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μ_3-Sulphido-tris[triphenylphosphinegold(I)] Hexafluorophosphate

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Abstract. $C_{54}H_{45}Au_3P_3S^+.PF_6^-$, $M_r = 1554{\cdot}81$, monoclinic, $P2_1/b$ (c axis unique), $a = 11{\cdot}079\ (4)$, $b = 18{\cdot}642\ (7)$, $c = 55{\cdot}53\ (3)$ Å, $\gamma = 96{\cdot}81\ (3)°$, $U = 11388$ Å^3, $D_x = 1{\cdot}814$ Mg m^{-3}, μ(Cu $K\alpha$) = 16·3 mm^{-1}, $Z = 8$. $R = 0{\cdot}075$ for 9330 unique observed reflexions. There are two formula units in the asymmetric unit, the cations of which are linked by weak Au···Au interactions. Several Au–S–Au angles deviate appreciably from 90°.

Introduction. The title compound was obtained as colourless needles in low yield from the reaction of Ph_3PAuCl, $Et_4P_2S_2$ and $AgPF_6$ in dichloromethane. An X-ray investigation was undertaken to determine the nature of the product.

Preliminary photographs established the space group as $P2_1/c$ with an extremely long b axis. It proved impossible to separate adjacent reflexions with Mo $K\alpha$ radiation; data were therefore collected with monochromated Cu $K\alpha$ radiation on a Syntex $P2_1$ diffractometer. 15 288 reflexions were measured ($2\theta_{max} = 115°$) by a profile-fitting method based on a Lehmann–Larsen algorithm (Blessing, Coppens & Becker, 1972) and programmed by D. Schwarzenbach.

After application of Lp and empirical absorption corrections (crystal size 0·65 × 0·075 × 0·05 mm) averaging equivalent reflexions gave 14 380 unique reflexions, 9344 with $F > 4\sigma(F)$. Because of the long axis, the non-standard setting of $P2_1/b$ was used for all calculations; the program system used (*SHELXTL*) imposes the restrictions $|h| < 50$, $|k| < 50$ but allows all values of l.

The Au atoms were located by direct methods, and other non-hydrogen atoms by difference syntheses. P and S atoms were distinguished only on chemical grounds. Refinement (Au, S and P anisotropic, phenyl rings as rigid groups with C–C 1·395 Å, angles 120°) proceeded to $R = R' [= \sum w^{1/2}\Delta / \sum w^{1/2}|F_o|] = 0{\cdot}075$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0{\cdot}001F^2$. 14 low-angle reflexions with $|F_o - F_c| > 7{\cdot}5\sigma$ were omitted. H atoms were not included. Final atomic coordinates are given in Table 1, selected bond lengths and angles in Table 2.*

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Discussion. X-ray analysis reveals that the product is the previously unknown title compound, $(Ph_3PAu)_3S^+.PF_6^-$. The O analogue of the cation has, however, been reported (Nesmeyanov, Grandberg, Dyadchenko, Lemenovskii & Perevalova, 1974).

The Au–S–Au angles are approximately 90°, as would be expected for bonding involving S atom p orbitals. Similar angles (at Cl) are observed in $(Ph_3PAu)_2Cl^+.ClO_4^-$, the only other Au compound with a bridging anionic ligand whose structure has been reported (Jones, Sheldrick, Usón & Laguna, 1980).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35445 (57 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

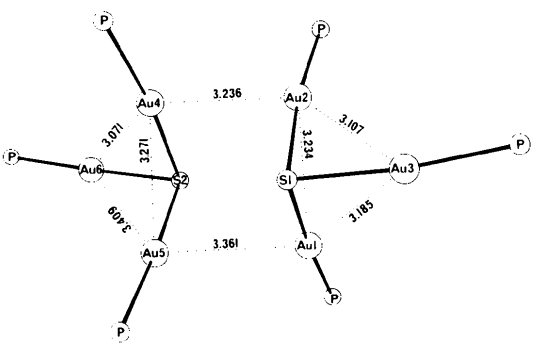

Fig. 1. Au, S and P atoms of the two independent cations, showing the atom numbering (for Au and S) and the short Au···Au contacts (e.s.d.'s 0·003 Å). P atom numbers are those of their attached Au atom. Phenyl rings have been omitted for clarity.

