

the phosphate atom O(2) and the second [H(7)] water atom is used in weak bifurcated hydrogen bonds.

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Synthesis and Structure of $[P(C_6H_5)_4]_4[M_2(WSe_4)_4]$ ($M = Pb, Sn$)

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Abstract. Tetrakis(tetraphenylphosphonium) bis(μ -tetraselenidotungstato-*Se, Se', μ -Se'*)-bis[(tetraselenidotungstato-*Se, Se'*)plumbate], $M_r = 3770.7$, triclinic, $P\bar{1}$, $a = 12.963$ (1), $b = 14.430$ (2), $c = 14.705$ (1) Å, $\alpha = 105.26$ (1), $\beta = 99.88$ (1), $\gamma = 94.06$ (1)°, $V = 2595$ (1) Å³, $Z = 1$, $D_x = 2.40$ g cm⁻³, $\lambda(Cu K\alpha_1) = 1.54056$ Å, $\mu = 218.0$ cm⁻¹, $F(000) = 1673.5$ (including anomalous dispersion), $T = 153$ K, $R[\text{on } F \text{ for } F_o^2 > 3\sigma(F_o^2)] = 0.047$, $wR[\text{on } F \text{ for } F_o^2 > 3\sigma(F_o^2)] = 0.048$, $R(F^2) = 0.075$, $wR(F^2) = 0.101$ for 10 498 unique reflections, 7747 having $F_o^2 > 3\sigma(F_o^2)$. The centrosymmetric $[Pb_2(WSe_4)_4]^{4-}$ ion is composed of two independent W atoms tetrahedrally coordinated by Se atoms and one independent Pb atom in a distorted octahedral coordination of Se atoms. Tetrakis(tetraphenylphosphonium) bis(μ -tetraselenidotungstato-*Se, Se', μ -Se'*)-bis[(tetraselenidotungstato-*Se, Se'*)stannate], $[PPh_4]_4[Sn_2(WSe_4)_4]$, is isostructural with $[PPh_4]_4[Pb_2(WSe_4)_4]$, $M_r = 3593.7$, triclinic, $P\bar{1}$, $a = 12.981$ (3), $b = 14.412$ (6), $c = 14.644$ (7) Å, $\alpha = 105.26$ (4), $\beta = 99.79$ (3), $\gamma = 94.56$ (3)°, $V = 2583$ (1) Å³, $Z = 1$, $D_x = 2.31$ g cm⁻¹, $\lambda(Cu K\alpha_1) = 1.54056$ Å, $T = 153$ K.

Introduction. The reaction of various divalent metal cations with the tetrathiometalates MoS_4^{2-} or WS_4^{2-} affords the bis(thiometalate) anions $[M'(MS_4)_2]^{2-}$ ($M' = Fe, Co, Ni, Pd, Zn, \text{etc.}$, $M = Mo, W$) (Müller, Diemann, Jostes & Bögge, 1981). In contrast, the reaction of Sn^{2+} with WS_4^{2-} affords $[Sn_2(WS_4)_4]^{4-}$ (Müller, Paulat-Böschchen, Krebs & Dornfeld, 1976).

Until quite recently, little related chemistry of the $MoSe_4^{2-}$ and WSe_4^{2-} ions was known (Ansari & Ibers, 1990). It was recently found that reaction of WSe_4^{2-} with Ni^{2+} affords not only $[Ni(WSe_4)_2]^{2-}$ {analogous to $[Ni(WS_4)_2]^{2-}$ } but also $[Ni(Se_2)-$

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$(WSe_4)]^{2-}$ for which there is no known sulfur analogue (Ansari, Chau, Mahler & Ibers, 1989). Thus the chemistry of the soluble selenides need not parallel that of the sulfides. In the present study, the reactions of Pb^{2+} and Sn^{2+} with WSe_4^{2-} were investigated. These reactions afford the $[M_2(WSe_4)_4]^{4-}$ ($M = Pb, Sn$) species.

