2P(OR)_2]$, R = Et or ^{i}Pr failed. The structures of the related silver dialkyldithiophosphinates, AgS_2PR_2, R = C_2H_5, C_3H_7, C_4H_9, are reported to be polymers [8]. The structure of AgDPP, R = ^{i}Pr, presented in this paper shows that it is a hexanuclear species, with a

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different structural arrangement for the DDP ligands from that of $Cu_6(DDP)_6$ [4a]. As a result of this observation other plausible structures have also been considered.

EXPERIMENTAL

Commercial CH_2Cl_2 was distilled from P_4O_{10} prior to use. The ^1H NMR was recorded on a Varian XL-200E spectrometer and referenced against the $CDCl_3$. The $^{31}P\{^1H\}$ solution NMR spectrum in CH_2Cl_2 was recorded on a Varian XL-200 spectrometer operated at 81 MHz and the solid state ^{31}P MAS NMR spectrum was obtained at the Bruker MSL-300 spectrometer operated at 121.5 MHz.

For the solid state NMR measurements, a single pulse with high power proton decoupling was used. The 90° pulse for ^{31}P was 5 μs with a recycle time of 90 s. The sample was packed into a 7 mm zirconium oxide rotor. The spectrum was recorded with magic angle spinning, MAS. The homogeneity of the magnetic field was checked by using the CP/MAS ^{13}C NMR spectrum of adamantane. A line width of 1.8 Hz at half height of the peak was obtained. All chemical shifts were referenced externally against H_3PO_4. Elemental analyses were performed by the Canadian Microanalytical Service, Vancouver, Canada. The melting point was measured on a Thomas Hoover capillary melting point apparatus.

Synthesis of hexakis(diisopropyldithiophosphato)hexasilver(I). $Ag_6[S_2P(OC_3H_7)_2]_6$, **1**

A solution of [9] of $[NH_4][S_2P(O^iPr)_2]$ (2 mmol in 10 mL H_2O) was added to a solution of [10] of $Ag(CH_3CN)_4PF_6$ (1.3 mmol in 10 mL CH_2Cl_2). After stirring for 4 h, the organic phase was separated and dried over anhydrous $MgSO_4$. Most of the solvent was removed by rotavaporization under reduced pressure. A white solid product was isolated in 90% yield. M.p.: 175°C. Anal. Calcd for $C_{36}H_{84}O_{12}P_6S_{12}Ag_6$: C, 22.44; H, 4.36. Found: C, 22.75; H, 4.43. ^1H NMR (in $CDCl_3$): 1.34 (d, 6.2 Hz; 72 H), 4.83 (m; 12 H); $^{31}P\{^1H\}$ NMR: 105 ppm.

The diethyldithiophosphate derivative can also be synthesized in a similar fashion. $^{31}P\{^1H\}$-NMR: 108.5 ppm. (lit. [6], 109 ppm).

Table 1. Crystallographic data of **1**

Formula	$C_{36}H_{84}Ag_6O_{12}P_6S_{12}$
fw	1926.79
space group	$P\bar{1}$
a (Å)	11.870(2)
b (Å)	12.435(2)
c (Å)	14.275(2)
α (°)	110.58(1)
β (°)	103.67(1)
γ (°)	102.83(1)
V (Å^3)	1805.6(5)
Z	1
D_{calc} (Mg/m^3)	1.772
μ(Mo-Kα) (cm^{-1})	21.19
temp (K)	293(2)
$F(000)$	960
λ(radiation) (Å)	0.71073
Max. and min. transmission	0.973, 0.714
Data/parameters	4733/326
Goodness-of-fit on $F^{2,a}$	1.027
R^b, $wR2^b$ [$I > 2\sigma(I)$]	0.0372, 0.0827
R^b, $wR2^b$ (all data)	0.0482, 0.0872

[a] Goodness-of-fit = $[\Sigma[w(F_0^2 - F_c^2)^2]/(M-N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

[b] $R1 = \Sigma\|F_0| - |F_c\|/\Sigma|F_0|$;
$wR2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_{02})^2]\}^{1/2}$.

X-ray diffraction analysis

Cubic, colorless crystals of **1**, suitable for X-ray diffraction were grown at ambient temperature from the vaporization of a CH_2Cl_2 solution. Refined cell parameters were determined from setting angles of 25 reflections with $20 < 2\theta < 30°$. Data collection was carried out at ambient temperature using a Nicolet R3/m diffractometer controlled by a Data General Nova 4 minicomputer utilizing the Wyckoff-scanning technique in a bisecting geometry and graphite-monochromated Mo-Kα radiation. The intensity of a check reflection indicated less than 3% decay took place throughout the data collection.

The data were corrected for absorption, Lorentz and polarization effects. An empirical absorption correction was made on the basis of azimuthal scans of 5 strong reflections spanning a range of 2θ values for **1**. All data processing was performed by a Data General Eclipse S140 minicomputer using the SHELXTL crystallographic computational package (version 5.1) and Siemens SHELXTL PLUS (Micro Vax II).

