Crystal structures of triphenyl thiophosphate and selenophosphate, $(C_6H_5)_3PO_3X$ (X = S, Se)

J. Clade[I] and M. Jansen*,[II]

[I] Fraunhofer-Institut für Silicatforschung, Neunerplatz 2, 97082 Würzburg, Germany
[II] Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany

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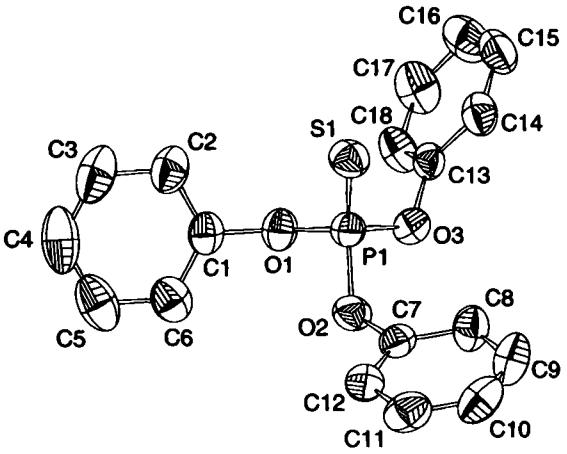

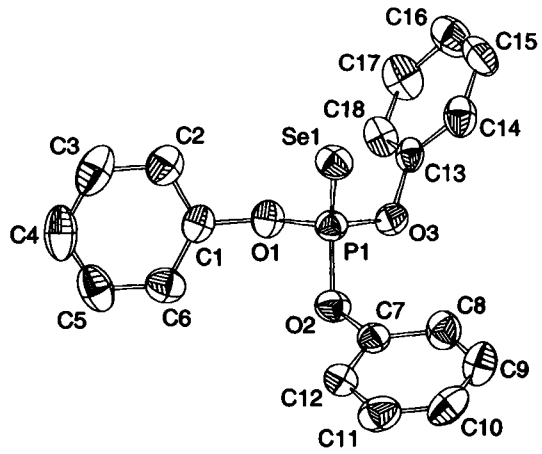

Abstract

$C_{18}H_{15}O_3PS$, orthorhombic, $P2_12_12_1$ (no. 19), a = 7.924(2) Å, b = 13.287(1) Å, c = 16.138(4) Å, V = 1699.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR_{obs}(F^2)$ = 0.075, T = 293 K.

$C_{18}H_{15}O_3PSe$, orthorhombic, $P2_12_12_1$ (no. 19), a = 7.839(8) Å, b = 13.559(1) Å, c = 16.1340(9) Å, V = 1714.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.036, $wR_{obs}(F^2)$ = 0.081, T = 293 K.

Source of material

The compounds were synthesized by dissolving elemental sulfur and selenium, respectively, in triphenyl phosphite diluted with ethanol. Crystals were obtained by recrystallization of the crude products from ethanol. Single crystals were sealed in glass capillaries under argon atmosphere for crystal structure determination.

* Correspondence author (e-mail: m.jansen@fkf.mpg.de)

Discussion

The isotypic triphenyl thiophosphate and triphenyl selenophosphate crystallize orthorhombically with one molecule per asymmetric unit. The coordination environments at phosphorus closely resemble each other, but are significantly different from the corresponding values found for P_4O_6S (d_{av}(P—O) = 1.595(3) Å, $\angle_{av}$O–P–O = 103.1(2)° [1]) and for P_4O_6Se (d_{av}(P—O) = 1.602(3) Å, $\angle_{av}$O–P–O = 102.5(2)° [2]), respectively. (Values are d_{av}(P—O) = 1.577(2) Å, $\angle_{av}$O–P–O = 100.4(1)° for $(C_6H_5)_3PO_3S$ and d_{av}(P—O) = 1.577(3) Å, $\angle_{av}$O–P–O = 100.4(2)° for the $(C_6H_5)_3PO_3Se$, respectively.) The Flack parameters were 0.0(1) for triphenyl thiophosphate and –0.00(1) for triphenyl selenophosphate, respectively [1].