Experimental. All reactions were carried out under a dry dinitrogen atmosphere with the use of standard Schlenk techniques. Solvents were dried and distilled before use. $[PPh_4]_4[M_2(WSe_4)_4]$ ($M = Pb, Sn$) was prepared by the reaction in DMF of $PbCl_2$ or $SnCl_2$ with $[NH_4]_2[WSe_4]$ in the presence of $[PPh_4]Br$. The ⁷⁷Se NMR spectrum of a DMF solution of the Pb complex exhibits resonances at δ 1653, 1563, 964, 938 and 894 (relative to Me_2Se at δ 0). These may be assigned to terminal W—Se at δ 1653 and 1563 and bridging W—Se at δ 964, 938 and 894 (Wardle, Mahler, Chau & Ibers, 1988). Such an assignment is consistent with a structure for an anion analogous to that of $[Sn_2(WS_4)_4]^{4-}$.

A tabular crystal $0.081 \times 0.139 \times 0.061$ mm was mounted in the cold stream ($T = 153$ K) of an Enraf–Nonius CAD-4 diffractometer. Cell constants were obtained from 23 reflections in the range $25 < \theta(Cu K\alpha_1) < 26^\circ$. Intensity data were collected by the ω - 2θ technique in the range $3 \leq \theta(Cu K\alpha_1) \leq 75^\circ$ ($-16 \leq h \leq 0$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$). The basic scan speed was 4° min^{-1} in ω but reflections having $F_o^2 < 3\sigma(F_o^2)$ were scanned more slowly up to a maximum time of 60 s. The scan range was 0.5° in ω below $K\alpha_1$ to 0.5° in ω above $K\alpha_2$. Six standards (081, 081, 643, 308, 600, 101) chosen from diverse regions of reciprocal space were monitored every 3 h during data collection and remained constant within

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters for $[\text{PPh}_4]_4[\text{Pb}_2(\text{WSe}_4)_4]$

