

Bis(triphenylphosphine)(phenyl trithiocarbonato)copper(I) Hemi(carbon disulfide)

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Abstract. $\text{CuP}_2\text{D}_4\text{C}_{43.5}\text{H}_{35}$, $M_r = 811.48$; CS_2 lost at 90–103 °C, m.p. 155–156 °C; monoclinic, $P2_1/c$, $a = 16.081$ (5), $b = 14.106$ (2), $c = 17.565$ (2) Å, $\beta = 93.99$ (2)°, $Z = 4$, $D_x = 1.356$, $D_m = 1.348$ g cm⁻³; $R = 0.059$, $R_w = 0.058$, for 2768 diffractometer reflections with $I \geq 2\sigma(I)$. The compound was originally suggested to have the adduct formulation $\text{Cu}(\text{PPh}_3)_2(\text{SPh}) \cdot \text{CS}_2$, but the X-ray structure solution reveals instead a symmetrically bidentate phenyl trithiocarbonate ligand bonded to pseudotetrahedral Cu. One half mole of lattice CS_2 is also present.

Introduction. Recently Reichle (1971) reported that CS_2 forms 1:1 adducts with $\text{Cu}(\text{PPh}_3)_2(\text{XPh})$ (where

$\text{X} = \text{O}$ and S) which readily release CS_2 on heating. A reversible interaction of CS_2 with the thiophenoxide compound is also found by us, but our X-ray diffraction study shows the product to be the result of CS_2 insertion into a Cu–SPh bond. Thus, CS_2 has been incorporated into a trithiocarbonate ligand rather than binding as a simple adduct ligand, giving a structure very similar to that reported earlier for $\text{Cu}(\text{PPh}_3)_2(\text{S}_2\text{CSEt})$ (Avdeef & Fackler, 1975). The results of our crystallographic investigation of the phenyl derivative are reported here.

Orange crystals are readily formed when $\text{Cu}(\text{PPh}_3)_2(\text{SPh})$ is dissolved in a CS_2 /ethanol mixture and the excess CS_2 is allowed to evaporate. The compound

Table 1. Fractional coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$)

Estimated standard deviations are given in parentheses. The form of the anisotropic thermal parameters is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos \gamma^* + 2U_{13}hla^*c^* \cos \beta^* + 2U_{23}klb^*c^* \cos \alpha^*)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	2245.6 (6)	52.5 (7)	4326.2 (5)	51 (1)	58.0 (8)	41.7 (7)	-1.6 (7)	12.7 (6)	-2.7 (6)
P(1)	2334 (1)	-1218 (1)	5107 (1)	36 (2)	53 (1)	38 (1)	2 (1)	9 (1)	-4 (1)
P(2)	2296 (1)	3395 (1)	9641 (1)	51 (2)	54 (1)	37 (1)	4 (1)	11 (1)	-1 (1)
S(1)	1488 (1)	-111 (1)	3073 (1)	39 (2)	84 (2)	52 (1)	2 (1)	5 (1)	-1 (1)
S(2)	3293 (1)	-292 (1)	3425 (1)	38 (2)	84 (2)	39 (1)	-3 (1)	7 (1)	-7 (1)
S(3)	2527 (1)	-439 (2)	1815 (1)	58 (2)	123 (2)	41 (1)	6 (2)	2 (1)	12 (1)
S(4)	-862 (3)	342 (3)	129 (3)	154 (4)	138 (3)	331 (6)	6 (3)	47 (4)	-21 (4)

