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# Solid State Structures of $[Ag_5(dppm)_4(S_2CC(CN)P(O)(OEt)_2)_2][PF_6]$ and $Ag_4(dppm)_4(S_2CC(CN)P(O)(OEt)_2)_2$: Variable Coordination Modes of 1,1-Dithiolate to Silver(I)

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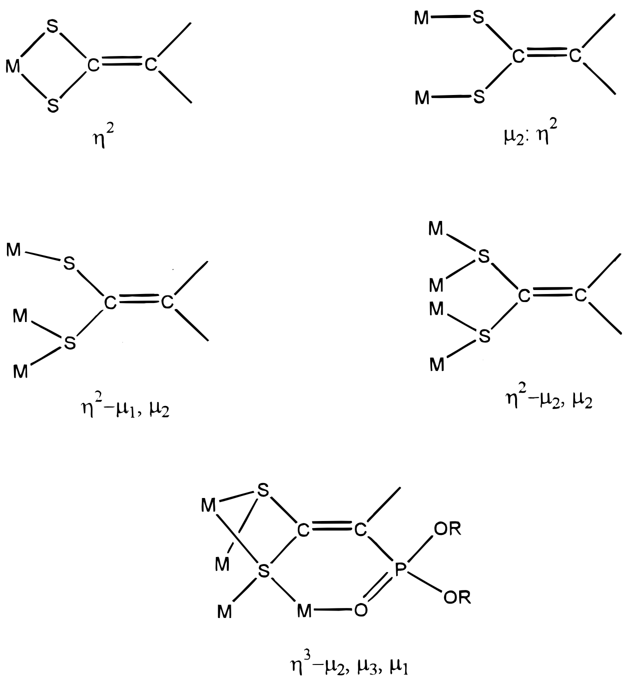
## Introduction

The chemistry of metal complexes containing 1,1-dithiolato ligands continues to attract broad attention followed the initial work by Delepine.[1] They have been used as fungicides, pesticides, vulcanization accelerators, flotation agents, and lubricant additives and more recently in the deposition of ZnS or CdS thin films by metal organic chemical vapor deposition.[2] In addition, the variable coordination modes of 1,1-dithiolate ligands to metal make the structural studies more interesting. They can act as chelating, bridging, tridentate[$\eta^2(\mu_2\text{-S-}\mu_1\text{-S})$], and tetradentate[$\eta^2(\mu_2\text{-S-}\mu_2\text{-S})$] ligands (Chart 1) of which the tetrametallic tetraconnective coordination mode, [$\eta^2(\mu_2\text{-S}, \mu_2\text{-S})$], is the least observed and only a handful of reports have appeared. Those include dinegative 1,1-dithiolates of copper[3] and silver,[4] uninegative dithiophosphates[5] of copper, and dithiocarboxylates[6] and dithiocarbamates[7] of silver. Herein, we report an unprecedented tetrametallic hexaconnective coordination pattern, $\eta^3(\mu_2\text{-S-}\mu_3\text{-S}'\text{−O})$, found in a novel pentanuclear silver complex, $[Ag_5(dppm)_4(S_2CC(CN)P(O)(OEt)_2)_2][PF_6]$, **1**, along with a neutral, tetranuclear silver compound, $Ag_4(dppm)_4(S_2CC(CN)P(O)(OEt)_2)_2$, **2**, containing a tetradentate ligand bridging mode. Surprisingly these two compounds are the first structurally characterized 2-(diethoxyphosphinyl)-2-cyanoethylene-1,1-dithiolato complexes of any element, and only two other complexes[8] containing this ligand have been synthesized prior to this study.

**Chart 1**



$\eta^2$ $\mu_2$: $\eta^2$

$\eta^2$−$\mu_1$, $\mu_2$ $\eta^2$−$\mu_2$, $\mu_2$

$\eta^3$−$\mu_2$, $\mu_3$, $\mu_1$

## Results and Discussion

Complexes **1** and **2** were isolated from the reaction of $[Ag_2(\mu\text{-dppm})_2(CH_3CN)_2](PF_6)_2$ and $K_2(S_2CC(CN)P(O)(OEt)_2)_2$ in $CH_2Cl_2$ having **1** as the major product. They can be easily separated by using $CH_3OH$ in which **1** barely dissolved. Two distinct spectroscopic characteristics are revealed in the $^{31}P$ NMR and IR spectra for these two compounds. While a broad peak centered at −1 ppm in the $^{31}P$ NMR is the resonance frequency of dppm ligands, the chemical shifts of 1,1-dithiolates are at 18 and 16 ppm for **1** and **2**, respectively. Also different are the $\nu_{CN}$ 2181 cm$^{-1}$ in **1** and 2172 cm$^{-1}$ in **2**, which exhibit high-energy shifts relative to the free ligand ($\nu_{CN} = 2162$ cm$^{-1}$).