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U		x	y	z	U
Au(1)	925 (1)	7774 (1)	3261 (1)	75 (1)*	C(51)	1991 (20)	11572 (10)	3797 (3)	134 (12)
Au(2)	1129 (1)	8546 (1)	3784 (1)	76 (1)*	C(52)	2991 (20)	11582 (10)	3950 (3)	126 (11)
Au(3)	2745 (1)	9197 (1)	3362 (1)	76 (1)*	C(53)	4000 (20)	11250 (10)	3879 (3)	180 (17)
Au(4)	989 (1)	7004 (1)	4056 (1)	75 (1)*	C(54)	4007 (20)	10910 (10)	3655 (3)	138 (12)
Au(5)	1174 (1)	6194 (1)	3537 (1)	75 (1)*	C(55)	−1154 (17)	6651 (7)	2935 (3)	80 (7)
Au(6)	−902 (1)	5682 (1)	3976 (1)	77 (1)*	C(56)	−2375 (17)	6397 (7)	2897 (3)	102 (8)
P(1)	641 (6)	7593 (3)	2993 (1)	78 (3)*	C(57)	2714 (17)	5667 (7)	2846 (3)	108 (9)
P(2)	−160 (6)	9172 (3)	3993 (1)	81 (3)*	C(58)	−1832 (17)	5193 (7)	2834 (3)	131 (11)
P(3)	2988 (7)	10362 (3)	3240 (1)	82 (3)*	C(59)	612 (17)	5448 (7)	2872 (3)	116 (10)
P(4)	2284 (7)	7165 (3)	4377 (1)	80 (3)*	C(60)	−273 (17)	6177 (7)	2923 (3)	98 (8)
P(5)	2711 (7)	5689 (4)	3361 (1)	81 (3)*	C(61)	−258 (18)	7964 (10)	2706 (3)	90 (7)
P(6)	−1503 (7)	4732 (3)	4217 (1)	80 (3)*	C(62)	910 (18)	8325 (10)	2676 (3)	96 (8)
S(1)	2511 (5)	8046 (3)	3533 (1)	71 (2)*	C(63)	1278 (18)	8603 (10)	2451 (3)	122 (10)
S(2)	−363 (6)	6685 (3)	3740 (1)	72 (2)*	C(64)	478 (18)	8522 (10)	2256 (3)	134 (12)
C(1)	3134 (16)	6379 (8)	4413 (3)	81 (7)	C(65)	−690 (18)	8162 (10)	2286 (3)	130 (11)
C(2)	2621 (16)	5704 (8)	4331 (3)	106 (9)	C(66)	1058 (18)	7883 (10)	2511 (3)	104 (9)
C(3)	3254 (16)	5105 (8)	4356 (3)	99 (8)	C(67)	1883 (15)	7991 (10)	3097 (3)	88 (7)
C(4)	4401 (16)	5181 (8)	4463 (3)	98 (8)	C(68)	−2135 (15)	7896 (10)	3342 (3)	104 (9)
C(5)	4915 (16)	5857 (8)	4545 (3)	93 (8)	C(69)	3212 (15)	8096 (10)	3437 (3)	159 (14)
C(6)	4282 (16)	6456 (8)	4520 (3)	101 (8)	C(70)	4036 (15)	8390 (10)	3287 (3)	134 (12)
C(7)	1565 (16)	7267 (9)	4667 (3)	78 (6)	C(71)	−3785 (15)	8485 (10)	3043 (3)	137 (12)
C(8)	552 (16)	7646 (9)	4676 (3)	100 (8)	C(72)	−2708 (15)	8285 (10)	2947 (3)	118 (10)
C(9)	38 (16)	7789 (9)	4897 (3)	108 (9)	C(73)	4137 (13)	5968 (9)	3515 (3)	83 (7)
C(10)	535 (16)	7555 (9)	5110 (3)	114 (10)	C(74)	4109 (13)	6237 (9)	3749 (3)	99 (8)
C(11)	1548 (16)	7176 (9)	5101 (3)	123 (10)	C(75)	5192 (13)	6463 (9)	3870 (3)	107 (9)
C(12)	2062 (16)	7032 (9)	4879 (3)	105 (9)	C(76)	6304 (13)	6421 (9)	3756 (3)	105 (9)
C(13)	3376 (14)	7934 (8)	4347 (3)	79 (7)	C(77)	6333 (13)	6152 (9)	3522 (3)	110 (9)
C(14)	3869 (14)	8103 (8)	4120 (3)	94 (8)	C(78)	5249 (13)	5926 (9)	3401 (3)	95 (8)
C(15)	4734 (14)	8704 (8)	4091 (3)	122 (11)	C(79)	3007 (17)	5958 (10)	3051 (3)	84 (7)
C(16)	5106 (14)	9136 (8)	4288 (3)	123 (10)	C(80)	3351 (17)	6691 (10)	3007 (3)	102 (9)
C(17)	4613 (14)	8968 (8)	4515 (3)	133 (12)	C(81)	3627 (17)	6929 (10)	2773 (3)	142 (12)
C(18)	3748 (14)	8366 (8)	4545 (3)	105 (9)	C(82)	3560 (17)	6434 (10)	2583 (3)	127 (11)