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} \rho_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
Pb	0.148114 (35)	0.085562 (29)	0.118175 (29)	2.00 (1)
W(1)	0.364729 (38)	0.227204 (32)	0.311431 (32)	1.72 (1)
W(2)	0.017196 (37)	-0.165498 (31)	0.087057 (31)	1.51 (1)
Se(1)	0.471861 (98)	0.354614 (82)	0.299786 (86)	2.45 (3)
Se(2)	0.41091 (11)	0.209509 (92)	0.462742 (84)	2.73 (3)
Se(3)	0.188427 (91)	0.256783 (78)	0.281940 (80)	2.12 (3)
Se(4)	0.374230 (98)	0.085846 (79)	0.190823 (82)	2.30 (3)
Se(5)	0.085657 (88)	-0.116824 (75)	-0.032983 (74)	1.88 (3)
Se(6)	0.07098 (10)	-0.041569 (80)	0.229202 (77)	2.33 (3)
Se(7)	-0.165612 (88)	-0.188081 (79)	0.041734 (79)	2.01 (3)
Se(8)	0.076881 (95)	-0.305418 (78)	0.106979 (86)	2.30 (3)
P(1)	-0.28710 (20)	-0.54648 (17)	0.08167 (17)	1.38 (6)
P(2)	-0.80568 (22)	0.22455 (20)	0.49251 (18)	1.90 (7)
C(1)	-0.16790 (80)	-0.55550 (72)	0.16066 (62)	1.7 (2)
C(2)	-0.14460 (89)	-0.64560 (77)	0.17363 (80)	2.3 (3)
C(3)	-0.05373 (91)	-0.64739 (85)	0.23842 (76)	2.6 (3)
C(4)	0.01083 (84)	-0.56457 (87)	0.28964 (73)	2.5 (3)
C(5)	-0.0141 (13)	-0.47517 (95)	0.27802 (87)	2.0 (4)
C(6)	-0.10240 (78)	-0.46981 (73)	0.21337 (76)	1.9 (3)
C(7)	-0.26298 (77)	-0.51747 (59)	-0.02313 (62)	1.7 (2)
C(8)	-0.34153 (76)	-0.54596 (72)	-0.10551 (72)	1.9 (3)
C(9)	-0.32550 (95)	-0.52200 (85)	-0.18747 (74)	2.8 (3)
C(10)	-0.2330 (10)	-0.46877 (80)	-0.18770 (83)	2.8 (3)
C(11)	-0.15541 (97)	-0.43971 (83)	-0.10807 (82)	2.6 (3)
C(12)	-0.16840 (90)	-0.46479 (71)	-0.02364 (72)	2.2 (3)
C(13)	-0.34372 (75)	-0.44932 (70)	0.15179 (68)	1.6 (2)
C(14)	-0.36669 (86)	-0.45619 (74)	0.24046 (70)	2.0 (3)
C(15)	-0.40604 (90)	-0.37830 (86)	0.29681 (61)	2.5 (3)
C(16)	-0.42017 (80)	-0.29630 (77)	0.27007 (72)	2.3 (3)
C(17)	-0.39633 (91)	-0.28885 (80)	0.18444 (79)	2.5 (3)
C(18)	-0.35750 (76)	-0.36527 (72)	0.12529 (72)	1.8 (3)
C(19)	-0.37153 (79)	-0.65914 (73)	0.04561 (71)	1.7 (3)
C(20)	-0.33625 (84)	-0.73981 (77)	-0.01155 (71)	1.9 (3)
C(21)	-0.3975 (10)	-0.82886 (76)	-0.04026 (74)	2.5 (3)
C(22)	-0.4932 (10)	-0.83618 (80)	-0.01119 (81)	2.8 (3)
C(23)	-0.52913 (89)	-0.75828 (82)	0.04350 (78)	2.5 (3)
C(24)	-0.46930 (82)	-0.66961 (75)	0.07198 (69)	1.9 (3)
C(25)	0.94350 (83)	0.21624 (81)	0.53371 (72)	2.1 (3)
C(26)	1.01407 (95)	0.21794 (95)	0.47302 (87)	3.1 (4)
C(27)	1.11891 (94)	0.2098 (11)	0.50448 (82)	3.4 (4)
C(28)	1.15383 (96)	0.20293 (95)	0.59545 (91)	3.0 (4)
C(29)	1.08526 (95)	0.20090 (90)	0.65533 (80)	2.9 (3)
C(30)	0.97813 (56)	0.20753 (68)	0.62522 (67)	2.0 (3)
C(31)	0.72960 (82)	0.18170 (76)	0.56654 (70)	2.1 (3)
C(32)	0.6714 (12)	0.09029 (91)	0.5342 (10)	3.7 (4)
C(33)	0.6163 (13)	0.05656 (86)	0.5934 (11)	4.5 (5)
C(34)	0.6160 (12)	0.1132 (11)	0.68420 (97)	4.1 (4)
C(35)	0.67382 (99)	0.20560 (94)	0.71720 (76)	2.9 (3)
C(36)	0.72870 (97)	0.23843 (88)	0.65914 (81)	2.6 (3)
C(37)	0.78291 (89)	0.34780 (71)	0.49705 (67)	2.1 (3)
C(38)	0.85486 (98)	0.40644 (82)	0.46955 (80)	2.6 (3)
C(39)	0.8343 (11)	0.49865 (84)	0.46572 (88)	3.3 (4)
C(40)	0.7461 (11)	0.53320 (88)	0.49404 (82)	3.1 (4)
C(41)	0.6722 (11)	0.47479 (85)	0.52050 (79)	3.1 (3)
C(42)	0.6915 (11)	0.38124 (83)	0.52030 (82)	2.9 (3)
C(43)	0.76829 (90)	0.15491 (81)	0.36913 (77)	2.4 (3)
C(44)	0.69845 (89)	0.18535 (83)	0.30503 (81)	2.7 (3)
C(45)	0.6707 (11)	0.13335 (98)	0.20918 (88)	3.4 (4)
C(46)	0.7173 (10)	0.0512 (11)	0.17777 (84)	4.0 (4)
C(47)	0.7858 (12)	0.0185 (10)	0.23962 (90)	4.5 (4)
C(48)	0.8143 (10)	0.0701 (10)	0.33623 (90)	4.0 (4)

counting statistics. In the solution and refinement of the structure, procedures standard in this laboratory were employed (Waters & Ibers, 1977). The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares methods. Upon correction for absorption, 11171 reflections were reduced to a set of 10498 unique reflections after averaging ($R = 0.031$). An analytical absorption correction was applied; minimum and maximum transmission factors were 0.182 and 0.399. In the final cycle of full-matrix least-squares refinement on F^2 all non-H atoms were allowed to vibrate anisotropically,

