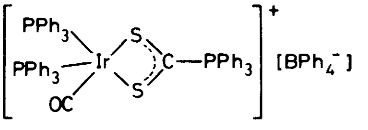
# Unprecedented Bridging Mode of the Triethylphosphine–Carbon Disulphide Adduct $PEt_3{\cdot}CS_2$. *X*-Ray Crystal Structure of the Binuclear Silver(I) Complex $[\{Ag(S_2CPEt_3)(\mu\text{-}S_2CPEt_3)\}_2][ClO_4]_2$ *

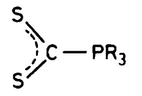
**Claudio Bianchini, Carlo A. Ghilardi, Andrea Meli, Annabella Orlandini, and Giancarlo Scapacci**
*Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, C.N.R., Via D. Guerrazzi, 27, Florence, Italy*

The binuclear complex $[\{Ag(S_2CPEt_3)_2\}_2][ClO_4]_2$ has been synthesized by reaction of the zwitterion $PEt_3{\cdot}CS_2$ with $AgClO_4{\cdot}H_2O$. The crystal and molecular structure of this silver(I) complex has been determined by standard *X*-ray methods. The compound is triclinic, space group $P\bar{1}$, with unit-cell parameters $a = 13.378(8)$, $b = 13.562(8)$, $c = 7.617(5)$ Å, $\alpha = 80.38(4)$, $\beta = 85.60(4)$, $\gamma = 67.44(4)°$, and $Z = 1$. Full-matrix least-squares refinement using 3 492 reflections having $I \geqslant 3\sigma(I)$ yielded a conventional $R$ factor of 0.058. The structure consists of centrosymmetric binuclear complexes, where the two metal centres are held together by two triethylphosphine–carbon disulphide adducts. Each silver atom displays a very distorted tetrahedral geometry, the S–Ag–S bond angles ranging from 65.5(1) to 136.5(1)° and the Ag–S bond distances ranging from 2.468(2) to 2.812(2) Å.

Since the synthesis of the first phosphoniodithiocarboxylate complex $[Ir(S_2CPPh_3)(CO)(PPh_3)_2][BPh_4]$ (1),[1] the chemical and physical properties of these compounds have been investigated extensively. Several metal complexes containing tertiary phosphine–carbon disulphide adducts (2) as ligands have been prepared and fully characterized.[2-7] Two routes are available to $PR_3{\cdot}CS_2$ metal complexes: (*i*) the reaction of CS with metal—phosphine complexes, and (*ii*) the addition of preformed $PR_3{\cdot}CS_2$ zwitterions to metal complexes.



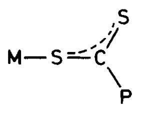
(1)

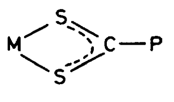


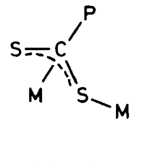
(2)

(R = Me, Et, $C_6H_{11}$ or Ph)

Among the $PR_3{\cdot}CS_2$ ligands available, that bearing ethyl substituents on the phosphorus atom, namely $PEt_3{\cdot}CS_2$, revealed itself to be the most suitable for testing the various hypotheses regarding structural and electronic properties of the complexes. Indeed, this zwitterion can act either as a uni- or bi-dentate σ donor by means of its electron-rich sulphur atoms,[2-7] or as a π donor through the conjugated $CS_2$ pseudo-allylic system [3] shown below.







A further bonding mode of the $PEt_3{\cdot}CS_2$ ligand has been recently found in the tetrahedral copper(I) complex $[Cu(S_2CPEt_3)(PPh_3)_2][BPh_4]$.[5] The Cu–S distances are so different that the phosphoniodithiocarboxylate ligand can be considered ' unsymmetrically ' chelated to the copper atom.

The most common strategy to synthesize metal complexes with $PEt_3{\cdot}CS_2$ usually exploits the reaction between this ligand and co-ordinatively unsaturated metal complexes. We have now found that the $PEt_3{\cdot}CS_2$ zwitterion exhibits a surprisingly versatile chemistry also toward ' naked ' metal ions.

Herein we report the synthesis and the crystal structure of the binuclear silver(I) complex $[\{Ag(S_2CPEt_3)_2\}_2][ClO_4]_2$ (3). This complex is of particular interest since it contains the $PEt_3{\cdot}CS_2$ ligand displaying an unprecedented bridging mode.

## Experimental

Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer as Nujol mulls between KBr disks. U.v.–visible spectra were measured on a Beckman DK-2A spectrophotometer.