Compound **1** crystallizes in the $P\bar{1}$ space group. The initial atomic coordinates for the silver atoms in the asymmetric unit were determined by direct methods, and subsequent atom positions were located on different Fourier maps. All but the hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated using fixed C—H bond lengths of 0.96 Å. The structure was refined using the SHELXL 93 crystallographic software package [11]. Crystal data and details of the crystallographic experimental parameters are given in Table 1. Atomic coordinates and isotropic thermal parameters are given in Table 2. Selected bonds distances and angles are given in Table 3.

RESULTS AND DISCUSSION

Synthesis

The title complex was originally synthesized from the reaction of a stoichiometric amount of $[NH_4][S_2$

Table 2. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å × 10^3] for **1**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Ag(1)	1975(1)	5721(1)	6586(1)	63(1)
Ag(2)	725(1)	4752(1)	3350(1)	68(1)
Ag(3)	1033(1)	7212(1)	5372(1)	71(1)
S(1)	3224(2)	8403(2)	5824(2)	93(1)
S(2)	2575(1)	5329(1)	4952(1)	56(1)
S(3)	2968(1)	7371(1)	8438(1)	56(1)
S(4)	893(1)	3489(1)	6176(1)	52(1)
S(5)	542(2)	5608(2)	2010(1)	62(1)
S(6)	−286(1)	2576(1)	3047(1)	51(1)
P(1)	3722(2)	6978(2)	5242(1)	59(1)
P(2)	355(1)	3322(1)	7392(1)	49(1)
P(3)	−1811(1)	1718(1)	1720(1)	43(1)
O(1)	5031(5)	7182(7)	5966(6)	149(3)
O(2)	3931(4)	6778(4)	4157(4)	69(1)
O(3)	1529(4)	3461(3)	8289(3)	57(1)
O(4)	−464(4)	1969(4)	7015(3)	60(1)
O(5)	−1428(4)	1276(3)	696(3)	54(1)
O(6)	−2420(3)	472(3)	1737(3)	48(1)
C(1)	5621(8)	7084(12)	6685(12)	173(7)
C(2)	6806(10)	8130(14)	7211(12)	296(14)
C(3)	5621(9)	6217(9)	7078(7)	112(3)
C(4)	4675(7)	7783(7)	4018(6)	78(2)
C(6)	5623(8)	7379(10)	3620(8)	125(4)
C(5)	3869(9)	8111(10)	3279(8)	125(4)
C(7)	−264(6)	887(6)	6344(6)	68(2)
C(8)	−1429(9)	−123(7)	5887(9)	137(4)
C(9)	727(12)	633(9)	6903(9)	206(8)
C(10)	2474(6)	4658(6)	8981(5)	59(2)
C(11)	2615(8)	4880(8)	10105(6)	93(2)
C(12)	3636(7)	4647(8)	8738(6)	87(2)
C(13)	−3583(5)	−433(5)	904(5)	54(2)
C(14)	−4425(8)	−783(10)	1412(7)	153(5)
C(15)	−3325(8)	−1483(8)	244(7)	129(4)
C(16)	−853(6)	2126(6)	304(6)	66(2)
C(17)	343(8)	2007(11)	308(9)	136(4)
C(18)	−1692(9)	1844(10)	−755(7)	122(4)

P(OEt)$_2$] with AgNO$_3$ in water [6] with a yield of 60%. However, a much higher yield synthesis is achieved by using [Ag(CH$_3$CN)$_4$]PF$_6$ as the starting material under biphasic conditions.

Two types of crystals were observed during the course of recrystallization. Cubic, colorless crystals were isolated along with the major portion of the material which forms extremely fine needle-shaped, crystals. The ^{31}P{^{1}H} NMR spectra of these two materials have the same chemical shift, 105 ppm in CH$_2$Cl$_2$ solution, and identical melting points and elemental analyses. The solid state ^{31}P MAS NMR spectrum of the crystalline materials, with proton decoupling, shows three different peaks with chemical shifts at 107.0, 106.6 and 104.5 ppm, respectively. (A rotor spinning rate of 4.0 kHz was used.) This indicates there exist three crystallographically non-equivalent phosphorus nuclei in the lattice. There are three independent diisopropyl dithiophosphate ligands in the asymmetric unit of **1** (*vide infra*).

Several dinuclear species, [Ag$_2$(DDP)$_2$L$_2$], L = phosphine, which have *syn* and *anti* arrangements of the phosphines, also have been characterized structurally with synthetic details and structural data to be reported elsewhere.

Structure

The molecular structure of **1** shown in Fig. 1 reveals a hexanuclear species. There is an idealized three-fold symmetry axis through two opposite unoccupied Ag$_3$ triangles of the distorted octahedron. There are three two-fold symmetry axes, each of which bisects the whole molecule, perpendicular to the three-fold axis. The idealized point group symmetry is D_{3d} although there is no molecular symmetry other than the inversion center for the complex in the solid state.