while phenyl H atoms were idealized [$\text{C}-\text{H} = 0.95 \text{ \AA}$; $B_{\text{H}} = B_{\text{eq}}(\text{C}) + 1 \text{ \AA}^2$]. This final cycle involved 10498 reflections and 550 variables. It converged to $R(F^2)$ and $wR(F^2)$ values of 0.075 and 0.101. The value of $R(F)$ for the 7747 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.047. $w = 1/\sigma^2(F^2)$, $\Delta/\sigma_{\text{max}} = 0.8$ and $\Delta\rho_{\text{min,max}} = -2.9, 3.0 \text{ e \AA}^{-3}$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A and 2.3.1). All calculations were performed on a Stellar GS1000 computer with the use of local programs.

Examination of a single crystal of $[\text{PPh}_4]_4[\text{Sn}_2(\text{WSe}_4)_4]$ on an Enraf-Nonius CAD-4 diffractometer led to cell constants in good agreement with those of $[\text{PPh}_4]_4[\text{Pb}_2(\text{WSe}_4)_4]$; we conclude that the compounds are isostructural.

Discussion. The final atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms of $[\text{PPh}_4]_4[\text{Pb}_2(\text{WSe}_4)_4]$ are given in Table 1.* A sketch of the anion is in Fig. 1. The $[\text{Pb}_2(\text{WSe}_4)_4]^{4-}$ anion, which has a crystallographically imposed center of symmetry, consists of two distorted PbSe_6 edge-shared octahedra. There are two crystallographically distinct W atoms in this

* Lists of anisotropic thermal parameters, H-atom parameters and structure amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53904 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

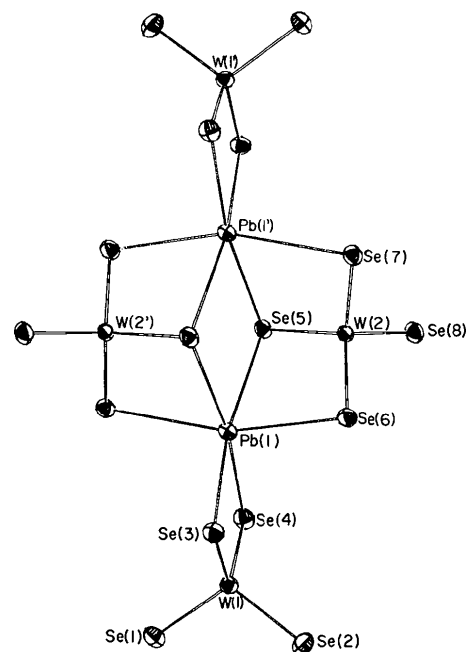


Fig. 1. A drawing of the $[\text{Pb}_2(\text{WSe}_4)_4]^{4-}$ anion showing the labeling scheme and the 50% probability ellipsoids.