Instead of the molecular ion peak of $[Ag_5(dppm)_4(S_2CC(CN)P(O)(OEt)_2)_2]^+$ ($M_{calc} = 2579.2$), the *m/z* 2194.7 peak observed in the positive FAB mass spectrum corresponds to the intact complex with loss of one dppm ligand, $[Ag_5(dppm)_3(S_2CC(CN)P(O)(OEt)_2)_2]^+$ ($M_{calc} = 2194.8$). The *m/z* 1810.9 peak can be attributed to loss of two dppm ligands, $[Ag_5(dppm)_2(S_2CC(CN)P(O)(OEt)_2)_2]^+$ ($M_{calc} = 1810.4$). On the other hand, only fragment peaks of **2** are revealed in the mass spectrum.

A crystallographic analysis reveals that the complex **1** is a pentanuclear cationic species. As shown in Figure 1, three kinds of silver environments are present: the Ag(1) atom by which the 2-fold rotational axis passes is surrounded by two sulfur

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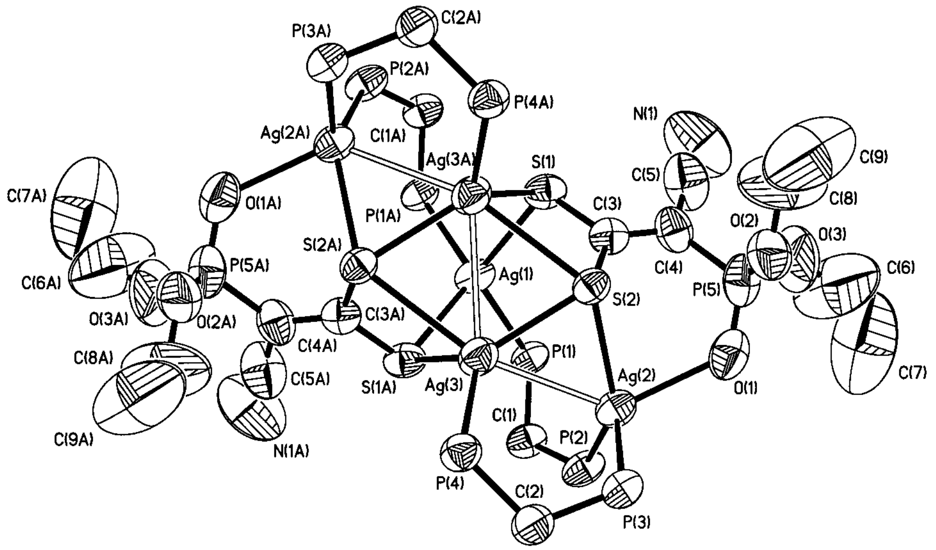

**Figure 1.** Thermal ellipsoid drawing (50% probability) of the cation $[Ag_5(dppm)_4(S_2CC(CN)P(O)(OEt)_2)_2]^+$. The phenyl rings are omitted for clarity. Atoms *n* and *n*A are related by a 2-fold axis.

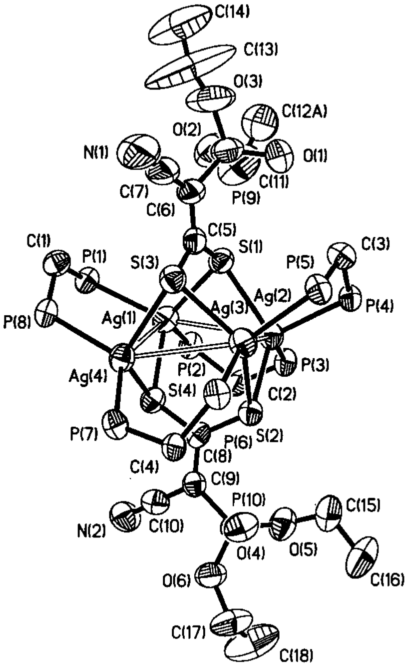

**Figure 2.** Thermal ellipsoid drawing (50% probability) of $[Ag_4(dppm)_4(S_2CC(CN)P(O)(OEt)_2)_2]$. The phenyl rings are omitted for clarity.