The silver atoms, each of which is trigonally coordinated to three sulfur atoms of the diisopropyldithiophosphate ligands, are located at the vertices of a distorted octahedron. The displacements of the silver atoms from the plane through the sulfur atoms range from 0.328(1) to 0.392(8) Å. The Ag—S distances range from 2.485(2) to 2.572(2) Å. The ligands are tridentate (μ_2-S; μ_1-S) and bridge across the Ag$_3$ triangles with bridging S atoms occupying all three edges of these *trans*-oriented triangles. The other six sulfur atoms [S(1), S(3), S(5), S(1a), S(3a), S(5a)] of the ligands are terminally coordinated to only one silver atom. The Ag—Ag distances within the Ag$_3$ triangles, which have only one edge bridged by S are in the range 3.1551(8)–4.128(4) Å. The average Ag—Ag distance within the two Ag$_3$ triangles having each edge occupied by the bridging S atoms is 4.063(6) Å. The mean distance between these two Ag$_3$ triangles through which the pseudo three-fold axis passes is 2.160(4) Å. The intraligand S—S 'bite' distance averages 3.417(6) Å. The phosphorous atoms are tetrahedrally coordinated to two sulfur atoms and two oxygen atoms. The torsion angles of Ag—S—P—S within the Ag$_6$S$_{12}$ unit range from 6.7(2) to 16.1(2)°.

Table 4 lists the octahedral Ag$_6$ clusters which contain sulfur–donor ligands that have been structurally characterized. All ligands are η^3 and span the Ag$_3$ triangles. One peculiar result noted in Table 4 is that the mean distance between two Ag$_3$ planes is not proportional to the intraligands 'bite' distance. The Ag$_6$[S$_2$CN(Et)$_2$]$_6$ is a polymeric chain material [17]. Hence, it is not included in Table 4, nor are the structures of Ag$_6$(SC$_6$H$_4$Cl)$_6$(PPh$_3$)$_5$ [18] or {[Mo$_2$Ag$_6$S$_6$(SCMe$_3$]$_2$](O)$_2$(PPh$_3$)$_4$} [19]. The molecular aggregate, Ag$_6$(SC$_6$H$_4$Cl)$_6$(PPh$_3$)$_5$, can be regarded as a (PPh$_3$)$_2$Ag$^+$ derivative of [(PPh$_3$)$_3$Ag$_5$(SAr)$_6$]$^-$. In the case of the double cubane-like molecule, {[Mo$_2$Ag$_6$S$_6$(SCMe$_3$]$_2$(O)$_2$(PPh$_3$)$_4$}, two hetero-cubanes are linked to each other through two SCMe$_3$ units.

Table 3. Selected bond lengths (Å) and angles (°) for **1**

Ag(1)—S(3)	2.496(2)	Ag(1)—S(2)	2.514(2)
Ag(1)—S(4)	2.572(2)	Ag(1)—Ag(3)	3.1551(8)
Ag(1)—Ag(2)#1	3.1567(9)	Ag(2)—S(5)	2.485(2)
Ag(2)—S(2)	2.518(2)	Ag(2)—S(6)	2.537(2)
Ag(2)—Ag(1)#1	3.1567(9)	Ag(2)—Ag(3)	3.2584(10)
Ag(3)—S(1)	2.490(2)	Ag(3)—S(4)#1	2.499(2)
Ag(3)—S(6)#1	2.565(2)	S(1)—P(1)	1.960(3)
S(2)—P(1)	2.032(2)	S(3)—P(3)#1	1.986(2)
S(4)—P(2)	2.045(2)	S(4)—Ag(3)#1	2.499(2)
S(5)—P(2)#1	1.973(2)	S(6)—P(3)	2.026(2)
S(6)—Ag(3)#1	2.565(2)	P(2)—S(5)#1	1.973(2)
P(3)—S(3)#1	1.986(2)		