	<i>x</i>	<i>y</i>	<i>z</i>	B (Å ²)		<i>x</i>	<i>y</i>	<i>z</i>	B (Å ²)
C(1)	2458 (5)	-290 (5)	2800 (4)	3.6 (2)	C(23)	7335 (5)	950 (6)	1140 (4)	5.3 (2)
C(2)	3605 (5)	-595 (5)	1719 (4)	4.3 (2)	C(24)	7796 (5)	1662 (6)	1477 (4)	5.1 (2)
C(3)	3988 (6)	-1421 (6)	1919 (4)	5.3 (2)	C(25)	7896 (5)	2526 (5)	1102 (4)	4.2 (2)
C(4)	4840 (6)	-1536 (6)	1836 (5)	6.1 (2)	C(26)	3295 (5)	3054 (5)	129 (4)	3.5 (2)
C(5)	5268 (6)	-827 (6)	1539 (4)	6.0 (2)	C(27)	3590 (5)	3589 (5)	747 (4)	4.6 (2)
C(6)	4909 (6)	-9 (6)	1323 (5)	5.9 (2)	C(28)	4365 (6)	3380 (6)	1126 (4)	5.3 (2)
C(7)	4056 (6)	131 (6)	1413 (4)	5.4 (2)	C(29)	4838 (5)	2676 (6)	874 (4)	5.5 (2)
C(8)	6742 (5)	1127 (5)	4242 (4)	3.3 (2)	C(30)	4560 (6)	2141 (6)	265 (5)	6.2 (2)
C(9)	5973 (5)	1028 (5)	4549 (4)	3.9 (2)	C(31)	3780 (5)	2320 (5)	-102 (4)	4.8 (2)
C(10)	5254 (5)	905 (5)	4080 (4)	4.9 (2)	C(32)	1535 (5)	2963 (5)	259 (4)	3.2 (2)
C(11)	5294 (5)	859 (5)	3303 (4)	5.1 (2)	C(33)	1685 (5)	2218 (6)	763 (4)	5.4 (2)
C(12)	6040 (5)	962 (5)	2989 (4)	4.7 (2)	C(34)	1051 (6)	1915 (6)	1232 (5)	6.2 (2)
C(13)	6776 (5)	1095 (5)	3451 (4)	4.3 (2)	C(35)	307 (6)	2385 (6)	1188 (5)	6.6 (2)
C(14)	8477 (5)	1449 (5)	4250 (4)	3.6 (2)	C(36)	145 (6)	3116 (6)	708 (5)	6.0 (2)
C(15)	8692 (5)	2327 (6)	4007 (4)	5.1 (2)	C(37)	764 (5)	3400 (5)	229 (4)	4.7 (2)
C(16)	9337 (6)	2429 (6)	3491 (5)	6.8 (2)	C(38)	2192 (5)	2413 (5)	3832 (4)	3.8 (2)
C(17)	9700 (6)	1643 (6)	3228 (4)	6.0 (2)	C(39)	1628 (5)	3126 (6)	3773 (4)	5.1 (2)
C(18)	9493 (6)	774 (6)	3440 (4)	5.7 (2)	C(40)	1569 (6)	3727 (6)	3125 (5)	6.7 (2)
C(19)	8873 (5)	662 (5)	3965 (4)	4.7 (2)	C(41)	2095 (6)	3558 (6)	2560 (5)	6.4 (2)
C(20)	7514 (5)	2646 (5)	375 (4)	3.3 (2)	C(42)	2653 (6)	2863 (6)	2589 (5)	6.3 (2)
C(21)	7036 (5)	1926 (5)	45 (4)	4.0 (2)	C(43)	2710 (5)	2252 (5)	3237 (4)	5.3 (2)
C(22)	6946 (5)	1077 (5)	431 (4)	5.2 (2)	C(44)	0	0	0	9.8 (5)

melts with effervescence at 90–103 °C to a red liquid, which crystallizes to a cream-colored solid that subsequently melts at 155–156 °C. The Cu(PPh₃)₂(SPh) starting material melts at 156–157 °C. Precession photographs revealed Laue symmetry $2/m$ and systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$, establishing the space group as $P2_1/c$. With graphite-monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) and a Picker FACS-I automated diffractometer, setting angles for 12 reflections in the 2θ range 81–96° were measured and used in a cell refinement. Crystal density was measured by flotation in a CCl₄/petroleum spirit mixture. Intensities were measured (with Cu $K\alpha$ radiation) by the θ – 2θ method to a 2θ limit of 90° in the reciprocal-space quadrant ($h, k, \pm l$). Of the 3199 unique reflections measured, 2768 had $I \geq 2\sigma(I)$ and were used in subsequent calculations. σ 's were calculated according to the formula

$\sigma(I) = \{T + B + [0.015(T - B)]^2\}^{1/2}$, where T and B represent the total count and total background.