**Table 1.** Crystallographic Data for $[Ag_5(dppm)_4(S_2CC(CN)P(O)(OEt)_2)_2](PF_6)$, **1**, and $[Ag_4(dppm)_4(S_2CC(CN)P(O)(OEt)_2)_2]$, **2**

| | $\mathbf{1}\cdot 2CH_2Cl_2$ | $\mathbf{2}\cdot Et_2O$ |
|---|---|---|
| formula | $C_{116}H_{112}Ag_5Cl_4F_6N_2O_6P_{11}S_4$ | $C_{118}H_{118}Ag_4N_2O_7P_{10}S_4$ |
| fw | 2894.14 | 2545.56 |
| $\lambda$(Mo K$\alpha$), Å | 0.71073 | 0.71073 |
| $T$, °C | 25 | 25 |
| space group | $C2/c$ | $P2_1/n$ |
| $a$, Å | 20.6267(11) | 20.7446(13) |
| $b$, Å | 23.0079(13) | 23.3690(14) |
| $c$, Å | 26.3660(15) | 23.9971(15) |
| $\beta$, deg | 90.914(10) | 90.423(1) |
| $V$, Å$^3$ | 12511(1) | 11633(1) |
| $Z$ | 4 | 4 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.537 | 1.453 |
| $\mu$, mm$^{-1}$ | 1.122 | 0.927 |
| R1$^a$ | 0.0545 | 0.0708 |
| wR2$^b$ | 0.1523 | 0.149 |

$^a$ R1 $= \sum||F_o| - |F_c||/\sum|F_o|$. $^b$ wR2 $= \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

atoms and two phosphorus atoms forming a tetrahedral arrangement; the Ag(3) and Ag(3A) atoms are each tetragonally surrounded by three sulfur atoms and one phosphorus atom; the remaining two are also tetragonally coordinated by two phosphorus atoms and one sulfur atom with the oxygen atom from the P═O group of the dithiolate ligand occupying the fourth coordination site. The Ag(2)−Ag(3) distance of 2.9827(6) Å is the shortest silver−silver bond length found in this complex, which is slightly longer than the distance in metallic silver (2.88 Å).[9] The sulfur atoms of the dithiolates display two distinct bridging modes: while the S(1) atom links two silver atoms, the S(2) atom connects three silver atoms. The Ag(3A)−S(2) bond is the longest (2.8919(14) Å) among the Ag−$\mu_3$-S bonds, and the rest fall in the range 2.5518(15)−2.5926(14) Å. This kind of bridging mode, $\mu_2$;$\mu_3$, in conjunction with the oxygen atom of the phosphinyl group makes the 1,1-dithiolate in the title complex an extremely rare example of a tetrametallic hexaconnective coordination mode. *To the best of our knowledge, this has never been observed in any 1,1-dithiolato metal complexes.* The dppm ligands act as normal bridging ligands, each connecting two silver atoms. The Ag−P bond distances are in the range 2.4592(15)−2.5145(15) Å. The Ag−O bond length, 2.510(5) Å, is slightly longer than those (2.489(2) and 2.388(5) Å) found in the compound $[Ag_4\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_4]$,[10] of which two silver atoms are four coordinated by the oxygen and the sulfur atoms from two $\eta^2$-(O−$\mu_2$-S) bridging bidentate thiolate ligands and fall in the 2.251(7)−2.64(2) Å range found in the other tetracoordinated silver−oxygen complexes.[11]

The compound **2** (Figure 2) structurally characterized as $[Ag_4(dppm)_4(S_2CC(CN)P(O)(OEt)_2)_2]$, which is similar in coordination to $[Ag_4(dppm)_4(i\text{-}MNT)_2]$ (i-MNT = [S$_2$C═C-

