Crystal and Molecular Structure of $[\{Ag[S_2P(OEt)_2]\cdot PPh_3\}_2]$ *

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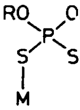
The reaction of $[Ag\{S_2P(OEt)_2\}]$ with triphenylphosphine yields $[\{Ag[S_2P(OEt)_2]\cdot PPh_3\}_2]$ (**1**). The crystal structure of compound (**1**) has been determined. The crystals are monoclinic, space group $P2_1/c$, $a = 14.965(13)$, $b = 9.753(8)$, $c = 18.438(12)$ Å, $\beta = 119.0(1)°$, and $Z = 2$. 2 401 Independent reflections above background were measured on a diffractometer and the structure was refined to $R = 0.056$. The structure contains the centrosymmetric species $[\{Ag[S_2P(OEt)_2]\cdot PPh_3\}_2]$, in which the two dithiophosphate ligands bridge the two metal centres in a unique fashion. The bonding mode of the two sulphur atoms of the dithiophosphate ligand is very different; while S(1) bridges two silver atoms [2.502(2) and 2.821(2) Å], S(2) is only bonded to one [2.810(2) Å]. The silver atoms are also bonded to triphenylphosphine [Ag–P 2.404(2) Å] to complete a distorted four-co-ordinate geometry.

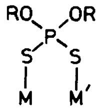
Dialkyl dithiophosphates exhibit a remarkable variety of forms of co-ordination (**A**)—(**E**) to a metal atom and types (**A**)—(**D**) have all been observed in transition-metal complexes. Such complexes are categorised in ref. 1. Within some categories there are additional variations between dimeric, oligomeric, or polymeric structures. The mode of bonding adopted depends upon the nature of the metal and the alkyl group of the ligand. The influence of the alkyl groups is illustrated by the zinc compounds $[Zn\{S_2P(OR)_2\}_2]$ (R = Et or Pr^i), both of structural type (**B**), where with R = Et a polymeric structure is formed[2] while a dimeric species is observed[3] when R = Pr^i. The effect of the metal atom is seen with $[M\{S_2P(OPr^i)_2\}]$ (M = Au or Cu). The gold compound consists of dimeric $[\{Au[S_2P(OPr^i)_2]\}_2]$ units [type (**B**)] which are linked *via* gold–gold bonds to give infinite chains.[4] In contrast the copper compound consists of tetrameric $[\{Cu[S_2P(OPr^i)_2]\}_4]$ molecules in which the ligand is tridentate, one sulphur atom bridging an edge of a Cu_4 tetrahedron while the other bonds to a third copper atom[5] [type (**D**)].

As part of our studies of oil additives we have been investigating the interaction of metal dialkyl dithiophosphates with bases.[6,7] We now report the preparation and structure of $[\{Ag[S_2P(OEt)_2]\cdot PPh_3\}_2]$ (**1**) in which the $[S_2P(OEt)_2]^-$ ligand is tridentate, acting in both a bridging and chelating manner [type (**E**)].

Experimental

$[Ag\{S_2P(OEt)_2\}]$.—A solution of $[NH_4][S_2P(OEt)_2]$ (0.01 mol in 10 cm^3 of water) was added to a solution of $AgNO_3$ (0.01 mol in 10 cm^3 of water). A white precipitate of $[Ag\{S_2P(OEt)_2\}]$ formed immediately. The product was isolated, air-dried, and recrystallised from acetone–toluene (3:1 v/v). Yield 60% (Found: C, 16.3; H, 3.3. $C_4H_{10}AgO_2PS_2$ requires C, 16.4; H, 3.4%). ^{31}P N.m.r. ($CDCl_3$, reference H_3PO_4): 109.74 p.p.m.


(**A**)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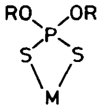
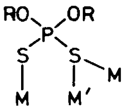
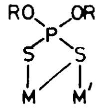

(**C**)


(**D**)


(**E**)

$[\{Ag[S_2P(OEt)_2]\cdot PPh_3\}_2]$.—To a solution of $[Ag\{S_2P(OEt)_2\}]$ (3.4 mmol in 5 cm^3 CH_2Cl_2) was added PPh_3 (3.4 mmol in 10 cm^3 EtOH). Over a period of 3 d at room temperature, white crystals formed. Yield 90% (Found: C, 49.1; H, 4.5. $C_{22}H_{25}AgO_2P_2S_2$ requires C, 47.6; H, 4.5%).