1. Triphenyl thiophosphate, $(C_6H_5)_3PO_3S$

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.5 × 0.6 × 0.8 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.96 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$ (profile fit)
$2\theta_{max}$:	49.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2965, 2509
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2135
$N(param)_{refined}$:	209
Programs:	SHELXS-86 [4], SHELXL-93 [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4a	–0.0097	–0.9202	–0.5624	0.097
H(3)	4a	0.1041	–1.0073	–0.4509	0.120
H(4)	4a	0.0478	–1.1744	–0.4341	0.126
H(5)	4a	–0.1201	–1.2588	–0.5264	0.117
H(6)	4a	–0.2280	–1.1743	–0.6405	0.092
H(8)	4a	0.0833	–1.2080	–0.8362	0.088
H(9)	4a	0.2219	–1.2487	–0.9580	0.102
H(10)	4a	0.1836	–1.1522	–1.0736	0.104
H(11)	4a	0.0071	–1.0180	–1.0704	0.108
H(12)	4a	–0.1327	–0.9739	–0.9498	0.089
H(14)	4a	–0.1745	–0.7382	–0.8664	0.083
H(15)	4a	–0.2698	–0.5777	–0.8329	0.103
H(16)	4a	–0.4736	–0.5570	–0.7344	0.112
H(17)	4a	–0.5899	–0.6937	–0.6710	0.110
H(18)	4a	–0.4960	–0.8540	–0.7023	0.087

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	4*a*	−0.1190(1)	−0.96175(5)	−0.76232(4)	0.0586(5)	0.0537(4)	0.0511(4)	−0.0031(4)	0.0016(3)	−0.0004(3)
S(1)	4*a*	0.0899(1)	−0.89199(6)	−0.75938(5)	0.0621(6)	0.0641(4)	0.0794(5)	−0.0085(4)	−0.0042(4)	0.0035(4)
O(1)	4*a*	−0.2048(3)	−0.9890(2)	−0.6769(1)	0.063(1)	0.076(1)	0.054(1)	0.006(1)	0.005(1)	0.0039(9)
O(2)	4*a*	−0.1222(3)	−1.0666(1)	−0.8077(1)	0.077(2)	0.055(1)	0.060(1)	−0.010(1)	0.014(1)	−0.0019(8)
O(3)	4*a*	−0.2723(3)	−0.9079(2)	−0.8063(1)	0.062(1)	0.064(1)	0.059(1)	−0.004(1)	−0.006(1)	−0.0035(9)
C(1)	4*a*	−0.1269(4)	−1.0408(2)	−0.6114(2)	0.059(2)	0.076(2)	0.050(1)	0.006(2)	0.015(1)	0.005(1)
C(2)	4*a*	−0.0301(5)	−0.9887(3)	−0.5556(2)	0.081(3)	0.106(3)	0.056(2)	−0.008(2)	0.003(2)	0.006(2)
C(3)	4*a*	0.0362(6)	−1.0406(4)	−0.4891(2)	0.080(3)	0.163(4)	0.057(2)	−0.009(3)	0.000(2)	0.011(3)
C(4)	4*a*	0.0025(6)	−1.1402(5)	−0.4792(3)	0.072(3)	0.164(5)	0.079(3)	0.028(3)	0.023(2)	0.051(3)
C(5)	4*a*	−0.0966(7)	−1.1909(3)	−0.5344(3)	0.094(3)	0.098(3)	0.101(3)	0.020(3)	0.036(3)	0.036(2)
C(6)	4*a*	−0.1615(5)	−1.1406(3)	−0.6020(2)	0.078(2)	0.079(2)	0.074(2)	0.006(2)	0.020(2)	0.008(2)
C(7)	4*a*	−0.0363(4)	−1.0874(2)	−0.8826(2)	0.057(2)	0.058(2)	0.054(2)	−0.007(1)	−0.002(1)	−0.006(1)
C(8)	4*a*	0.0681(5)	−1.1692(2)	−0.8836(2)	0.095(3)	0.058(2)	0.066(2)	0.007(2)	−0.006(2)	−0.005(2)
C(9)	4*a*	0.1504(5)	−1.1933(3)	−0.9562(2)	0.082(3)	0.085(2)	0.088(2)	0.016(2)	−0.004(2)	−0.026(2)
C(10)	4*a*	0.1272(5)	−1.1361(3)	−1.0248(2)	0.070(3)	0.126(3)	0.064(2)	−0.002(3)	0.001(2)	−0.023(2)
C(11)	4*a*	0.0227(6)	−1.0560(4)	−1.0227(2)	0.093(3)	0.125(3)	0.053(2)	0.008(3)	−0.003(2)	0.007(2)
C(12)	4*a*	−0.0614(5)	−1.0294(3)	−0.9512(2)	0.076(2)	0.085(2)	0.061(2)	0.016(2)	−0.006(2)	0.006(2)
C(13)	4*a*	−0.3245(4)	−0.8097(2)	−0.7850(2)	0.049(2)	0.059(2)	0.051(2)	−0.002(1)	−0.009(1)	0.008(1)
C(14)	4*a*	−0.2571(5)	−0.7291(3)	−0.8261(2)	0.063(2)	0.078(2)	0.067(2)	−0.007(2)	−0.003(2)	0.017(2)
C(15)	4*a*	−0.3148(6)	−0.6336(3)	−0.8062(3)	0.084(3)	0.071(2)	0.102(3)	−0.011(2)	−0.026(3)	0.031(2)
C(16)	4*a*	−0.4367(6)	−0.6213(3)	−0.7481(3)	0.085(3)	0.069(2)	0.127(4)	0.021(2)	−0.010(3)	0.015(2)
C(17)	4*a*	−0.5047(5)	−0.7025(3)	−0.7099(3)	0.080(3)	0.093(3)	0.102(3)	0.027(2)	0.021(2)	0.015(2)
C(18)	4*a*	−0.4489(5)	−0.7983(2)	−0.7284(2)	0.066(2)	0.069(2)	0.083(2)	0.005(2)	0.014(2)	0.023(2)