S(3)—Ag(1)—S(2)	131.80(6)	S(3)—Ag(1)—S(4)	122.78(5)
S(2)—Ag(1)—S(4)	97.86(5)	S(3)—Ag(1)—Ag(3)	99.96(4)
S(2)—Ag(1)—Ag(3)	69.15(4)	S(4)—Ag(1)—Ag(3)	126.68(4)
S(3)—Ag(1)—Ag(2)#1	94.89(4)	S(2)—Ag(1)—Ag(2)#1	126.41(4)
S(4)—Ag(1)—Ag(2)#1	67.51(4)	Ag(3)—Ag(1)—Ag(2)#1	79.56(2)
S(5)—Ag(2)—S(2)	127.78(6)	S(5)—Ag(2)—S(6)	127.74(6)
S(2)—Ag(2)—S(6)	98.10(5)	S(5)—Ag(2)—Ag(1)#1	99.18(4)
S(2)—Ag(2)—Ag(1)#1	122.92(4)	S(6)—Ag(2)—Ag(1)#1	67.92(4)
S(5)—Ag(2)—Ag(3)	97.05(5)	S(2)—Ag(2)—Ag(3)	67.31(4)
S(6)—Ag(2)—Ag(3)	126.05(4)	Ag(1)#1-Ag(2)—Ag(3)	77.68(2)
S(1)—Ag(3)—S(4)#1	134.39(7)	S(1)—Ag(3)—S(6)#1	116.06(6)
S(4)#1—Ag(3)—S(6)#1	104.25(5)	S(1)—Ag(3)—Ag(1)	88.04(6)
S(4)#1—Ag(3)—Ag(1)	128.29(4)	S(6)#1—Ag(3)—Ag(1)	67.66(4)
S(1)—Ag(3)—Ag(2)	100.15(5)	S(4)#1—Ag(3)—Ag(2)	66.51(4)
S(6)#1—Ag(3)—Ag(2)	129.29(4)	Ag(1)—Ag(3)—Ag(2)	80.10(2)
P(1)—S(1)—Ag(3)	95.45(9)	P(1)—S(2)—Ag(1)	104.32(8)
P(1)—S(2)—Ag(2)	106.89(8)	Ag(1)—S(2)—Ag(2)	110.22(6)
P(3)#1—S(3)—Ag(1)	95.45(7)	P(2)—S(4)—Ag(3)#1	106.45(8)
P(2)—S(4)—Ag(1)	112.57(8)	Ag(3)#1—S(4)—Ag(1)	105.03(6)
P(2)#1—S(5)—Ag(2)	95.49(8)	P(3)—S(6)—Ag(2)	110.74(7)
P(3)—S(6)—Ag(3)#1	106.40(7)	Ag(2)—S(6)—Ag(3)#1	104.65(6)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y+1$, $-z+1$.

The same ligand bridging mode (μ_2-S; μ_1-S) observed in **1** also has been observed in the Cu_4 cluster, $Cu_4[S_2P(O^iPr)_2]_4$, and in the Cu_6 cluster, $Cu_6[S_2P(OEt)_2]_6$ [4]. The DDP ligands can also become tetradentate (μ_2-S; μ_2-S) ligand as found in the centered [4,20] Cu_8 cubane clusters. While dithiocarbamates [21] and dithiophosphates [3] of Cu^I generally form tetranuclear clusters, the Ag^I complexes of these same ligands appear to be hexanuclear clusters. Hexanuclear clusters are found in the monothiocarbamates [14,22] of both Cu^I and Ag^I. The thermodynamics of the self assembly process appears to play a crucial role in determining the specific cluster nuclearity and geometry.

In $Cu_6[S_2P(OEt)_2]_6$ [4], which crystallizes in the $R\bar{3}$ space group, the basic structure of the Cu_6S_{12} core is similar to that of **1**. The mean distance between the two empty Cu_3 planes is 1.898(2) Å. The Cu–Cu distances within the empty Cu_3 triangle plane and between the two uncapped Cu_3 triangles are 4.307(3) and 3.129(3) Å, respectively. The intraligand bite distance is 3.441(3) Å. The bridging sulfur atom positions are different, however, in these two molecules. In the case of Ag_6 cluster, the six bridging sulfur atoms are located on the two uncapped Ag_3 triangles while the terminally coordinated sulfur atoms are in the belt positions of an octahedron. In the Cu_6 cluster, the bridging sulfur atom positions are in the belt positions of the octahedron.

Recently the structure of $Ag_4(i\text{-MNT})_4^{4-}$, *i*-MNT = $[S_2CC(CN)_2]^{2-}$, was reported from our laboratory [23]. Its structural arrangement [24] is like that of Cu_4DDP_4 and the dithiocarbamates [3,21]. Reaction with $Ag(PPh_3)_2NO_3$ in acetonitrile produces Ag_7, Ag_8, and Ag_9 clusters built upon the hexanuclear $Ag_6(i\text{-MNT})_6^{6-}$ moiety reported by Dietrich [12(a)]. The hexanuclear entity within the Ag_8 and Ag_9 clusters has the same approximate D_{3d} arrangement as found in **1**.

Structural possibilities

The different structures for Cu_6DDP_6 and **1** are presented with space filling models in Fig. 2(a) and (b). In order to represent these structures easily in