*Preparation of* (3).—$PEt_3{\cdot}CS_2$ [8] (0.39 g, 2 mmol) in acetone (20 cm$^3$) was added under nitrogen to a solution of $AgClO_4{\cdot}H_2O$ (0.21 g, 1 mmol) in acetone (20 cm$^3$). Brick-red crystals were obtained in a short time from the resultant red-orange solution. They were filtered off and washed with 4 : 1 acetone–ethanol and light petroleum (b.p. 40—70 °C) before being dried in a stream of nitrogen, yield 85% (Found: C, 28.05; H, 5.15; Ag, 18.0; S, 21.4. Calc. for $C_{28}H_{60}Ag_2Cl_2O_8P_4S_8$: C, 28.20; H, 5.05; Ag, 18.10; S, 21.5%).

X-*Ray Crystal Structure of Complex* (3).—*Crystal data.* $C_{28}H_{60}Ag_2Cl_2O_8P_4S_8$, $M = 1\,191.83$, $a = 13.378(8)$, $b = 13.562(8)$, $c = 7.617(5)$ Å, $\alpha = 80.38(4)$, $\beta = 85.60(4)$, $\gamma = 67.44(4)°$, $U = 1\,258.1$ Å$^3$, $Z = 1$, $D_c = 1.572$ g cm$^{-3}$, $F(000) = 608$, space group $P\bar{1}$, Mo-$K_\alpha$ radiation (graphite monochromator), $\lambda = 0.710\,7$ Å, and $\mu = 13.60$ cm$^{-1}$.

*Collection and reduction of data.* A brick-red parallelepiped of approximate dimensions $0.07 \times 0.09 \times 0.50$ mm was selected and mounted in a Philips PW 1100 automatic computer-controlled diffractometer. Data were measured using the $\omega$—$2\theta$ scan method with a scan speed of 0.1° s$^{-1}$ and scan width $0.8 + 0.3 \tan\theta$. Three standard reflections were measured in every 120, the maximum deviations being ±1.

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* Bis[μ-(triethylphosphoniodithiocarboxylato-*SS'*)]-(triethylphosphoniodithio-carboxylato-*SS'*)silver] bis(perchlorate).

*Supplementary data available* (No. SUP 23652, 23 pp.): structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

**Table 1.** Positional parameters ($\times 10^4$) for complex (3)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ag | 1 019(1) | 64(1) | −712(1) |
| S(1) | −275(2) | −1 922(2) | −8(3) |
| S(2) | 749(2) | −883(2) | −3 068(3) |
| S(3) | 3 273(2) | −515(2) | −1 054(3) |
| S(4) | 2 148(2) | −1 355(2) | 1 981(3) |
| P(1) | 764(2) | −3 019(2) | −3 130(2) |
| P(2) | 4 476(2) | −1 893(2) | 2 209(3) |
| C(1) | 377(5) | −1 856(5) | −1 973(9) |
| C(2) | 439(7) | −4 087(6) | −1 783(11) |
| C(3) | 762(8) | −5 081(8) | −2 697(14) |
| C(4) | 103(7) | −2 589(7) | −5 260(11) |
| C(5) | −1 084(9) | −2 044(10) | −5 067(16) |
| C(6) | 2 203(8) | −3 454(8) | −3 619(13) |
| C(7) | 2 851(10) | −3 594(10) | −2 010(16) |
| C(8) | 3 241(5) | −1 219(5) | 928(9) |
| C(9) | 5 600(7) | −1 791(7) | 893(12) |
| C(10) | 6 689(8) | −2 318(9) | 1 831(15) |
| C(11) | 4 278(9) | −1 225(9) | 4 141(15) |
| C(12) | 3 944(10) | −63(10) | 3 763(17) |
| C(13) | 4 659(11) | −3 275(10) | 3 074(17) |
| C(14) | 4 659(12) | −3 836(12) | 1 679(20) |
| Cl | 2 902(2) | 4 019(2) | 2 753(4) |
| O(1) * | 3 262(15) | 2 885(15) | 3 153(25) |
| O(2) * | 3 139(21) | 4 331(20) | 941(34) |
| O(3) * | 3 186(17) | 4 450(18) | 4 107(29) |
| O(4) * | 1 800(33) | 4 538(33) | 2 733(54) |
| O(11) † | 4 006(21) | 3 791(19) | 2 320(33) |
| O(22) † | 2 318(22) | 3 890(20) | 1 361(36) |
| O(33) † | 2 541(43) | 3 629(42) | 4 417(69) |
| O(44) † | 2 430(34) | 5 152(33) | 2 732(52) |

* Population 0.55. † Population 0.45.

