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Tetraphenylarsonium *O,O'*-Dimethyldithiophosphate

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Abstract. $[As(C_6H_5)_4][P(CH_3O)_2S_2]$, $M_r = 540{\cdot}52$, triclinic, $P\bar{1}$ (No. 2), $a = 9{\cdot}637\,(4)$, $b = 11{\cdot}875\,(4)$, $c = 13{\cdot}119\,(6)$ Å, $\alpha = 66{\cdot}34\,(4)$, $\beta = 68{\cdot}62\,(4)$, $\gamma = 78{\cdot}85\,(3)°$, $V = 1278{\cdot}7\,(8)$ Å^3, $Z = 2$, $D_x = 1{\cdot}404$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71073$ Å, $\mu = 15{\cdot}6$ cm^{-1}, $F(000) = 556$, $T = 294\,(1)$ K, $R_F = 0{\cdot}043$ for 2005 unique observed reflections. Both the cation and the anion have tetrahedral geometry. There is some asymmetry in the phosphorus-to-sulfur binding [P—S = 1·954 (3) and 1·944 (2) Å].

Experimental. Obtained as a by-product in the synthesis of $(C_6H_5)_4As.Yb[S_2P(OCH_3)_2]_4$ from $YbCl_3.6H_2O$ and $Na[S_2P(OCH_3)_2]$ and crystallized from 2-propanol. Colorless plate, 0·18 × 0·18 × 0·09 mm mounted on a glass fiber. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, unit cell from the angular settings of 25 reflections ($16 < 2\theta < 28°$). 3922 total intensities measured, 3575 unique, 1570 unobserved, 2005 with $F_o^2 > 3{\cdot}0\sigma(F_o^2)$, maximum $2\theta = 52{\cdot}0°$, $0 < h < 11$, $-14 < k < 14$, $-15 < l < 16$ using θ–2θ scans. Corrections: Lorentz–polarization, linear decay (from 0·962 to 1·115 on I), reflection averaging (agreement on $I = 4{\cdot}3\%$), empirical absorption (from 0·896 to 0·996 on I). Centrosymmetric space group judged correct based on successful refinement. Solution by Patterson and Fourier methods. Refinement by full-matrix least squares. H atoms refined as riding atoms. 289 parameters refined, $R_F = 0{\cdot}043$, $wR = 0{\cdot}047$, e.s.d. of observation of unit weight = 1·20, largest shift < 0·01σ. Minimization function $\sum w(|F_o| - |F_c|)^2$, $w = 4F_o^2/\sigma^2(F_o^2)$, instrument instability factor 0·040, max. $\Delta\rho = 0{\cdot}40\,(7)$ e Å^{-3}, min. $\Delta\rho = -0{\cdot}30\,(7)$ e Å^{-3}. *SDP*/VAX program package (Frenz, 1978). Atomic parameters are given in Table 1, bond distances and angles in Table 2.* The anion structure is shown in Fig. 1. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Related literature. We have been interested in the chemistry and structures of dithiophosphate and dithiophosphinate complexes of transition-metal ions for many years (Pinkerton, Schwarzenbach & Spiliadis,

Table 1. *Positional parameters and their e.s.d.'s*

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(\frac{4}{3})\,[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

	x	y	z	B (Å^2)
As	0·11184 (7)	0·40654 (6)	0·21225 (6)	3·20 (2)
S1	0·4988 (2)	0·9855 (2)	0·2445 (2)	5·95 (6)
S2	0·3430 (3)	0·7108 (2)	0·3668 (2)	5·92 (7)
P	0·3358 (2)	0·8869 (2)	0·2784 (2)	4·18 (5)
O1	0·3109 (5)	0·8977 (4)	0·1601 (4)	5·0 (1)
O2	0·1895 (5)	0·9564 (4)	0·3402 (4)	5·3 (1)
C1	0·0111 (6)	0·5643 (5)	0·2002 (5)	3·1 (2)
C2	−0·1376 (7)	0·5812 (6)	0·2092 (5)	3·9 (2)
C3	−0·2100 (7)	0·6959 (6)	0·1995 (5)	4·4 (2)
C4	−0·1356 (7)	0·7935 (6)	0·1787 (5)	4·9 (2)
C5	0·0144 (8)	0·7767 (6)	0·1662 (6)	4·8 (2)
C6	0·0884 (7)	0·6620 (5)	0·1779 (5)	3·9 (2)
C7	0·2684 (6)	0·4197 (5)	0·0687 (5)	3·4 (2)
C8	0·2865 (7)	0·5284 (6)	−0·0261 (5)	4·1 (2)
C9	0·3946 (7)	0·5371 (6)	−0·1315 (5)	4·8 (2)
C10	0·4842 (7)	0·4351 (6)	−0·1430 (5)	4·4 (2)
C11	0·4685 (7)	0·3262 (6)	−0·0504 (6)	5·0 (2)
C12	0·3605 (7)	0·3167 (6)	0·0589 (6)	4·4 (2)
C13	−0·0273 (6)	0·2955 (5)	0·2387 (5)	3·1 (2)
C14	−0·0219 (7)	0·2545 (5)	0·1528 (5)	4·0 (2)
C15	−0·1285 (7)	0·1768 (6)	0·1763 (6)	4·8 (2)
C16	−0·2388 (7)	0·1414 (6)	0·2815 (6)	5·1 (2)
C17	−0·2439 (7)	0·1823 (6)	0·3677 (6)	4·9 (2)
C18	−0·1366 (7)	0·2589 (6)	0·3479 (6)	4·5 (2)
C19	0·1922 (6)	0·3456 (5)	0·3388 (5)	3·1 (2)
C20	0·2615 (7)	0·2291 (6)	0·3654 (5)	4·4 (2)
C21	0·3272 (7)	0·1886 (7)	0·4515 (6)	5·2 (2)
C22	0·3249 (8)	0·2605 (7)	0·5110 (6)	5·3 (2)
C23	0·2537 (8)	0·3745 (7)	0·4862 (6)	5·9 (2)
C24	0·1867 (8)	0·4193 (6)	0·3992 (5)	5·0 (2)
C25	0·0462 (8)	0·9113 (7)	0·3799 (7)	6·7 (3)
C26	0·2970 (8)	1·0154 (6)	0·0736 (6)	5·8 (2)