The direct-methods technique was used to locate the heavy atoms, and C atoms were located by straightforward Fourier/least-squares methods. H atoms were included in fixed positions of idealized D_{6h} geometry (with one position omitted) with adjacent H–H distances of 2.34 Å and a fixed B value of 3.0 Å². Neutral-atom scattering factors were used (Cromer, 1976) and anomalous dispersion terms were used for Cu, S and P (Cromer & Liberman, 1970). Absorption corrections were applied with transmission coefficients ranging between 0.53 and 0.75 [$\mu = 36.2 \text{ cm}^{-1}$, crystal dimensions 0.014 × 0.033 × 0.010 cm, crystal faces (01 $\bar{1}$), (001), {100}, (011), (0 $\bar{1}\bar{1}$)]. Other computational details were as previously described (Ryan & Swanson, 1974).

The maximum parameter shift in the final least-squares cycle was less than 0.1 e.s.d., and a final difference Fourier synthesis revealed the principal peaks to have $|\rho| < 0.46 \text{ e \AA}^{-3}$ in the vicinity of a phenyl group. The final R values were $R_F = 0.059$ and $R_F^w = 0.058$.^{*} Atomic parameters are given in Table 1, distances and angles in Table 2, and a view of the structure in Fig. 1.

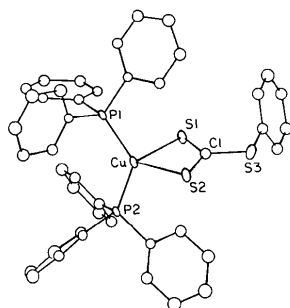


Fig. 1. A view of the structure of Cu(PPh₃)₂(S₂CSPH).

Table 2. Selected distances (Å) and angles (°)

Cu–P(1)	2.255 (2)	P(1)–Cu–P(2)	128.47 (8)
Cu–P(2)	2.258 (2)	P(1)–Cu–S(1)	118.54 (8)
Cu–S(1)	2.452 (2)	P(1)–Cu–S(2)	102.68 (8)
Cu–S(2)	2.440 (2)	P(2)–Cu–S(1)	108.55 (8)
Cu–C(1)	2.769 (6)	P(2)–Cu–S(2)	109.68 (8)
P(1)–C(8)	1.815 (7)	S(1)–Cu–S(2)	73.77 (7)
P(1)–C(14)	1.814 (7)	S(1)–C(1)–S(2)	122.1 (4)
P(1)–C(20)	1.837 (7)	S(1)–C(1)–S(3)	115.0 (4)
P(2)–C(26)	1.832 (7)	S(2)–C(1)–S(3)	122.9 (4)
P(2)–C(32)	1.798 (7)	C(1)–S(3)–C(2)	103.8 (4)
P(2)–C(38)	1.820 (7)	Cu–S(1)–C(1)	81.8 (2)
C(1)–S(1)	1.681 (7)	Cu–S(2)–C(1)	82.3 (2)
C(1)–S(2)	1.675 (7)		
C(1)–S(3)	1.754 (7)		
C(2)–S(3)	1.767 (8)		
C(44)–S(4)	1.500 (4)		

Average

C–C	1.33 (1)–1.43 (1)	1.38
Cu–P–C	110.0 (2)–120.3 (3)	115.0
C–P–C	102.3 (3)–104.7 (3)	103.3
P–C–C	116.6 (5)–124.6 (5)	120.5
S–C–C	119.3 (6)–121.0 (7)	120.2
C–C–C	118.0 (8)–123.4 (8)	120.0