C(19)	−1225 (14)	8651 (8)	4209 (3)	75 (6)	C(83)	3216 (17)	5702 (10)	2627 (3)	155 (14)
C(20)	−1692 (14)	7953 (8)	4141 (3)	81 (7)	C(84)	2940 (17)	5464 (10)	2861 (3)	115 (10)
C(21)	−2450 (14)	7522 (8)	4298 (3)	100 (8)	C(85)	2464 (24)	4711 (9)	3352 (4)	112 (9)
C(22)	−2742 (14)	7789 (8)	4522 (3)	103 (9)	C(86)	1296 (24)	4392 (9)	3409 (4)	131 (11)
C(23)	−2275 (14)	8487 (8)	4590 (3)	97 (8)	C(87)	1041 (24)	3641 (9)	3415 (4)	135 (12)
C(24)	−1517 (14)	8918 (8)	4434 (3)	98 (8)	C(88)	1953 (24)	3209 (9)	3363 (4)	124 (11)
C(25)	578 (19)	9877 (10)	4176 (3)	91 (8)	C(89)	3120 (24)	3528 (9)	3305 (4)	148 (13)
C(26)	75 (19)	10515 (10)	4221 (3)	114 (10)	C(90)	3376 (24)	4279 (9)	3300 (4)	145 (13)
C(27)	658 (19)	11031 (10)	4378 (3)	157 (14)	C(91)	2920 (16)	4201 (11)	4115 (3)	91 (8)
C(28)	1744 (19)	10908 (10)	4489 (3)	152 (14)	C(92)	−3791 (16)	4547 (11)	3995 (3)	115 (10)
C(29)	2248 (19)	10271 (10)	4443 (3)	145 (13)	C(93)	−4880 (16)	4155 (11)	3922 (3)	155 (14)
C(30)	1665 (19)	9755 (10)	4287 (3)	119 (10)	C(94)	−5097 (16)	3416 (11)	3969 (3)	142 (13)
C(31)	−1133 (18)	9603 (10)	3789 (3)	89 (7)	C(95)	−4225 (16)	3069 (11)	4090 (3)	139 (12)
C(32)	−760 (18)	9791 (10)	3555 (3)	121 (10)	C(96)	−3136 (16)	3462 (11)	4163 (3)	117 (10)
C(33)	−1550 (18)	10086 (10)	3398 (3)	143 (13)	C(97)	−279 (16)	4145 (9)	4234 (4)	90 (7)
C(34)	−2714 (18)	10193 (10)	3474 (3)	132 (11)	C(98)	144 (16)	3948 (9)	4459 (4)	103 (9)
C(35)	−3088 (18)	10005 (10)	3708 (3)	133 (12)	C(99)	1070 (16)	3504 (9)	4473 (4)	122 (10)
C(36)	−2297 (18)	9710 (10)	3865 (3)	126 (11)	C(100)	1574 (16)	3257 (9)	4262 (4)	126 (11)
C(37)	1827 (16)	10629 (10)	3045 (3)	82 (7)	C(101)	1151 (16)	3454 (9)	4038 (4)	156 (14)
C(38)	1840 (16)	11343 (10)	2969 (3)	104 (9)	C(102)	225 (16)	3898 (9)	4024 (4)	129 (11)
C(39)	954 (16)	11529 (10)	2810 (3)	115 (10)	C(103)	1868 (18)	4988 (11)	4520 (3)	93 (8)
C(40)	55 (16)	11000 (10)	2726 (3)	130 (11)	C(104)	−2705 (18)	4552 (11)	4660 (3)	99 (8)
C(41)	41 (16)	10286 (10)	2802 (3)	142 (13)	C(105)	−3008 (18)	4778 (11)	4890 (3)	122 (10)
C(42)	927 (16)	10100 (10)	2961 (3)	120 (10)	C(106)	−2475 (18)	5440 (11)	4979 (3)	116 (10)
C(43)	4375 (15)	10630 (11)	3081 (3)	87 (7)	C(107)	1639 (18)	5876 (11)	4839 (3)	151 (14)
C(44)	4937 (15)	11340 (11)	3089 (3)	126 (11)	C(108)	1335 (18)	5650 (11)	4609 (3)	129 (11)
C(45)	5976 (15)	11541 (11)	2952 (3)	132 (11)	P(7)	4246 (9)	2632 (5)	4764 (1)	118 (4)*
C(46)	6454 (15)	11032 (11)	2807 (3)	134 (12)	F(1)	2825 (26)	2554 (15)	4825 (5)	209 (11)
C(47)	5892 (15)	10322 (11)	2799 (3)	155 (14)	F(2)	4105 (22)	2205 (13)	4539 (4)	178 (9)
C(48)	4852 (15)	10121 (11)	2936 (3)	101 (8)	F(3)	4019 (27)	3346 (16)	4616 (5)	213 (11)
C(49)	3007 (20)	10900 (10)	3502 (3)	88 (7)	F(4)	5618 (23)	2789 (13)	4714 (4)	185 (9)
C(50)	1999 (20)	11231 (10)	3573 (3)	111 (9)	F(5)	4398 (32)	3029 (18)	5000 (6)	257 (14)