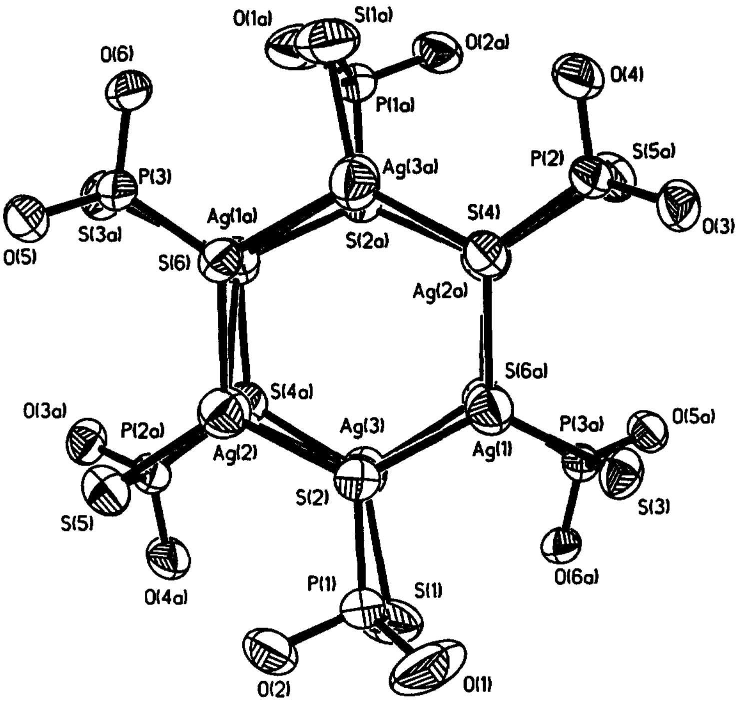


Fig. 1. The thermal ellipsoid drawing (50% probability) of $\{Ag[S_2P(OC_3H_7)_2]\}_6$. The isopropyl groups were omitted for clarity.

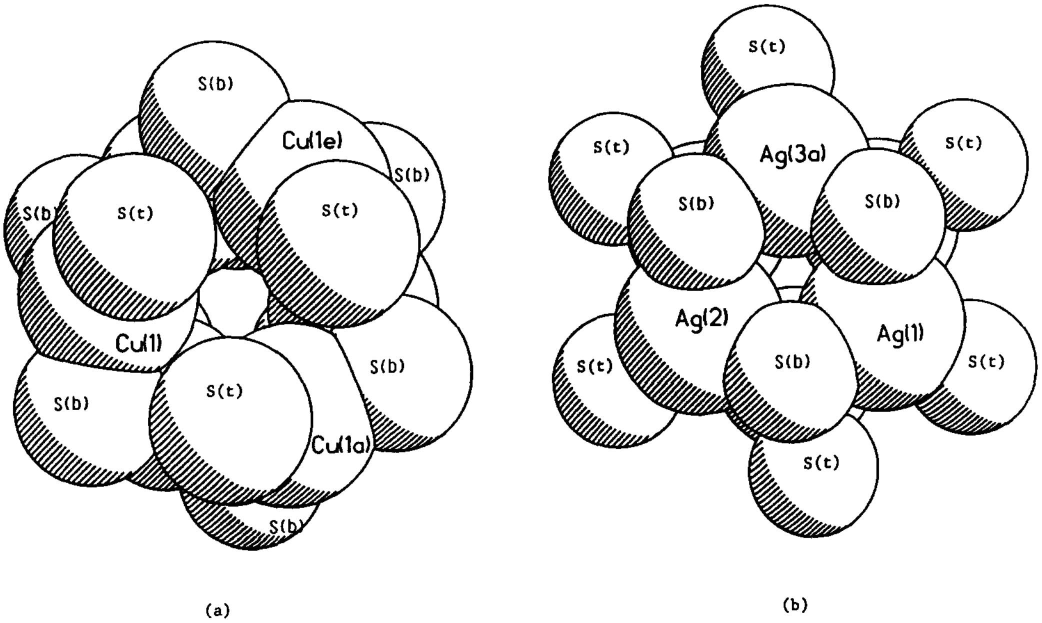


Fig. 2. Space-filling models of the M_6S_{12} cores in the complex, $M_6(DPP)_6$, view down the pseudo-three-fold axis, (a) $Cu_6[S_2P(OEt)_2]_6$; (b) $\{Ag[S_2P(OC_3H_7)_2]\}_6$. S(b) and S(t) denote a bridging sulfur atom and terminally coordinated sulfur atom, respectively.

Table 4. The octahedral hexasilver clusters containing sulfur-donor ligand which have been structurally characterized

Compounds	Geometry of each silver (donor set)[a]	Structure[b] of Ag_6 core	mpln[c]	bite distance	Ag–Ag[d]	Ag–Ag[e]	Ref.
$[Me_4N]_6[Ag_6(i\text{-MNT})_6]\cdot H_2O$	Trigonal ($2S_b$, S_t)	o	2.331(2)	2.996(3)	3.610(2)	3.127(3)	[12]
$\{Ag_6[S_2CN(^nPr)_2]_6\}$	Trigonal ($2S_b$, S_t)	o	2.096(2)	3.002(6)	3.770(5)	3.023(1)	[13]
$\{Ag_6[S(O)CN(^nPr)_2]_6\}$	Trigonal ($2S_b$, O_t)	o	2.457(3)	2.638(5)	3.153(4)	3.060(3)	[14]
$[Ag_6(SC_5H_3N\text{-}3\text{-}SiMe_2Ph)_6]$	Trigonal ($2S_b$, N_t)	o	2.397(2)	2.317(4)	3.157(2)	3.016(2)	[15]
$[Ag_6(C_5H_3NSSiMe_3)_6]$	Trigonal ($2S_b$, N_t)	o	[f]	[f]	[f]	3.323(1)	[16]
$\{Ag_6[S_2P(OC_3H_7)]_6\}$	Trigonal ($2S_b$, S_t)	o	2.160(4)	3.417(6)	4.063(6)	3.190(4)	This work

[a] Suffixes b and t denote bridging and terminal coordination modes, respectively.