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

Numbers in parentheses are estimated standard deviations in the least-significant digits.

S1—P	1·954 (3)	S2—P	1·944 (2)
P—O1	1·608 (6)	P—O2	1·606 (5)
O1—C26	1·423 (7)	O2—C25	1·415 (9)
As—C1	1·910 (6)	As—C7	1·906 (5)
As—C13	1·906 (7)	As—C19	1·906 (7)

S1—P—S2	120·1 (1)	S1—P—O1	111·5 (2)
S1—P—O2	103·9 (2)	S2—P—O1	104·2 (2)
S2—P—O2	112·1 (2)	O1—P—O2	104·2 (3)
P—O1—C26	120·2 (5)	P—O2—C25	121·1 (5)
C1—As—C7	109·3 (2)	C1—As—C13	108·6 (3)
C1—As—C19	110·8 (3)	C7—As—C13	108·9 (3)
C7—As—C19	109·7 (3)	C13—As—C19	109·5 (3)

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44483 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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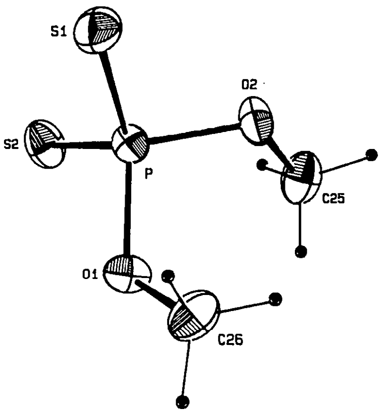

Fig. 1. A single anion showing 30% probability ellipsoids.

1987). Comparison of bond lengths and angles in free and complexed ligands has rarely been possible due to the lack of structures of the free ligands. The only structures known to date of this type of ligand are the potassium salt of the present anion determined from photographic data (Coppens, McGillavry, Hovenkamp & Douwes, 1962), the dimethylammonium salt of the isopropyl analog (Kalinin, Andrianov & Struchkov, 1979) and the potassium salt of the benzyl-substituted anion (Hazel & Collin, 1972).

In general the P—S bond lengths are essentially equivalent (in the potassium salt by symmetry). The small asymmetry here [1·954 (3) *vs* 1·944 (2) Å] is much less than observed in the free acids *e.g.* in diphenyldithiophosphinic acid, P=S = 1·954 (1) Å and P—SH = 2·077 (1) Å (Krebs & Henkel, 1981). The value for the potassium salt was 1·96 (1) Å and in the isopropyl and benzyl analogs the values were 1·974 (6), 1·965 (6), 1·969 (2) and 1·945 (2) Å respectively. The P atoms are formally tetrahedral, the major distortion being the larger angle between the two S atoms [120·1 (1)°] owing to steric effects as has been observed for the cited analogs [118·2° in the potassium salt, 116·6 (3)° for the isopropyl analog and 120·0 (1)° for the benzyl-substituted anion].

On complexation there is typically a small lengthening of the P—S bonds and a concomitant closing of the S—P—S angle.

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Structure of Hexacarbonylbis(pentamethylcyclopentadienyl)dimolybdenum(*Mo–Mo*)

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Abstract. $[Mo_2(C_{10}H_{15})_2(CO)_6]$, $M_r = 630·4$, monoclinic, $P2_1/n$, $a = 9·3922$ (4), $b = 9·1125$ (3), $c = 15·5643$ (6) Å, $\beta = 97·319$ (4)°, $V = 1321·24$ Å^3, $Z = 2$, $D_x = 1·584$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·96$ mm^{-1}, $F(000) = 636$, $T = 293$ K, $R = 0·0245$ for 1818 unique reflections with $F > 4\sigma(F)$. The molecule consists of a mutually bonded dimolybdenum core, each Mo atom being additionally bonded to three carbonyl and one pentamethylcyclopentadienyl ligand, and contains the longest recorded unsupported Mo—Mo bond, 3·281 (1) Å.

Experimental. The compound was isolated in good yield from a reaction between bismuth metal and $[Mo_2(\eta\text{-}C_5Me_5)_2(CO)_4]$(Mo≡Mo), the only other major product being the *cis* isomer of the dimolybdenum tetraoxo compound, $[Mo_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}O)_2(O)_2]$, which has been previously characterized by X-ray crystallography (Arzoumanian, Baldy, Pierrot & Petrignani, 1985). Reaction is presumed to occur by oxo transfer from the bismuth surface to $[Mo_2(\eta\text{-}C_5Me_5)_2(CO)_4]$ and subsequent carbonyl loss to give $[Mo_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}O)_2(O)_2]$. Additional molecules of $[Mo_2(\eta\text{-}C_5Me_5)_2\text{-}$

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