2. Triphenyl selenophosphate, $(C_6H_5)_3PO_3Se$

Table 4. Data collection and handling.

Crystal:	colorless block, size 0.4 × 0.5 × 0.9 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	22.94 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$ (profile fit)
$2\theta_{max}$:	45°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5228, 2241
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1931
$N(param)_{refined}$:	209
Programs:	SHELXS-86 [4], SHELXL-93 [5]

Table 5. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*a*	−0.0002	−0.9163	−0.5616	0.085
H(3)	4*a*	0.1147	−1.0007	−0.4488	0.106
H(4)	4*a*	0.0600	−1.1677	−0.4321	0.104
H(5)	4*a*	−0.1102	−1.2473	−0.5231	0.095
H(6)	4*a*	−0.2204	−1.1671	−0.6377	0.080
H(8)	4*a*	0.0850	−1.2047	−0.8293	0.076
H(9)	4*a*	0.2198	−1.2502	−0.9507	0.091
H(10)	4*a*	0.1774	−1.1631	−1.0694	0.089
H(11)	4*a*	−0.0011	−1.0293	−1.0694	0.092
H(12)	4*a*	−0.1431	−0.9840	−0.9514	0.080
H(14)	4*a*	−0.1779	−0.7466	−0.8734	0.077
H(15)	4*a*	−0.2734	−0.5873	−0.8451	0.091
H(16)	4*a*	−0.4738	−0.5611	−0.7447	0.096
H(17)	4*a*	−0.5873	−0.6922	−0.6743	0.095
H(18)	4*a*	−0.4880	−0.8496	−0.6972	0.074