**Table 2.** Bond distances (Å) and bond angles (°) for complex (3)

(*a*) Cation

| | | | |
|---|---|---|---|
| Ag−Ag′ | 2.914(1) | P(2)−C(8) | 1.819(7) |
| Ag−S(1′) | 2.468(2) | P(2)−C(9) | 1.780(9) |
| Ag−S(2) | 2.495(2) | P(2)−C(11) | 1.805(11) |
| Ag−S(3) | 2.812(2) | P(2)−C(13) | 1.808(12) |
| Ag−S(4) | 2.668(2) | C(2)−C(3) | 1.52(1) |
| S(1)−C(1) | 1.680(6) | C(4)−C(5) | 1.48(1) |
| S(2)−C(1) | 1.661(7) | C(6)−C(7) | 1.50(1) |
| S(3)−C(8) | 1.653(7) | C(9)−C(10) | 1.53(1) |
| S(4)−C(8) | 1.671(7) | C(11)−C(12) | 1.45(1) |
| P(1)−C(1) | 1.817(6) | C(13)−C(14) | 1.41(2) |
| P(1)−C(2) | 1.805(8) | S(1) · · · S(2) | 3.031(4) |
| P(1)−C(4) | 1.807(8) | S(3) · · · S(4) | 2.968(4) |
| P(1)−C(6) | 1.813(9) | | |

| | | | |
|---|---|---|---|
| S(1′)−Ag−S(2) | 136.5(1) | C(1)−P(1)−C(4) | 108.5(3) |
| S(1′)−Ag−S(3) | 106.3(1) | C(1)−P(1)−C(6) | 107.9(4) |
| S(1′)−Ag−S(4) | 111.7(1) | C(2)−P(1)−C(4) | 112.6(3) |
| S(2)−Ag−S(3) | 99.1(1) | C(2)−P(1)−C(6) | 111.2(4) |
| S(2)−Ag−S(4) | 110.8(1) | C(4)−P(1)−C(6) | 106.0(4) |
| S(3)−Ag−S(4) | 65.5(1) | C(8)−P(2)−C(9) | 109.9(4) |
| Ag−S(1′)−C(1′) | 105.8(2) | C(8)−P(2)−C(11) | 106.4(4) |
| Ag−S(2)−C(1) | 104.9(2) | C(8)−P(2)−C(13) | 111.1(5) |
| Ag−S(3)−C(8) | 81.7(2) | C(9)−P(2)−C(11) | 111.3(5) |
| Ag−S(4)−C(8) | 86.0(2) | C(9)−P(2)−C(13) | 112.5(5) |
| S(1)−C(1)−S(2) | 130.3(4) | C(11)−P(2)−C(13) | 105.4(5) |
| S(1)−C(1)−P(1) | 116.9(4) | P(1)−C(2)−C(3) | 112.1(6) |
| S(2)−C(1)−P(1) | 112.8(4) | P(1)−C(4)−C(5) | 111.8(7) |
| S(3)−C(8)−S(4) | 126.5(4) | P(1)−C(6)−C(7) | 112.4(7) |
| S(3)−C(8)−P(2) | 119.6(4) | P(2)−C(9)−C(10) | 115.0(7) |
| S(4)−C(8)−P(2) | 113.8(4) | P(2)−C(11)−C(12) | 115.1(9) |
| C(1)−P(1)−C(2) | 110.4(3) | P(2)−C(13)−C(14) | 110.3(10) |

(*b*) Anion

| | | | |
|---|---|---|---|
| Cl−O(1) | 1.41(2) | Cl−O(11) | 1.41(2) |
| Cl−O(2) | 1.42(2) | Cl−O(22) | 1.43(2) |
| Cl−O(3) | 1.41(2) | Cl−O(33) | 1.41(5) |
| Cl−O(4) | 1.37(4) | Cl−O(44) | 1.42(4) |

| | | | |
|---|---|---|---|
| O(1)−Cl−O(2) | 110(1) | O(11)−Cl−O(22) | 113(2) |
| O(1)−Cl−O(3) | 111(1) | O(11)−Cl−O(33) | 123(2) |
| O(1)−Cl−O(4) | 114(2) | O(11)−Cl−O(44) | 105(2) |
| O(2)−Cl−O(3) | 120(1) | O(22)−Cl−O(33) | 109(2) |
| O(2)−Cl−O(4) | 99(2) | O(22)−Cl−O(44) | 101(2) |
| O(3)−Cl−O(4) | 102(2) | O(33)−Cl−O(44) | 102(2) |