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**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **1**·$2CH_2Cl_2$

| | | | |
|---|---|---|---|
| Ag(1)−P(1) | 2.5143(14) | Ag(1)−P(1)#1 | 2.5143(14) |
| Ag(1)−S(1)#1 | 2.5817(15) | Ag(1)−S(1) | 2.5817(15) |
| Ag(2)−P(2) | 2.4617(15) | Ag(2)−O(1) | 2.510(5) |
| Ag(2)−P(3) | 2.5145(15) | Ag(2)−S(2) | 2.5926(14) |
| Ag(2)−Ag(3) | 2.9827(6) | Ag(3)−P(4) | 2.4592(15) |
| Ag(3)−S(2) | 2.5518(15) | Ag(3)−S(1)#1 | 2.5797(17) |
| Ag(3)−S(2)#1 | 2.8919(14) | Ag(3)−Ag(3)#1 | 3.1114(9) |
| S(1)−Ag(3)#1 | 2.5797(17) | S(1)−C(3) | 1.747(6) |
| S(2)−C(3) | 1.740(6) | S(2)−Ag(3)#1 | 2.8919(14) |
| P(5)−O(1) | 1.469(6) | P(5)−O(2) | 1.566(6) |
| P(5)−O(3) | 1.569(6) | P(5)−C(4) | 1.786(7) |
| N(1)−C(5) | 1.152(11) | C(3)−C(4) | 1.376(9) |
| C(4)−C(5) | 1.428(10) | | |
| P(1)−Ag(1)−P(1)#1 | 115.68(7) | P(1)−Ag(1)−S(1)#1 | 93.91(5) |
| P(1)#1−Ag(1)−S(1)#1 | 118.47(5) | P(1)−Ag(1)−S(1) | 118.47(5) |
| P(1)#1−Ag(1)−S(1) | 93.91(5) | S(1)#1−Ag(1)−S(1) | 118.43(7) |
| P(2)−Ag(2)−O(1) | 111.10(12) | P(2)−Ag(2)−P(3) | 112.81(5) |
| O(1)−Ag(2)−P(3) | 107.60(13) | P(2)−Ag(2)−S(2) | 135.90(5) |
| O(1)−Ag(2)−S(2) | 79.49(12) | P(3)−Ag(2)−S(2) | 103.26(5) |
| P(2)−Ag(2)−Ag(3) | 101.47(4) | O(1)−Ag(2)−Ag(3) | 133.27(12) |
| P(3)−Ag(2)−Ag(3) | 88.46(4) | S(2)−Ag(2)−Ag(3) | 53.93(3) |
| P(4)−Ag(3)−S(2) | 116.84(5) | P(4)−Ag(3)−S(1)#1 | 117.97(5) |
| S(2)−Ag(3)−S(1)#1 | 122.97(5) | P(4)−Ag(3)−S(2)#1 | 107.10(5) |
| S(2)−Ag(3)−S(2)#1 | 110.50(4) | S(1)#1−Ag(3)−S(2)#1 | 66.47(4) |
| P(4)−Ag(3)−Ag(2) | 92.94(4) | S(2)−Ag(3)−Ag(2) | 55.20(3) |
| S(1)#1−Ag(3)−Ag(2) | 107.37(4) | S(2)#1−Ag(3)−Ag(2) | 159.68(3) |
| P(4)−Ag(3)−Ag(3)#1 | 132.84(4) | S(2)−Ag(3)−Ag(3)#1 | 60.46(3) |
| S(1)#1−Ag(3)−Ag(3)#1 | 91.93(3) | S(2)#1−Ag(3)−Ag(3)#1 | 50.15(3) |
| Ag(2)−Ag(3)−Ag(3)#1 | 113.02(2) | Ag(3)#1−S(1)−Ag(1) | 93.59(6) |
| Ag(3)−S(2)−Ag(2) | 70.87(4) | Ag(3)−S(2)−Ag(3)#1 | 69.40(4) |
| Ag(2)−S(2)−Ag(3)#1 | 135.81(6) | O(1)−P(5)−O(2) | 109.4(3) |
| O(1)−P(5)−O(3) | 114.2(4) | O(2)−P(5)−O(3) | 105.4(5) |
| O(1)−P(5)−C(4) | 116.7(3) | O(2)−P(5)−C(4) | 109.9(3) |
| O(3)−P(5)−C(4) | 100.3(4) | P(5)−O(1)−Ag(2) | 124.6(3) |
| N(1)−C(5)−C(4) | 178.1(11) | | |

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x, y, -z + \frac{1}{2}$; #2, $-x + 1, -y, -z + 1$.