[b] o = distorted octahedral.

[c] The distance between two Ag_3 planes through which the pseudo-three-fold axis passes.

[d] The averaged Ag–Ag distance within the Ag_3 triangle which is not capped by the ligand.

[e] The averaged Ag–Ag distances between two Ag_3 planes through which the pseudo-three-fold axis passes.

[f] The data were not available at Cambridge Structural Database.

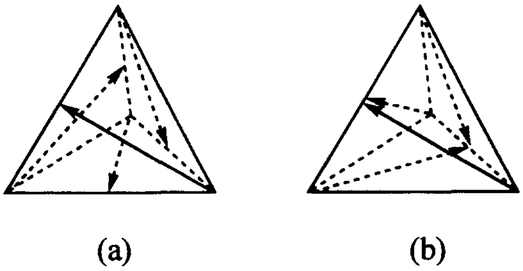


Fig. 3. A sketch of possible tetrahedral structures for M_4L_4 dithiolates, each with terminal and bridging ligand atoms spanning triangular faces of the tetrahedron. (a) is commonly observed with Cu^I dithiolates and was thoroughly described and discussed by Hesse [21,22]. A third possible dithiolate structure with three coordination at each metal atom center and with triangular face capping ligands (not sketched here) has two ligands with both S atoms bridging and two ligands with both S atoms terminal.

order to determine the number of different possibilities that might be formed, a line drawing arrangement was devised. Figure 3 presents the only possibilities plausible for the tetranuclear species in which each metal atom is three coordinate and the ligands span triangular faces of the polygon. Figure 3(a) is the classical dithiocarbamate structure seen for cu_4DDP_4. Figure 3(b) is a representation of the case in which two of the edges of the tetrahedron have double S bridges. These are the only possibilities if (1) the metal centers are three coordinate and (2) the ligands do not chelate to a single metal center but bond to one metal terminally and bridge two other metal atoms. The arrowheads represent the bridging S atom (μ_2) of the dithiolate with the arrow's tail the terminally bonded (μ_1) ligand atoms. For M_6 clusters the situation becomes considerably more complicated with the different structures observed represented in Fig. 4(a) (b). The remainder of the plausible structures with uncapped triangular faces across the octahedron are sketched in Fig. 4(c)–(f). Each figure shows two drawings: the octahedral structure and the ligand configurations in the belt triangles. Space filling models of the two observed M_6S_{12} core units viewed down the pseudo three fold axis are presented in Fig. 2. *To our knowledge, two geometrical forms have not been described previously for octahedral dithiolate clusters.*

Given the existence of these two experimentally verified, geometrically distinct octahedral structures, it was of interest to ask what other distinct octahedral structures might be theoretically plausible assuming trigonal MS_3 coordination about each metal atom with the ligands spanning the triangular faces of the octahedron. Under similar hypotheses stated below, it is shown that exactly six geometrically distinct shapes occur. Given that three of these shapes conform to point groups containing only proper rotation, there are nine distinct isomers (counting the enantiomeric forms).

The following assumptions are made: *There are six terminally coordinated ligand atoms, one at each of the six vertices of the octahedron. There are six bridging atoms, each joined to a terminally coordinated atom by a single ligand bridge. There are two opposite uncapped triangular faces. Each of the remaining six triangular faces in the belt of the octahedron contains exactly one ligand. This ligand joins a terminally coordinated atom at a vertex of that face to a bridging atom on the opposite edge of the face.*

Under these hypotheses the 4-fold axes are removed, reducing the symmetries of the octahedral structure from 48 to the 12 of the D_{3d} point group. These 12 symmetries are characterized as those which transform six triangular faces in the belt into themselves while preserving both *u-ligands*, those that terminate on the uncapped faces, and *b-ligands*, those that terminate on the belt positions. These transformations are generated by an S_6 rotation (or bar 6, $(2\pi/6) \times I$) and reflection through a plane containing the rotation axis. The classification is completed by considering several cases.

Case 1. The structure contains only u-ligands. Only one structure results. It has the full D_{3d} symmetry Fig. 4(a).