4 421 Reflections were collected in the range $5 \leqslant 2\theta \leqslant 50°$ of which 3 492 with $I \geqslant 3\sigma(I)$ were used in the refinement. A least-squares fit of 20 carefully centred reflections yielded the cell dimensions. The intensities, after correction for background, were assigned a standard deviation $\sigma(I)$, calculated as described elsewhere,[9] by using the value of 0.03 for the instability factor *k*. The raw intensity data were corrected for Lorentz and polarization effects, and an absorption correction giving transmission factors ranging from 0.69 to 0.82 was applied. Atomic scattering factors for non-hydrogen atoms were taken from International Tables [10] and those for hydrogen atoms from Stewart *et al.*[11] Both the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms.[12]

*Solution and refinement of the structure.* All calculations were carried out on a SEL 32/70 computer using the SHELX 76 crystallographic system of programs.[13] The function minimized during refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The structure was solved by assuming $P\bar{1}$ to be the correct space group. A three-dimensional Patterson function yielded the positions of the silver and of one sulphur atom. All the non-hydrogen atoms were located from successive Fourier maps. Cycles with isotropic thermal motion on all the non-hydrogen atoms were followed by cycles where anisotropic thermal vibration was assigned to the silver, sulphur, and phosphorus atoms. Hydrogen atoms were introduced in their calculated positions, but not refined. Some disorder was detected in the region of the perchlorate anion. Such disorder, which is not unusual in groups like $ClO_4^-$, was rationalized by discerning from a difference-Fourier map two different models: indeed eight peaks were located at bond distance from the chlorine atom. While the chlorine atom was assigned a population parameter of 1, the two groups of oxygen atoms were given multiplicities of $\alpha$ and $1 - \alpha$. The parameter $\alpha$, allowed to vary, converged to 0.55. The refinement converged to *R* and *R′* factors of 0.058 and 0.064 respectively. Final positional parameters are given in Table 1.

## Results and Discussion

An acetone solution of $AgClO_4 \cdot H_2O$ reacts with the zwitterion adduct $PEt_3 \cdot CS_2$ producing a red solution, from which brick-red crystals of empirical formula $[Ag(S_2CPEt_3)_2][ClO_4]$ are obtained in good yield.

This complex is reasonably air-stable in the solid state but decomposes rapidly in solution even in an inert atmosphere, and thus has not been studied in solution. The electronic spectrum exhibits absorption maxima at 13 800 (sh) and 22 200 cm$^{-1}$.

Although the $-CS_2$ stretching region is partially masked by vibrations associated both with the perchlorate anion and with the triethylphosphine group, a band at 1 070 cm$^{-1}$ in the i.r. spectrum of (3) can be positively attributed to $\nu_{asym}(CS_2)$. Bands between 1 070 and 970 cm$^{-1}$ assigned to $\nu_{sym}(CS_2)$ have

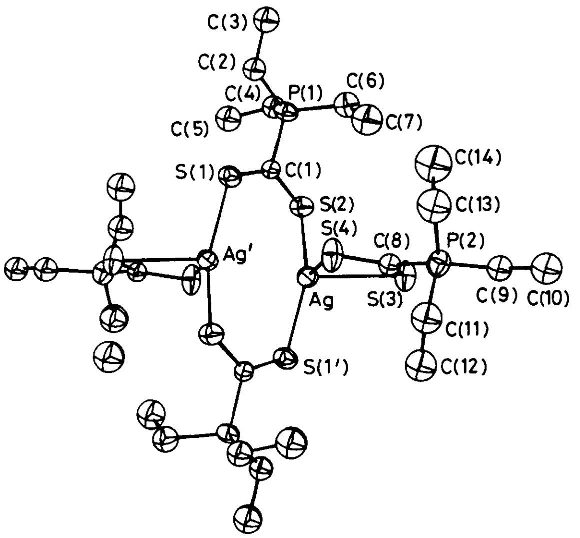

**Figure 1.** Perspective view of the complex cation $[\{Ag(S_2CPEt_3)(\mu\text{-}S_2CPEt_3)\}_2]^{2+}$: ORTEP drawing with 30% probability ellipsoids

been reported for a variety of phosphoniodithiocarboxylate complexes.[2-7] In the i.r. spectra of the free ligands $PMe_3{\cdot}CS_2$, $PEt_3{\cdot}CS_2$, and $P(C_6H_{11})_3{\cdot}CS_2$ the corresponding $-CS_2$ stretching frequencies are observed at 1 042, 1 065, and 1 050 $cm^{-1}$, respectively.[14,15] The i.r. data therefore indicate that the asymmetric $-CS_2$ stretching vibration is poorly affected by the bonding mode of the phosphoniodithiocarboxylate ligands. Only in the case of the $PEt_3{\cdot}CS_2$ adduct π-bonded to the metal is this stretching vibration not observed.[3]

The crystal structure of (3) consists of dimeric complex cations $[Ag_2(S_2CPEt_3)_4]^{2+}$ and perchlorate anions. A perspective view of the complex cation is shown in Figure 1. Selected bond distances and angles are given in Table 2.