$(CN)_2]^{2-}$),[4c] has a much distorted $Ag_4$ planar-like geometry. Each silver atom is tetrahedrally coordinated by two sulfur atoms and two phosphorus atoms. Two kinds of bridging ligands surround the $Ag_4$ unit: two 1,1-dithiolate ligands exhibiting a “tetrametallic tetraconnective” ($\mu_2$,$\mu_2$) coordination pattern are bonded from both sides of the $Ag_4$ plane and are perpendicular to each other, while the four dppm ligands bridge the edges having two-up and two-down conformation. The geometry of $Ag_4$ is so distorted that the torsion angle of Ag1−Ag2−Ag3−Ag4 is 15.2(1)° and the Ag−Ag bond lengths range from 3.186 to 3.595 Å. The averaged sulfur−sulfur bite distance of 1,1-dithiolates is 3.074(2) Å.

A close example having a similar coordination mode as revealed in **1** is $[Cu_{10}(HBu^t\text{-DED})_6(Bu^t\text{-DED})_2]$,[12] where DED = $[S_2C{=}C(COOR)_2]^{2-}$, which has two $Cu_4S_8$ tetrahedra linked by two trigonal $CuS_2O$ units. The oxygen atom in the carbonyl group of $Bu^t\text{-DED}^{2-}$ provides the third coordination site for the bridging copper(I) atom. Hence the ($Bu^t$-DED) ligand dispalys a $\eta^3$($\mu_2$-S-$\mu_2$-S′−O) coordination pattern. This intriguing decanuclear copper cluster containing six dithio acid monoanions, $(HBu^t\text{-DED})^-$, and two 1,1-ethylenedithiolate dianions, $(Bu^t\text{-DED})^{2-}$, is formed upon the addition of 4 equiv of acid to a $CH_3CN$ solution of $K_4Cu_8(Bu^t\text{-DED})_6$.

The potential donating ability of the oxygen atom in the phosphinyl group of the 1,1-dithiolate ligand apparently induces the cluster rearrangement which may account for the difference in obtained cluster nuclearities. It will be of great interest to utilize all possible coordination sites of 1-(diethoxyphosphinyl)-1-cyanoethylene-2,2-dithiolates to other metals.

## Experimental Section

**Apparatus.** All infrared spectra were recorded on a Bio-Rad spectrometer at 25 °C using KBr plates. NMR spectra were recorded on a Bruker AC-F200 Fourier transform spectrometer. The $^{31}P\{^1H\}$ NMR are referenced externally against 85% $H_3PO_4$. Elemental analyses were performed by Taipei Instrumental Center.

**Reagents.** Bis(diphenylphosphino)methane, $Ag_2O$, $HPF_6$, and $CS_2$ were purchased from Aldrich. $K_2S_2CC(CN)(P(O)(OEt)_2)$[13] was prepared according to the literature reports. All reactions were performed in oven-dried Schlenk glassware by using standard inert-atmosphere techniques. Commercial $CH_2Cl_2$ was distilled from $P_4O_{10}$ before use. Ether and hexanes were distilled from Na/K.

**Reaction of $[Ag_2(\mu\text{-dppm})_2(CH_3CN)_2](PF_6)_2$ and $K_2S_2CC(CN)P(O)(OEt)_2$.** Dichloromethane (50 mL) was added to $Ag_2(dppm)_2(CH_3CN)_2(PF_6)_2$ (500 mg, 5 mmol) and $K_2S_2CC(CN)P(O)(OEt)_2$ (146 mg, 6 mmol) in a Schlenk bottle (100 mL) and stirred for 48 h at ambient temperature. The solution underwent color changes from pale yellow to orange during the reaction. It was then evaporated to dryness to give an orange residue. The residue was redissolved in $CH_3OH$ (30 mL), from which orange-yellow material of **1** was precipitated out in a few minitues (164 mg, 40% yield). Diffusion of hexanes to the yellow methanol filtrate afforded yellow crystalline material of **2** in 20% yield (82 mg).