Crystal Structure Determination for Compound (**1**).—*Crystal data.* $C_{44}H_{50}Ag_2O_4P_4S_4$, $M = 1\,110.8$, monoclinic, space group $P2_1/c$, $a = 14.965(13)$, $b = 9.753(8)$, $c = 18.438(12)$ Å, $\beta = 119.0(1)°$, $U = 2\,353.77$ Å^3, $D_m = 1.57$ g cm^{-3} (flotation), $Z = 2$, $D_c = 1.56$ g cm^{-3}, $F(000) = 1\,128$, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 10.8$ cm^{-1}.

Data were collected on a Stoe STADI-2 diffractometer as described previously. A crystal of approximate size 0.4 × 0.5 × 0.4 mm was set to rotate about the *a* axis. 3 145 Independent reflections with $2\theta < 45°$ were measured of which 2 401 with $I > 3\sigma(I)$ were used in subsequent calculations. The structure was determined by heavy-atom methods, no absorption correction being applied. All atoms except hydrogen were refined anisotropically. Hydrogen atoms were placed in trigonal or tetrahedral positions. Their thermal parameters were refined, although those of atoms bonded to the same carbon atom were constrained to be the same. The weighting scheme used was $w = 1/[\sigma(F) + 0.0098F^2]$ where $\sigma(F)$ was taken from counting statistics. Calculations were carried out using SHELX 76[8] and some of our own programs on the Amdahl V7 at this University. The final R value was 0.056 ($R' = 0.057$). Atomic co-ordinates are given in Table 1 and selected dimensions in the molecule in Table 2.

Results and Discussion

There have been a number of structural determinations of gold(I) and copper-(I) and -(II) dialkyl dithiophosphate compounds but none for silver has been reported. All attempts we made to obtain crystals of $[Ag\{S_2P(OR)_2\}]$ (R = Et or Pr^i)

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* Bis(μ-diethyl dithiophosphato-*S*,μ-*S'*)-bis[(triphenylphosphine)-silver(I)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates (× 10^4) of compound (**1**) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Ag	8 777.3(4)	4 592.6(5)	4 784.8(3)	C(25)	5 130(6)	4 029(10)	2 559(5)
P(1)	7 280(1)	4 669(2)	4 950(1)	C(26)	5 981(6)	4 456(8)	3 269(4)
S(1)	9 953(1)	7 016(2)	5 269(1)	C(31)	7 296(4)	3 781(7)	5 828(3)
S(2)	8 385(1)	5 942(2)	3 313(1)	C(32)	7 947(5)	2 682(7)	6 185(4)
P(2)	9 041(1)	7 472(2)	4 075(1)	C(33)	7 976(7)	2 014(7)	6 860(5)
C(11)	6 930(4)	6 407(7)	5 078(3)	C(34)	7 375(6)	2 425(8)	7 183(4)
C(12)	7 643(6)	7 156(8)	5 735(4)	C(35)	6 732(6)	3 529(9)	6 830(4)
C(13)	7 397(6)	8 439(9)	5 899(5)	C(36)	6 700(5)	4 206(8)	6 162(4)
C(14)	6 466(7)	9 007(9)	5 412(5)	O(1)	8 160(3)	8 465(4)	3 991(3)
C(15)	5 761(6)	8 286(8)	4 737(5)	C(101)	8 429(7)	9 717(8)	4 493(6)
C(16)	5 984(5)	6 995(7)	4 570(4)	C(102)	7 529(6)	10 632(8)	4 141(5)
C(21)	6 145(4)	4 031(6)	4 035(4)	O(2)	9 718(3)	8 396(5)	3 815(3)
C(22)	5 446(5)	3 145(7)	4 075(4)	C(201)	9 293(7)	8 850(11)	2 962(5)
C(23)	4 587(5)	2 725(8)	3 343(5)	C(202)	9 761(8)	10 129(10)	2 938(6)
C(24)	4 436(6)	3 167(8)	2 597(5)				