Discussion. The structure consists of discrete Cu(PPh₃)₂(S₂CSPH) molecules at a general position and lattice CS₂ molecules at a center of symmetry. The coordinated CS₂ molecule is not present as a simple adduct ligand, but is part of a trithiocarbonate ligand resulting from insertion into the Cu–SPh bond. The compound is, therefore, very similar to Cu(PPh₃)₂–(S₂CSEt), which had previously been prepared by an indirect route and determined structurally (Avdeef, 1973; Avdeef & Fackler, 1975). The trithiocarbonate ligand is a symmetrically bonded bidentate ligand with C–S distances in the range 1.681 (7)–1.754 (7) Å. The CS₃ group is approximately planar, the C atom lying 0.01 Å from the four-atom unweighted least-squares plane. The Cu^I is pseudotetrahedrally coordinated to the two triphenylphosphine ligands [Cu–P 2.255 (2), 2.258 (2) Å] and to the bidentate S ligand [Cu–S 2.440 (2), 2.452 (2) Å]. The structural parameters are in close agreement with the previously reported structure of Cu(PPh₃)₂(S₂CSEt), with two exceptions. The Cu–S bond lengths are similar in the present case and differ by 0.11 Å in the ethyl compound. Unlike the earlier structure, the four-atom CuS₂C moiety is planar within

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32196 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

0.01 Å in the present case; the dihedral angles between the CuS₂ and S₂C planes are 1.7 and 12.7° in the two determinations. By similar means, we have also prepared the related compounds Cu(PPh₃)₂(SMe)·CS₂ and Ag(PPh₃)₂(SPh)·CS₂; presumably the trithiocarbonate formulation applies to these compounds as well.

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Osmium Tetroxide–9-Methylbenzanthracene–Bis(pyridine) Adduct (Toluene Solvate)

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Abstract. C₃₆H₂₄N₂O₄Os; monoclinic, *P*2₁/*c*; *a* = 11.285 (4), *b* = 32.507 (6), *c* = 8.044 (5) Å; β = 93.04° and *Z* = 4. The structure was refined to an *R* of 9.8%. Distortion from idealized octahedral geometry occurs around the Os atom; the aromatic parts of the molecule are folded in two parts about the saturated C ring.

Introduction. A single crystal of the title adduct (II) (Fig. 1) obtained from toluene was mounted on a PW 1100 four-circle automatic diffractometer with graphite-monochromatized Mo *K*α radiation. 5506 reflexions were scanned in the θ–2θ mode above the background (3σ). No absorption corrections were made. The position of the Os atom was easily obtained

from the Patterson map, and successive Fourier syntheses revealed step by step the whole molecule. An additional molecule of solvent (toluene) was also located in the asymmetric unit.

Refinement was carried out by full-matrix least squares with a modified version of *ORFLS* (Busing, Martin & Levy, 1962). The thermal parameters of the non-hydrogen atoms were anisotropic and the H atoms were situated at their theoretical positions (except those of benzanthracene and toluene methyl groups). The scattering factors were those given in *International Tables for X-ray Crystallography* (1974). The final *R* is 9.8%.*

The coordinates and thermal parameters for the heavy atoms are listed in Table 1.

Discussion. The addition of osmium tetroxide to olefins gives an adduct which under smooth reductive conditions leads to a pure *cis*-diol (Criegee, 1936). This convenient synthesis can be extended, in some cases, to

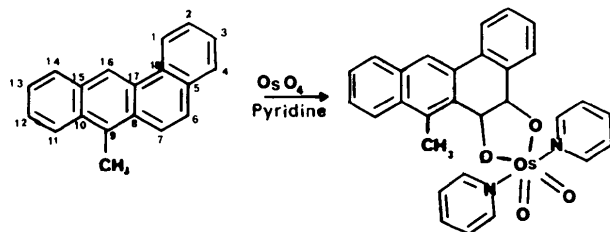


Fig. 1. Synthesis of the title adduct.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32230 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.