**1:** $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 18 [s; 2P, $P$(O)], −1 [b; 8P]; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 1.36 [t; 12H, $CH_2CH_3$], 3.42 [b; 8H], 4.14 [m; 8H, $CH_2CH_3$]; 6.9−7.2 (m, 80H); FAB MS, *m/z* 2194.7 ($M^+$ − dppm), 1810.9 ($M^+$ − 2dppm); IR (KBr, $cm^{-1}$) $\nu$(CN), 2181. Anal. Calcd for $C_{114}H_{108}$-

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**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **2**·$Et_2O$

| | | | |
|---|---|---|---|
| Ag(1)−P(1) | 2.538(2) | Ag(1)−P(2) | 2.543(2) |
| Ag(1)−S(1) | 2.582(2) | Ag(1)−S(4) | 2.592(2) |
| Ag(1)−Ag(2) | 3.3016(10) | Ag(2)−P(3) | 2.526(2) |
| Ag(2)−P(4) | 2.558(2) | Ag(2)−S(2) | 2.566(2) |
| Ag(2)−S(1) | 2.594(2) | Ag(2)−Ag(3) | 3.1857(9) |
| Ag(3)−P(6) | 2.524(2) | Ag(3)−P(5) | 2.547(2) |
| Ag(3)−S(3) | 2.603(2) | Ag(3)−S(2) | 2.649(2) |
| Ag(4)−P(7) | 2.515(2) | Ag(4)−P(8) | 2.522(2) |
| Ag(4)−S(4) | 2.564(2) | Ag(4)−S(3) | 2.625(2) |
| S(1)−C(5) | 1.738(8) | S(2)−C(8) | 1.739(8) |
| S(3)−C(5) | 1.738(8) | S(4)−C(8) | 1.746(8) |
| P(9)−O(1) | 1.470(8) | P(9)−O(2) | 1.577(10) |
| P(9)−O(3) | 1.599(9) | P(9)−C(6) | 1.775(9) |
| P(10)−O(4) | 1.460(6) | P(10)−O(5) | 1.585(7) |
| P(10)−O(6) | 1.588(6) | P(10)−C(9) | 1.774(9) |
| O(2)−C(11) | 1.455(15) | O(3)−C(13) | 1.4499(10) |
| O(5)−C(15) | 1.459(13) | O(6)−C(17) | 1.480(12) |
| N(1)−C(7) | 1.143(12) | N(2)−C(10) | 1.152(11) |
| C(5)−C(6) | 1.384(11) | C(6)−C(7) | 1.442(13) |
| C(8)−C(9) | 1.399(10) | C(9)−C(10) | 1.421(11) |
| C(11)−C(12A) | 1.51(3) | C(13)−C(14) | 1.5499(10) |
| C(15)−C(16) | 1.541(18) | C(17)−C(18) | 1.483(17) |