Table 2. Dimensions involving heavy atoms, distances in Å, angles in °

P(1)–Ag	2.404(2)	S(1^i)–Ag	2.502(2)
S(1)–Ag	2.821(2)	P(2)–S(1)	2.000(2)
S(2)–Ag	2.810(2)	P(2)–S(2)	1.957(2)
Ag–Ag^i	3.441(1)		
S(1)–Ag–P(1)	114.25(6)	S(1^i)–Ag–S(2)	93.57(6)
S(2)–Ag–P(1)	109.66(6)	S(1^i)–Ag–Ag^i	53.91(4)
Ag^i–Ag–P(1)	156.36(4)	P(2)–S(1)–Ag	81.36(6)
S(1^i)–Ag–P(1)	142.79(6)	Ag–S(1)–Ag^i	80.29(5)
S(2)–Ag–S(1)	73.73(5)	Ag^i–S(1)–P(2)	102.82(9)
Ag^i–Ag–S(1)	45.80(4)	P(2)–S(2)–Ag	82.34(8)
S(1^i)–Ag–S(1)	99.71(6)	S(2)–P(2)–S(1)	117.25(10)
Ag^i–Ag–S(2)	79.37(4)		

failed. However the reaction between [Ag{$S_2P(OEt)_2$}] and PPh_3 gave a crystalline product from which suitable crystals for *X*-ray analysis were obtained, and we now report the structure of [{Ag[$S_2P(OEt)_2$]·PPh_3}$_2$] (**1**).

Compound (**1**) forms a centrosymmetric species (see Figure for the atomic numbering scheme) in which two [$S_2P(OEt)_2$]$^-$ ligands bridge two silver atoms. The bonding of the dithiophosphate sulphur atoms is very different; S(1) is bonded to both silver atoms [Ag^i–S(1) 2.502(2), Ag–S(1) 2.821(2) Å; symmetry element i $-x$, $1-y$, $1-z$] to form a planar $\overline{\text{Ag–S(1)–Ag}^{i}\text{–S(1}^{i})}$ four-membered ring, whilst S(2) is bonded to only one metal [Ag–S(2) 2.810(2) Å]. Thus the ligand is tridentate, acting as a bidentate ligand in both bridging and chelating modes. This type of bonding is unique for the dialkyl dithiophosphate ligand although it has been observed in the dialkyldithiophosphinate compound [{Re(CO)$_4$(S_2PEt_2)}$_2$].[9]

The silver atom is four-co-ordinate, being bonded to three sulphur atoms (see above) and a phosphorus atom of a PPh_3 molecule [Ag–P(1) 2.404(2) Å]. The co-ordination sphere of the silver atom is highly irregular with wide variation in angles as well as bond lengths. There are only two bonds of single length, *viz.* Ag–S(1^i) 2.502(2) and Ag–P(1) 2.404(2) Å. The latter bond can be compared with a range of distances (2.363—2.529 Å) for other Ag–PPh_3 complexes found in the Cambridge Data Centre files.

While the present structure is unique, it does contain an $\overline{\text{Ag–S(2)–P(2)–S(1)–Ag}^{i}\text{–S(2}^{i})\text{–P(2}^{i})\text{–S(1}^{i})}$ chair-shaped ring and similar eight-membered rings have been observed in a number of dimeric dialkyl dithiophosphate[3,7] and dialkyldithiophosphinate complexes.[10,11] However there is no bond across the ring in the complexes with zinc[3,10,11] (Zn ··· S distances >3.35 Å) or with copper[7] (Cu ··· S distances >3.69 Å) as is found in (**1**), where Ag–S(1) is 2.821(2) Å, and this bond has a profound effect on the geometry of the present compound as shown when the dihedral angles of the ring are compared with the equivalent angles[7] in [{Cu[$S_2P(OEt)_2$]·bipy}$_2$] (bipy = 2,2′-bipyridyl).