Table 2. Selected bond distances (Å) and angles (°) for [PPh₄]₄[Pb₂WSe₄]₄

Pb—W(1)	3.679 (1)	W(1)—Se(4)	2.352 (1)
Pb—W(2)	3.769 (1)	W(2)—Se(5)	2.345 (1)
Pb—W(2)'	3.872 (1)	W(2)—Se(6)	2.325 (1)
Pb—Se(3)	2.904 (1)	W(2)—Se(7)	2.324 (1)
Pb—Se(4)	2.942 (1)	W(2)—Se(8)	2.283 (1)
Pb—Se(5)	3.124 (1)	P(1)—C(1)	1.770 (10)
Pb—Se(5)'	3.185 (1)	P(1)—C(7)	1.795 (10)
Pb—Se(6)	2.984 (1)	P(1)—C(13)	1.794 (10)
Pb—Se(7)	3.121 (1)	P(1)—C(19)	1.803 (10)
W(1)—Se(1)	2.285 (1)	P(2)—C(25)	1.809 (10)
W(1)—Se(2)	2.298 (1)	P(2)—C(31)	1.785 (11)
W(1)—Se(3)	2.343 (1)	P(2)—C(37)	1.813 (10)
		P(2)—C(43)	1.794 (11)
Se(3)—Pb—Se(4)	79.23 (3)	Se(1)—W(1)—Se(4)	110.69 (5)
Se(3)—Pb—Se(5)	169.32 (4)	Se(2)—W(1)—Se(3)	110.33 (5)
Se(3)—Pb—Se(5)'	96.71 (3)	Se(2)—W(1)—Se(4)	112.41 (5)
Se(3)—Pb—Se(6)	93.40 (3)	Se(3)—W(1)—Se(4)	105.12 (4)
Se(3)—Pb—Se(7)	98.10 (3)	Se(5)—W(2)—Se(6)	107.33 (4)
Se(4)—Pb—Se(5)	102.97 (3)	Se(5)—W(2)—Se(7)	107.76 (4)
Se(4)—Pb—Se(5)'	170.90 (3)	Se(5)—W(2)—Se(8)	111.51 (5)
Se(4)—Pb—Se(6)	96.13 (4)	Se(6)—W(2)—Se(7)	110.46 (5)
Se(4)—Pb—Se(7)	98.91 (3)	Se(6)—W(2)—Se(8)	109.75 (5)
Se(5)—Pb—Se(5)'	82.54 (3)	Se(7)—W(2)—Se(8)	109.98 (4)
Se(5)—Pb—Se(6)	76.01 (3)	W(1)—Se(3)—Pb	88.36 (4)
Se(5)—Pb—Se(6)	92.22 (3)	W(1)—Se(4)—Pb	87.29 (4)
Se(5)—Pb—Se(7)	91.92 (3)	W(2)—Se(5)—Pb	85.89 (3)
Se(5)′—Pb—Se(7)	73.46 (3)	W(2)—Se(5)—Pb'	87.51 (4)
Se(6)—Pb—Se(7)	162.53 (4)	W(2)—Se(6)—Pb	89.55 (4)
Se(1)—W(1)—Se(2)	108.65 (5)	W(2)—Se(7)—Pb'	89.43 (4)
Se(1)—W(1)—Se(3)	109.59 (5)	Pb—Se(5)—Pb'	97.46 (3)

structure. Each is tetrahedrally coordinated by four Se atoms. One WSe₄ tetrahedron is edge shared to a PbSe₆ octahedron while the other contributes the Se vertices that are edge shared between PbSe₆ octahedra. The distances (Table 2) from Pb to the doubly bridging Se are 2.904 (1) to 3.121 (1) Å, shorter than those to the triply bridging Se atoms 3.124 (1)–

3.185 (1) Å. The angles around Pb vary from 73.46 (3) to 170.90 (3)°; the distortion in part probably arises from the lone-pair electrons on the Pb²⁺ center. The Se—W(1)—Se angles range from 105.12 (4) to 112.41 (5)°, showing slightly wider variation than the Se—W(2)—Se angles [107.33 (4) to 111.51 (5)°]. The distances from W(2) atoms to the triply bridging Se(5) atoms [2.345 (1) Å] are slightly longer than those to the doubly bridging Se(6) [2.325 (1) Å] or Se(7) [2.324 (1) Å] atoms. The terminal W—Se distances of 2.283 (1)–2.289 (1) Å are comparable with those of 2.281 (1)–2.292 (1) Å in the W₂Se₆²⁻ (Lu, Ansari & Ibers, 1989) and 2.281 (1)–2.288 (1) Å in the NiWSe₆²⁻ anions (Ansari, Chau, Mahler & Ibers, 1989).

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Structure of Dichloro[1-(4-methoxyphenyl)iminomethyl-2-naphtholato]-diphenyltin(IV)

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Abstract. [SnCl₂(C₁₈H₁₅NO₂)₂(C₆H₅)₂], C₄₈H₄₀Cl₂N₂O₄Sn, *M_r* = 898.46, triclinic, *P* $\bar{1}$, *a* = 10.291 (1), *b* =

12.332 (1), *c* = 8.895 (1) Å, α = 70.62 (1), β = 80.30 (1), γ = 72.62 (1)°, *V* = 1013 (1) Å³, *Z* = 1, *D_m* = 1.451 (floatation), *D_x* = 1.473 Mg m⁻³, λ (Mo *K*α) = 0.71069 Å, μ = 0.728 mm⁻¹, *F*(000) = 458, *T* =

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