In the dimeric complex cation, which possesses $C_i$-$\bar{1}$ crystallographic symmetry, the two metal centres are held together by two bridging zwitterionic ligands, two other zwitterion groups being co-ordinated respectively to the two metal atoms. Thus each silver atom is four-co-ordinated by the two sulphur atoms of the chelating zwitterion and by two sulphur atoms of two different bridging ligands, displaying a very distorted tetrahedral geometry.

The distortion from idealized geometry is evidenced by the S–Ag–S bond angles, whose values range from 65.5(1) to 136.5(1)°. In particular the value for S(3)–Ag–S(4) of 65.5(1)° is surprisingly small even in comparison with the corresponding values reported for other metal zwitterionic complexes, showing a bidentate attachment to the metal, where the S–M–S angle reaches at least the value of 71.5(1)°.[1,2,4,5]

The Ag–S bond distances also appear to be very irregular: while the Ag–S bonds involving the bridging zwitterionic ligands are rather similar [2.468(2) and 2.495(2) Å], the other two linkages are much larger and are not comparable [2.668(2) and 2.812(2) Å]. The different hybridization states of the sulphur atoms appear to be largely responsible for these irregularities. Indeed the values of the C–S–Ag angles for the chelating [81.7(2) and 86.0(2)°] and bridging [104.9(2) and 105.8(2)°] ligands indicate that the orbitals used by the sulphur are of the types *p* pure and $sp^2$ respectively.[16] With regard to the difference between the values of Ag–S involving the non-bridging zwitterion, a similar unsymmetrical arrangement around the metal atom is not unusual: indeed in other monomeric copper(I) complexes, significant differences between the M–S distances are observed, which have been attributed to the tendency of the copper to be three- as well as four-co-ordinated.[5,17] In the present compound support to this hypothesis is given by the planarity of the AgS(2)S(1')S(4) fragment, the value of the displacement (0.14 Å) of the silver atom from the S(2)S(1')S(4) plane being extremely small. The loose bonding of the non-bridging zwitterion is evidenced by the value of the S(3)–C(8)–S(4) angle, 126.5(4)°, which matches that of the free ligand [127(1)°].[18]

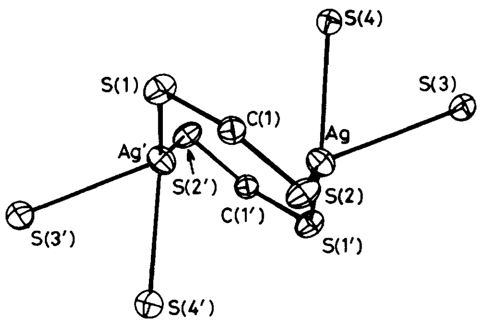

**Figure 2.** ORTEP drawing of the eight-membered ring

It is interesting to note the arrangement of the bridging zwitterions, which with the two silver atoms form an eight-membered ring (Figure 2): in this ring the six atoms belonging to the ligands lie on a plane, their maximum displacement being within 0.05 Å, while the silver atoms are pushed out. The dihedral angle between the plane passing through the two $-CS_2$ fragments and the plane passing through the S(1')–Ag–S(2) group has the value of 68.5°.

Although the nature and extent of metal–metal interaction in $Ag^I$ compounds is still uncertain, the Ag–Ag distance deserves some comment. The value of this distance, 2.914(1) Å, is undoubtedly rather short.[19] This fact together with the rather small values of the C–S–Ag angles [104.9(2), 105.8(2)°] in the bridging zwitterion seems to indicate that a small interaction exists.

Binuclear complexes containing phosphoniodithiocarboxylates as bridging ligands are so far limited to complex (3) and $[\{Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)\}_2]$.[3] In a recent review Werner[6] reported the synthesis of a series of palladium complexes of general formula $[Pd(PR_3)(S_2CPR'_3)]_2$ ($PR_3$ = $PMe_3$ or $PMePh_2$; $PR'_3$ = $PMe_3$, $PMePh_2$, $PPr^i_3$, or $PPh_3$) which are suggested to contain bridging $PR'_3{\cdot}CS_2$ groups. However, the bridging mode of the zwitterion as well as the complexities of the structure of these complexes are so far unresolved.

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