| | | | |
|---|---|---|---|
| P(1)−Ag(1)−P(2) | 111.70(8) | P(1)−Ag(1)−S(1) | 105.58(7) |
| P(2)−Ag(1)−S(1) | 115.45(7) | P(1)−Ag(1)−S(4) | 107.35(7) |
| P(2)−Ag(1)−S(4) | 99.37(7) | S(1)−Ag(1)−S(4) | 117.28(7) |
| P(1)−Ag(1)−Ag(2) | 153.33(6) | P(2)−Ag(1)−Ag(2) | 91.76(6) |
| S(1)−Ag(1)−Ag(2) | 50.53(5) | S(4)−Ag(1)−Ag(2) | 79.82(5) |
| P(3)−Ag(2)−P(4) | 104.82(7) | P(3)−Ag(2)−S(2) | 105.00(7) |
| P(4)−Ag(2)−S(2) | 113.19(7) | P(3)−Ag(2)−S(1) | 110.36(8) |
| P(4)−Ag(2)−S(1) | 97.31(7) | S(2)−Ag(2)−S(1) | 124.67(7) |
| P(3)−Ag(2)−Ag(3) | 158.50(6) | P(4)−Ag(2)−Ag(3) | 87.17(5) |
| S(2)−Ag(2)−Ag(3) | 53.53(5) | S(1)−Ag(2)−Ag(3) | 85.13(5) |
| P(3)−Ag(2)−Ag(1) | 83.65(6) | P(4)−Ag(2)−Ag(1) | 146.58(6) |
| S(2)−Ag(2)−Ag(1) | 94.94(5) | S(1)−Ag(2)−Ag(1) | 50.20(5) |
| Ag(3)−Ag(2)−Ag(1) | 96.19(2) | P(6)−Ag(3)−P(5) | 108.56(8) |
| P(6)−Ag(3)−S(3) | 106.08(7) | P(5)−Ag(3)−S(3) | 103.82(8) |
| P(6)−Ag(3)−S(2) | 100.22(7) | P(5)−Ag(3)−S(2) | 120.05(7) |
| S(3)−Ag(3)−S(2) | 117.12(7) | P(6)−Ag(3)−Ag(2) | 151.39(6) |
| P(5)−Ag(3)−Ag(2) | 89.16(5) | S(3)−Ag(3)−Ag(2) | 90.53(5) |
| S(2)−Ag(3)−Ag(2) | 51.17(5) | P(7)−Ag(4)−P(8) | 116.95(8) |
| P(7)−Ag(4)−S(4) | 105.73(7) | P(8)−Ag(4)−S(4) | 109.34(7) |
| P(7)−Ag(4)−S(3) | 115.06(7) | P(8)−Ag(4)−S(3) | 94.86(8) |
| S(4)−Ag(4)−S(3) | 114.98(7) | Ag(1)−S(1)−Ag(2) | 79.27(6) |
| Ag(2)−S(2)−Ag(3) | 75.30(6) | Ag(3)−S(3)−Ag(4) | 82.62(7) |
| Ag(4)−S(4)−Ag(1) | 88.42(7) | O(1)−P(9)−O(2) | 114.3(5) |
| O(1)−P(9)−O(3) | 107.8(6) | O(2)−P(9)−O(3) | 105.7(6) |
| O(1)−P(9)−C(6) | 114.4(5) | O(2)−P(9)−C(6) | 110.1(5) |
| O(3)−P(9)−C(6) | 103.6(4) | O(4)−P(10)−O(5) | 112.7(4) |
| O(4)−P(10)−O(6) | 114.4(4) | O(5)−P(10)−O(6) | 102.4(4) |
| O(4)−P(10)−C(9) | 116.9(4) | O(5)−P(10)−C(9) | 109.3(4) |
| O(6)−P(10)−C(9) | 99.5(4) | C(11)−O(2)−P(9) | 124.7(9) |
| C(13)−O(3)−P(9) | 121.6(15) | C(15)−O(5)−P(10) | 122.7(7) |
| C(17)−O(6)−P(10) | 118.9(7) | P(8)−C(1)−P(1) | 114.6(4) |
| P(2)−C(2)−P(3) | 113.7(4) | P(5)−C(3)−P(4) | 110.1(4) |
| P(7)−C(4)−P(6) | 113.0(4) | C(6)−C(5)−S(1) | 117.3(6) |
| C(6)−C(5)−S(3) | 118.7(6) | S(1)−C(5)−S(3) | 123.9(5) |
| C(5)−C(6)−C(7) | 119.9(8) | C(5)−C(6)−P(9) | 123.4(6) |
| C(7)−C(6)−P(9) | 115.8(6) | N(1)−C(7)−C(6) | 176.9(14) |
| C(9)−C(8)−S(2) | 118.6(6) | C(9)−C(8)−S(4) | 117.3(6) |
| S(2)−C(8)−S(4) | 124.1(4) | C(8)−C(9)−C(10) | 119.5(8) |
| C(8)−C(9)−P(10) | 122.7(6) | C(10)−C(9)−P(10) | 117.7(6) |
| N(2)−C(10)−C(9) | 178.1(10) | O(2)−C(11)−C(12A) | 107.2(16) |
| O(3)−C(13)−C(14) | 92.2(17) | O(5)−C(15)−C(16) | 108.1(10) |
| O(6)−C(17)−C(18) | 108.5(10) | | |

$Ag_5F_6O_6N_2P_{11}S_4 \cdot 2CH_2Cl_2$: C, 48.14; H, 3.90; N, 0.97; S, 4.43. Found: C, 48.62; H, 4.15; N, 1.03; S, 4.56. Mp: 191 °C.