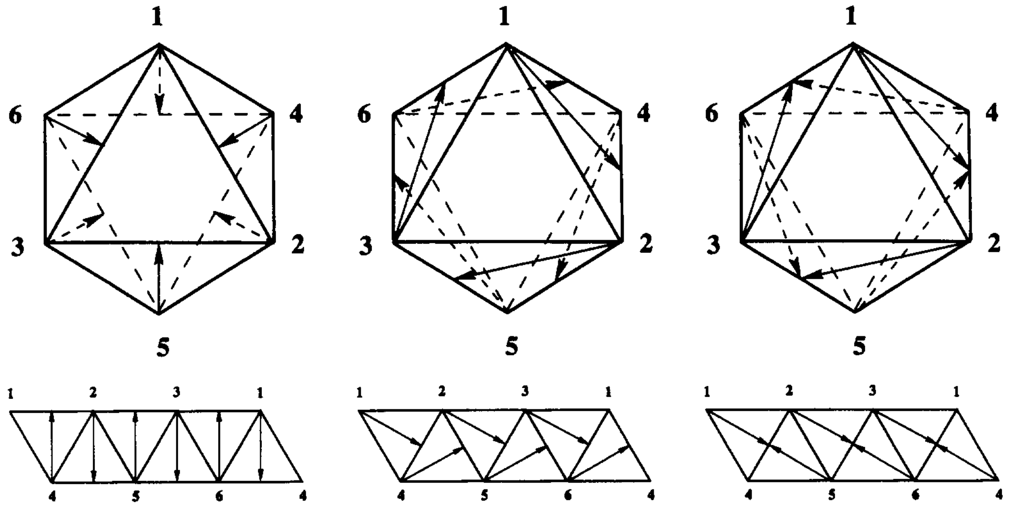
Case 2. The structure contains only b-ligands. The b-ligands in triangles **235** and **316** are uniquely determined. There are two choices of b-ligands in triangle **245**, one with a vertex at **4** and the other with a vertex at **5**. In both cases, there is only one choice for the b-ligands in the remaining two faces. The two possible structures are 4(b), S_6 symmetry and 4(c), D_3 symmetry. The latter structure contains three doubly bridging edges on the octahedron.

Case 3. The structure contains both u-ligands and b-ligands. By applying a suitable transformation, we assume without loss of generality that triangle **124** contains a u-ligand and triangle **164** a b-ligand (which necessarily originates at vertex **6**). The ligand originating at vertex **1** must therefore be a b-ligand in triangle **316**. It remains to consider triangles **245, 235,** and **356**.

Subcase 3(*a*). Triangle **245** contains a b-ligand. This ligand must originate at vertex **5**, which forces the ligand originating at **2** to the a b-ligand contained in triangle **235**. This in turn forces triangle **356** to contain a u-ligand from vertex **3**. The structure with C_{2h} symmetry, 4(d), results.

Subcase 3(*b*). Triangle **245** contains a u-ligand. This ligand must originate at vertex **2**. If the ligand in triangle **235** is a b-ligand, then it must originate at vertex **3** which forces triangle **356** to contain the b-ligand originating at vertex **5**. This gives structure 4(e). Otherwise triangle **235** contains the u-ligand from vertex **5** which forces triangle **356** to contain a u-ligand from vertex **3**. The resulting structure is shown in 4(f). Both 4(e) and 4(f) have C_2 symmetry.

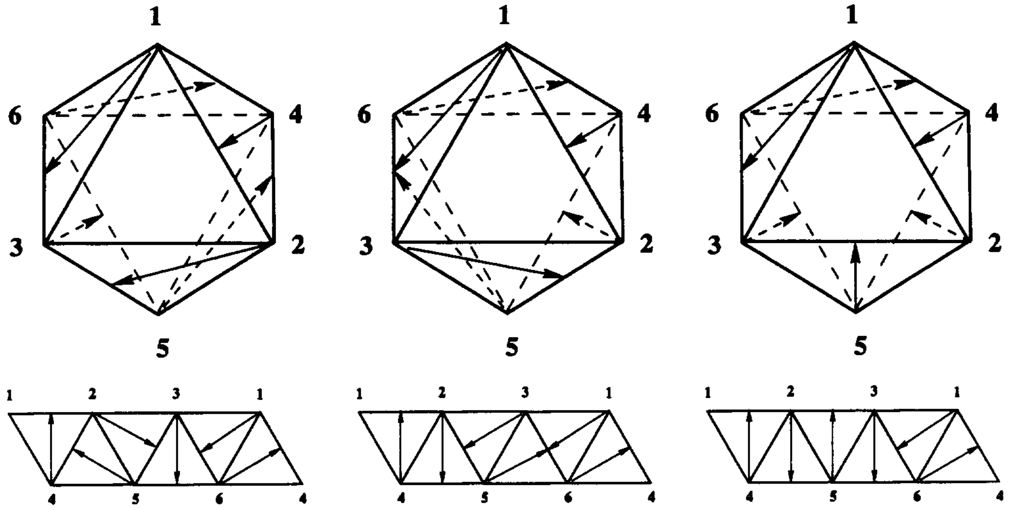
Why only two structural types have been observed to date with M_6DDP_6 complexes cannot be answered at this time. Structures 4(c) and 4(e) with double S atom bridges clearly are very different from the other



(a) D_{3d} (Observed in Ag_6DDP_6)

(b) S_6 (Observed in Cu_6DDP_6)