* Equivalent isotropic U calculated from anisotropic U.

Table 1 (*cont.*)

	x	*y*	*z*	*U*
F(6)	4382 (26)	1913 (15)	4902 (5)	207 (10)
P(8)	5236 (19)	3520 (8)	2686 (3)	200 (9)*
F(7)	4908 (33)	4222 (21)	2817 (6)	267 (15)
F(8)	4489 (26)	3704 (15)	2453 (5)	197 (10)
F(9)	5711 (29)	2847 (18)	2576 (6)	232 (12)
F(10)	6310 (30)	3982 (18)	2566 (6)	226 (12)
F(11)	4266 (34)	2987 (20)	2810 (6)	252 (14)
F(12)	5862 (47)	3373 (27)	2922 (10)	348 (24)

Table 2. *Bond lengths* (Å) *and angles* (°)

Au(1) P(1)	2·281 (8)	Au(1)–S(1)	2·326 (7)
Au(2) P(2)	2·270 (8)	Au(2)–S(1)	2·342 (7)
Au(3)–P(3)	2·259 (7)	Au(3)–S(1)	2·333 (7)
Au(4)–P(4)	2·284 (8)	Au(4) S(2)	2·338 (7)
Au(5) P(5)	2·262 (8)	Au(5) S(2)	2·320 (7)
Au(6)–P(6)	2·257 (7)	Au(6)–S(2)	2·303 (7)
P(1)–Au(1) S(1)	175·9 (3)	P(2) Au(2)–S(1)	171·9 (3)
P(3) Au(3)–S(1)	173·3 (3)	P(4)–Au(4)–S(2)	172·8 (3)
P(5) Au(5)–S(2)	176·5 (3)	P(6) Au(6) S(2)	176·9 (3)
Au(1)–S(1)–Au(2)	87·7 (3)	Au(1)–S(1)–Au(3)	86·3 (3)
Au(2)–S(1) Au(3)	83·3 (3)	Au(4)–S(2)–Au(5)	89·2 (3)
Au(4)–S(2)–Au(6)	82·9 (3)	Au(5)–S(2)–Au(6)	95·0 (3)

Au–P lengths fall in the expected range for two-coordinate Au, and the P–Au–S angles are all close to linear (maximum deviation 8·1°). The Au–S lengths vary from 2·303 (7) to 2·342 (7) Å; no other Au–sulphide bond lengths are available for comparison, although the dimeric organic sulphide derivative $[AuSCH_2PEt_2]_2$ has Au–S = 2·31 Å (Crane & Beall, 1978).

The cations are arranged in pairs with short contacts between the Au atoms [Au(1)···Au(5) 3·361 (3), Au(2)···Au(4) 3·236 (3) Å] (Fig. 1). Such contacts are a common feature of the structural chemistry of Au[1], although no theoretical explanation for them has been proposed. It is also striking that the angles at S(1) are all rather less than 90°, associated with further short Au···Au distances. It is thus feasible that weak Au···Au interactions cause these distortions; a similar effect is seen in $(Ph_3PAu)_2Cl^+$ (Jones *et al.*, 1980). However, the angles at S(2) show a different pattern, only Au(4)–S(2)–Au(6) being appreciably less than 90°. This leads to a more varied set of Au···Au distances, Au(5)···Au(6) being rather long and Au(4)···Au(6) short. The two cations also show appreciable differences in the orientation of the phenyl rings.

The PF_6 ions show high thermal motion, but do not appear to be disordered. The temperature factors of the cations are also somewhat high; both this and the rather high *R* may be attributed to the difficulty of performing accurate absorption corrections for a needle-shaped crystal with high μ.

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A Complex of 1,15-Bis(2-bromophenyl)-2,5,8,11,14-pentaoxapentadecane and Mercury Dibromide

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Abstract. $C_{22}H_{28}Br_2O_5.HgBr_2$, $M_r = 892·7$, $C2/c$, $a = 31·805$ (7), $b = 7·954$ (3), $c = 23·826$ (5) Å, $\beta = 113·22$ (4)°, $Z = 8$, $d_c = 2·141$ Mg m^{-3}, $\mu_{MoK\alpha} = 11·30$ mm^{-1}; $R_w = 0·066$ for 3504 data [weight = $1/\sigma^2(F_o)$]. The ligand wraps around the cation in a nearly circular manner such that all its O atoms (in

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