**2:** $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 16 [s; 2P, *P*(O)], −1 [b; 8P]; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 1.36 [t; 12H, $CH_2CH_3$], 3.1 [b; 8H], 4.14 [m; 8H, $CH_2CH_3$]; 6.9−7.2 (m, 80H); IR (KBr, $cm^{-1}$) $\nu$(CN), 2172. Anal. Calcd for $C_{114}H_{108}Ag_4O_6N_2P_{10}S_4$: C, 55.4; H, 4.40; N, 1.13; S, 5.18. Found: C, 55.23; H, 4.92; N, 1.26; S, 5.51. Mp: 194 °C.

**X-ray Structure Determination.** Crystals were mounted on the tip of glass fibers with epoxy resin. Data were collected at 298 K on a Siemens SMART CCD (charged coupled device) diffractometer. For both crystals, data were measured with $\omega$ scans of 0.3° per frame for 90 s. A total of 1271 frames were collected with a maximum resolution of 0.84 Å. Cell parameters were retrieved with SMART software[14] and refined with SAINT software[15] on all observed reflections ($I > 10\sigma(I)$). Data reduction was performed with SAINT, which corrects for Lorentz and polarization. An empirical absorption correction was applied. The structure was solved by the use of direct methods, and refinement was performed by the least-squares methods on $F^2$ with the SHELXL-97 package,[16] incorporated in SHELXTL/PC V5.10.[17] Pertinent crystallographic data for both compounds are listed in Table 1 and selected bond lengths and angles in Tables 2 and 3.

**(a) 1·2CH$_2$Cl$_2$.** Crystals suitable for X-ray diffraction were grown from $CH_2Cl_2$ layered with hexanes. A yellow crystal (0.36 × 0.38 × 0.46 mm) was mounted in the manner described above, and data were collected. A total of 17123 reflections were collected, of which 9744 were unique ($R_{int} = 0.0265$) and 9016 were observed with $I > 2\sigma(I)$. Five carbon atoms on one of the phenyl rings, all terminal carbon atoms on the ethyl groups, and chlorine atoms of the solvent molecule were found disordered. They were refined isotropically, and hydrogen atoms attached to these disordered atoms were not included in the calculation. F atoms on the $PF_6^-$ anion were located from difference Fourier syntheses and were riding on the P atom during the refinements, and so were Cl atoms on the $CH_2Cl_2$ solvent molecules. The final cycle of the full-matrix least-squares refinement was based on 9016 observed reflections and 641 parameters, and converged with unweighted and weighted agreement factors of R1 = 0.0545 and wR2 = 0.1523, respectively. The largest residual peak and hole are 1.552 e/Å$^3$ and −0.925 e/Å$^3$, respectively.

**(b) 2·Et$_2$O.** Crystals suitable for X-ray diffraction were grown from $CH_2Cl_2$ layered with diethyl ether. A pale yellow crystal (0.12 × 0.28 × 0.28 mm) was mounted in the manner described above, and data were collected. A total of 32015 reflections were collected, of which 17568 were unique ($R_{int} = 0.0487$) and 12975 were observed with $I > 2\sigma(I)$. Three carbon atoms were found disordered: C12, C13, and C14. Whereas two positions having a 0.5 site occupancy factor were treated for C12, a model with fixed C−C (1.550 Å) and O−C (1.450 Å) distances was introduced for O3, C13, and C14. One carbon atom of the solvated diethyl ether molecule cannot be located from the difference Fourier map. Hydrogen atoms were not included. All but disordered C atom and solvent molecule were refined anisotropically. The final cycle of the full-matrix least-squares refinement was based on 12975 observed reflections, 2 restraints, and 1266 parameters, and converged with unweighted and weighted agreement factors of R1 = 0.0708 and wR2 = 0.1497, respectively. The largest residual peak and hole are 0.640 e/Å$^3$ and −0.666 e/Å$^3$, respectively.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) SMART V4.043: *Software for the CCD Detector System*; Bruker Analytical X-ray System: Madison, WI, 1995.

(15) SAINT V4.035: *Software for the CCD Detector System*; Bruker Analytical X-ray System: Madison, WI, 1995.

(16) SHELXL-97: Sheldrick, G. M. *Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997.

(17) SHELXTL 5.10 (PC version): *Program Library for Structure Solution and Molecular Graphics*; Bruker Analytical X-ray Systems: Madison, WI, 1998.