(c) D_3



(d) C_{2h}

(e) C_2

(f) C_2

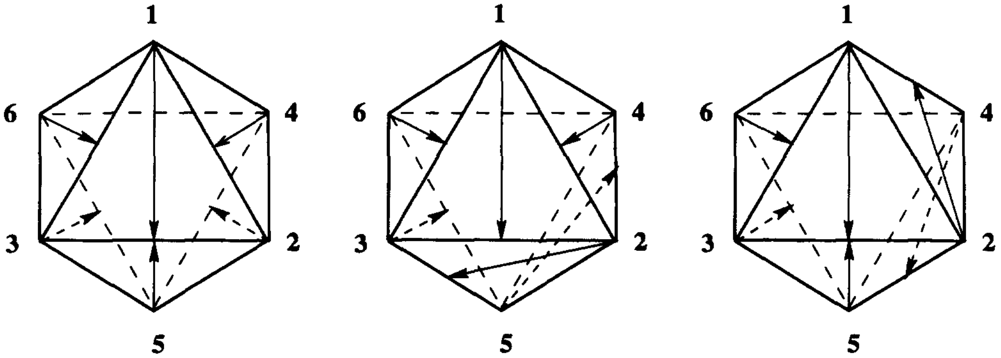
Fig. 4. Theoretically possible octahedral structures for M_6L_6 dithiolates with *trans* uncapped triangular faces, configurations and symmetries.

structures, but double S atom bridges are known. Further, there is no apparent reason to exclude structures in which the open triangular faces are adjacent to each other or those in which open triangular faces share a common vertex.

Figure 5 considers those structures with adjacent open faces (common edge). Mathematically all cases have been considered in these sketches. None satisfy the requirement of three coordination for each metal center. Three structural types require double bridges between two metal centers. The other three structures have both two and four coordinate metal centers. While both types of coordination are known for Ag^I, we are unaware of structural examples wherein both four and two coordination exist in the same molecule.

Open faces sharing a common vertex give the structures presented in Fig. 6. None of these structures satisfy the requirement of three coordination at each metal center. Arguments similar to those used to generate the structures of Fig. 4 were used to create these geometries of Figs 5 and 6.

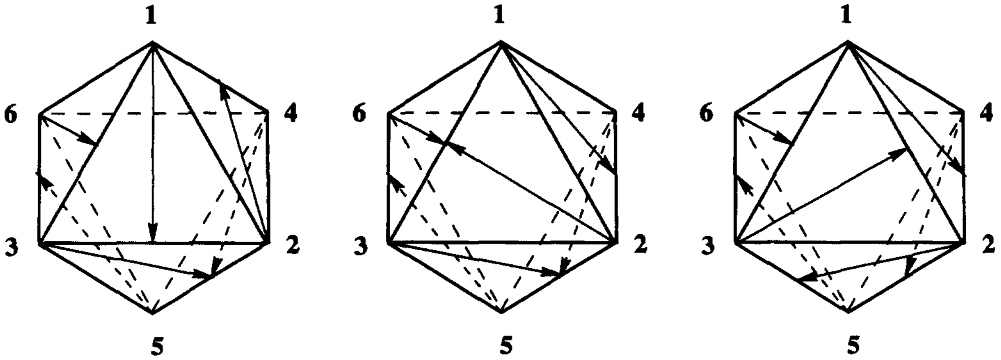
Given the condition that each ligand bonds to a vertex metal atom and bridges two others, there 16 structural types of octahedral M_6L_6, L = dithiolate, clusters to be considered of which 12 are in point groups which contain no improper rotations. Hence 28 molecular structures results, of which only two have been observed to date. Where are the rest? Some of the unknown structures simply have less symmetry than the two established structural types, others have



(a) Cis (Edge) - C_s - One double bridge - No enantiomorph

(b) Cis (Edge) - C_1 - No double bridges - One enantiomorph

(c) Cis (Edge) - C_1 - One double bridge - One enantiomorph



(d) Cis (Edge) - C_1 - One double bridge - One enantiomorph

(e) Cis (Edge) - C_1 - Two double bridges - One enantiomorph

(f) Cis (Edge) - C_1 - No double bridges - One enantiomorph

Fig. 5. Theoretically possible octahedral structures for M_6L_6 dithiolates with adjacent uncapped triangular faces, configurations and symmetries.

(a) Cis (Vertex) - C_1 - Two double bridges - One enantiomorph

(b) Cis (Vertex) - C_1 - One double bridge - One enantiomorph

(c) Cis (Vertex) - C_1 - No double bridges - One enantiomorph

(d) Cis (Vertex) - C_1 - No double bridges - One enantiomorph

Fig. 6. Theoretically possible octahedral structures for M_6L_6 dithiolates with uncapped triangular faces sharing a common vertex, configurations and symmetries.

double ligand atom bridges and still others have two different coordination numbers for the metal atoms. However, there is not an obvious explanation for the fact that none have been observed. The subtleties of *supramolecular cluster formation* remain to be understood for structures of this type.

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Supplementary material available. Tables of crystallographic data, position parameters, bond distances and angles, anisotropic thermal parameters and H atom coordinates (7 pages). Ordering information is given on the current masthead page.

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