Table 6. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	4*a*	−0.1168(2)	−0.96135(8)	−0.76187(7)	0.0476(6)	0.0478(6)	0.0501(6)	−0.0045(5)	0.0005(7)	−0.0015(5)
Se(1)	4*a*	0.11331(6)	−0.88918(4)	−0.76326(4)	0.0500(3)	0.0588(3)	0.0746(4)	−0.0099(2)	−0.0027(3)	0.0016(3)
O(1)	4*a*	−0.1999(4)	−0.9842(3)	−0.6750(2)	0.053(2)	0.068(2)	0.053(2)	0.002(2)	0.005(2)	0.003(2)
O(2)	4*a*	−0.1242(5)	−1.0660(2)	−0.8045(2)	0.064(2)	0.051(2)	0.056(2)	−0.010(2)	0.014(2)	−0.003(2)
O(3)	4*a*	−0.2724(4)	−0.9093(3)	−0.8059(2)	0.055(2)	0.057(2)	0.055(2)	−0.009(2)	−0.011(2)	−0.001(2)
C(1)	4*a*	−0.1212(7)	−1.0349(4)	−0.6091(3)	0.046(3)	0.071(3)	0.048(3)	0.003(3)	0.007(3)	0.000(2)
C(2)	4*a*	−0.0214(7)	−0.9832(5)	−0.5540(4)	0.063(4)	0.087(5)	0.062(4)	−0.005(3)	0.005(3)	−0.002(4)
C(3)	4*a*	0.0467(8)	−1.0338(7)	−0.4869(4)	0.060(4)	0.149(8)	0.056(4)	−0.014(4)	−0.003(3)	0.000(4)
C(4)	4*a*	0.0133(8)	−1.1337(7)	−0.4767(4)	0.064(4)	0.134(8)	0.062(4)	0.016(4)	0.015(3)	0.035(5)
C(5)	4*a*	−0.0862(9)	−1.1809(5)	−0.5313(4)	0.080(4)	0.080(4)	0.078(4)	0.018(4)	0.024(4)	0.025(4)
C(6)	4*a*	−0.1540(7)	−1.1332(4)	−0.5994(4)	0.066(4)	0.061(4)	0.073(4)	0.002(3)	0.012(3)	−0.007(3)
C(7)	4*a*	−0.0398(6)	−1.0890(4)	−0.8787(3)	0.046(3)	0.047(3)	0.055(3)	−0.008(2)	−0.007(2)	−0.002(2)
C(8)	4*a*	0.0671(7)	−1.1692(4)	−0.8778(4)	0.079(4)	0.048(3)	0.062(4)	0.000(3)	−0.008(3)	0.001(3)
C(9)	4*a*	0.1473(8)	−1.1960(5)	−0.9503(4)	0.075(4)	0.071(4)	0.083(4)	0.015(3)	−0.007(4)	−0.023(3)
C(10)	4*a*	0.1221(8)	−1.1445(5)	−1.0209(3)	0.064(3)	0.104(5)	0.054(3)	−0.005(4)	0.005(3)	−0.025(3)
C(11)	4*a*	0.0150(8)	−1.0649(6)	−1.0207(4)	0.080(4)	0.098(5)	0.052(3)	0.006(4)	0.000(3)	0.003(3)

Table 6. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(12)	4*a*	–0.0682(7)	–1.0371(4)	–0.9507(4)	0.064(4)	0.071(4)	0.066(4)	0.013(3)	–0.009(3)	0.003(3)
C(13)	4*a*	–0.3250(6)	–0.8109(4)	–0.7861(3)	0.037(2)	0.058(3)	0.046(3)	–0.001(2)	–0.010(2)	0.008(2)
C(14)	4*a*	–0.2587(7)	–0.7350(5)	–0.8323(3)	0.055(3)	0.080(4)	0.059(3)	–0.008(3)	0.001(2)	0.015(3)
C(15)	4*a*	–0.3169(8)	–0.6405(5)	–0.8154(4)	0.073(4)	0.056(4)	0.099(5)	–0.009(3)	–0.018(4)	0.029(4)
C(16)	4*a*	–0.4367(8)	–0.6248(5)	–0.7562(5)	0.070(3)	0.062(3)	0.108(5)	0.016(3)	–0.010(4)	0.013(4)
C(17)	4*a*	–0.5023(7)	–0.7029(5)	–0.7135(4)	0.059(3)	0.083(4)	0.095(5)	0.019(3)	0.016(3)	0.013(4)
C(18)	4*a*	–0.4451(6)	–0.7968(4)	–0.7274(4)	0.048(3)	0.066(3)	0.070(4)	0.004(2)	0.006(3)	0.016(3)

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