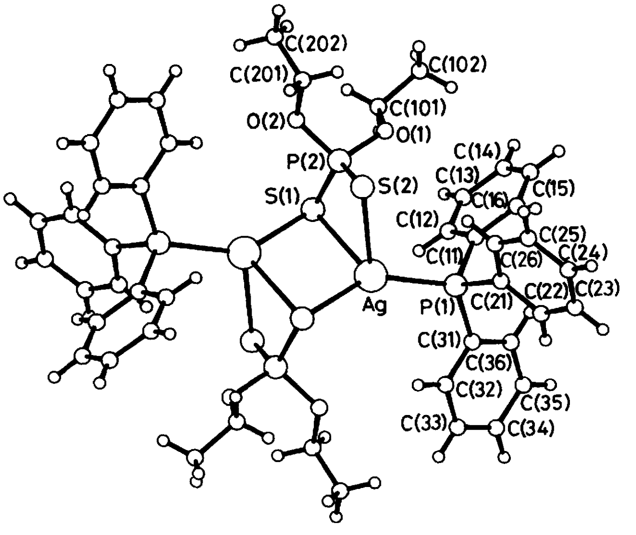

Figure. The structure of [{Ag[$S_2P(OEt)_2$]·PPh_3}$_2$]

It is interesting that whilst [Ag{$S_2P(OEt)_2$}] forms a 1:1 complex with PPh_3, copper(I) forms a 1:2 species in which the [$S_2P(OEt)_2$]$^-$ ligand is chelating[7] and the copper atom has a four-co-ordinate distorted tetrahedral environment [Cu–P 2.282(2) and 2.265(1), Cu–S 2.453(2) and 2.440(2) Å]. We attribute the difference in stoicheiometry to the combined steric requirements of the [$S_2P(OEt)_2$]$^-$ and PPh_3 ligands, and the relative size and geometric requirements of the copper and silver atoms.

The effect of the bulkiness of the [$S_2P(OEt)_2$]$^-$ ligand upon metal geometry is shown by a series of four-co-ordinate tetrahedral copper(I) complexes. The P–Cu–P angle in [Cu{$S_2P(OEt)_2$}]·2PPh_3 is only 115.1(1)° compared with[12] 127.1(1)° in [Cu(S_2COEt)]·2PPh_3 and 126.6(1)° in [Cu(S_2CNHPh)]·2PPh_3. The influence of PPh_3 on complex geometry is demonstrated in our previous paper,[7] where we showed that although copper(I) forms dimeric [{Cu[S_2P(OEt)$_2$]·bipy}$_2$], in which two four-co-ordinate tetrahedral copper centres are bridged by two S–P–S moieties, the steric requirements of the bulky PPh_3 groups and the preferred four-co-ordinate tetrahedral geometry of copper(I) preclude such dimerisation in $[Cu\{S_2P(OEt)_2\}]\cdot 2PPh_3$.

Clearly a similar tetrahedral 1:2 complex to that with copper would be sterically viable with the larger silver atom. However, its size and geometric requirements, and its tendency towards linear co-ordination, lead instead to the present structure with bridging $[S_2P(OEt)_2]^-$ ligands, two long and one normal Ag–S bond and thus only one PPh_3 group.

The angle subtended at silver by the two normally bonded donor atoms, the S(1ⁱ)–Ag–P(1) angle, is 142.8(1)° and so the observed ring structure could be visualised as arising *via* the dimerisation of monomeric, linear $Ag\{S_2P(OEt)_2\}\cdot PPh_3$ units through the formation of two long silver–sulphur bonds. Gold(I) has a greater propensity to linear co-ordination than silver(I), and a related monomeric unit has been observed in $[Au(S_2CNEt_2)]\cdot PPh_3$[13] [Au–S 2.338(3), Au–P 2.251(3) Å, S–Au–P 175.7(1)°], though even in that ostensibly linear two-dimensional structure there is an additional weak Au···S interaction of 3.01 Å. In compound (**1**) the Ag,S(1),S(2) plane is almost perpendicular to the Ag,S(1ⁱ),P(1) plane, with an angle of intersection of 86.9°, but the chelate ring is non-planar, with Ag 1.03 Å from the S_2P plane, and the P–S bond lengths differ significantly [0.043(3) Å]. Such distortions can be correlated to the difference in bonding pattern of the two sulphur atoms.[6]

Acknowledgements

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