Table IV. Atomic Coordinates (×10⁴) for $(PPh_4)_2[W_3S_{10}]\cdot{}^1/_2CH_2Cl_2$ (**4**)

	x	*y*	*z*
W(1)	2606 (1)	847 (1)	3485 (1)
W(2)	4590 (1)	327 (1)	2447 (1)
W(3)	6017 (1)	–939 (1)	1365 (1)
S(1)	1296 (6)	142 (5)	3764 (3)
S(2)	2411 (7)	2174 (5)	4088 (3)
S(3)	4550 (5)	–584 (4)	3565 (3)
S(4)	2348 (5)	1553 (4)	2408 (2)
S(5)	6237 (5)	–1595 (4)	2459 (3)
S(6)	4091 (5)	611 (4)	1298 (2)
S(7)	7431 (6)	–361 (5)	1118 (3)
S(8)	6634 (9)	–2830 (7)	1097 (4)
S(9)	5513 (10)	–1569 (9)	426 (4)
S(10)	5410 (6)	1465 (5)	2554 (3)
P(1)	1758 (5)	6194 (4)	985 (2)
P(2)	2389 (5)	6653 (4)	4492 (2)
C(1)	4289 (12)	5580 (8)	914 (6)
C(2)	5556	4787	902
C(3)	5900	3602	881
C(4)	4977	3209	871
C(5)	3709	4002	883
C(6)	3366	5188	904
C(7)	2040 (9)	4857 (10)	2191 (6)
C(8)	1603	4484	2771
C(9)	314	4941	2877
C(10)	–537	5772	2404
C(11)	–100	6146	1825
C(12)	1189	5688	1719
C(13)	1526 (13)	7958 (10)	1696 (5)
C(14)	1480	9041	1776
C(15)	1548	9772	1228
C(16)	1661	9420	600
C(17)	1708	8337	520
C(18)	1640	7606	1068
C(19)	1360 (9)	5564 (9)	–207 (6)
C(20)	639	5680	–762
C(21)	–591	6563	–842
C(22)	–1100	7331	–367
C(23)	–378	7215	188
C(24)	852	6331	268
C(25)	3543 (12)	6901 (7)	3337 (6)
C(26)	4267	6501	2789
C(27)	4833	5308	2722
C(28)	4675	4516	3202
C(29)	3950	4917	3750
C(30)	3384	6110	3818
C(31)	3066 (12)	5109 (11)	5640 (6)
C(32)	3037	4195	6074
C(33)	2342	3623	5908
C(34)	1677	3965	5307
C(35)	1706	4879	4872
C(36)	2401	5451	5039
C(37)	–148 (12)	8129 (11)	4608 (4)
C(38)	–1378	8798	4364
C(39)	–1655	8871	3696
C(40)	–702	8276	3273
C(41)	528	7607	3517
C(42)	805	7534	4184
C(43)	2436 (10)	7817 (11)	5533 (6)
C(44)	2963	8318	5923
C(45)	4062	8401	5730
C(46)	4634	7982	5148
C(47)	4108	7482	4759
C(48)	3009	7399	4951
C(49)[a]	8987 (54)	2200 (45)	2326 (25)
Cl(1)[a]	8343 (15)	1498 (12)	2132 (7)
Cl(2)[a]	8227 (18)	3436 (15)	2641 (8)

[a] Occupancy factor 0.5.

presence of trinuclear M_3 units[14b,e] or a chainlike arrangement of the metal atoms[14c,d] in the noncrystalline materials, which contain (beside the S_2^{2-} groups) only bridging sulfide ligands.[14b–d]

The decrease of the average oxidation state of tungsten from +6 to +5.33 accompanied by the corresponding balanced increase for sulfur from –2 to –1.8 in **1** applies in a similar way to the formation of WS_3 and explains why the stoichiometry of a W^{VI} compound is retained during the decomposition of $[WS_4]^{2-}$.

During a preparation of **2** without addition of manganese chloride a compound $(PPh_4)_2[W_3S_{10}]\cdot{}^1/_2CH_2Cl_2$ (**4**) could also be isolated; however, reproduction of this experiment turned out to be rather difficult. Initially we wanted to obtain a W–S–Mn cluster compound from the reaction with manganese chloride, which however yielded the new $[W_3S_{10}]^{2-}$ anion. For the reason unknown to us, the presence of manganese chloride is essential for the reproducibility of the preparation of **2**. Notably there exists precedence in literature for the necessicity of manganese chloride to prepare W–S clusters,[15,16] and the reaction did not proceed in this direction even when manganese chloride was substituted by magnesium chloride.

The formation of $[W_3S_9]^{2-}$ is always a competitive reaction; on the other hand, small amounts of **1** may also be present during all preparations of $[W_3S_9]^{2-}$ salts.[17]

Note Added in Proof. The corresponding WOS_4^{2-} ligand has been found in the species $[Br_2FeS_2WO(S_2)]^{2-}$.[18]

Supplementary Material Available: For **2**–**4**, crystal data (Table S1), bond lengths (Table S2), bond angles (Table S3), anisotropic thermal parameters (Table S4), H atom and isotropic thermal parameters (Table S5), and isotropic parameters for non-hydrogen atoms (Table S6) (7 pages); tables of calculated and observed structure factors (67 pages). Ordering information is given on any current masthead page.

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(15) Manoli, J. M.; Potvin, C.; Sécheresse, F. *Inorg. Chem.* **1987**, *21*, 340.
(16) Manoli, J. M.; Potvin, C. *Inorg. Chim. Acta* **1987**, *133*, 27.
(17) For a possible mechanism for the formation of the thermodynamically more stable $[W_3S_9]^{2-}$, see ref 1.
(18) Müller, A.; et al. *Monatsh. Chem.* **1989**, *120*, 367.

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Synthesis and Characterization of $[PPh_4]_2[W_2Se_6]$

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An extensive solution chemistry of Mo/S anions has been developed, mainly by Coucouvanis and co-workers.[1,2] Among those anions containing two Mo atoms, various isomers of $Mo_2S_n^{2-}$, n = 6–12, are known, as is some of the chemistry of their interconversions.[1] The recent synthesis of the first oligomeric W/Se anions[3] makes possible the study of their reaction chemistry. Here we report the preparation of the new $W_2Se_6^{2-}$ ion from the reaction of BH_4^- with two isomers of $W_2Se_{10}^{2-}$, namely the symmetrical isomer $[(Se_3)SeW(\mu\text{-}Se)_2WSe(Se_3)]^{2-}$ and the unsymmetrical one $[(Se_4)SeW(\mu\text{-}Se)_2WSe(Se_2)]^{2-}$. Although, at this stage in the development of the chemistry of soluble selenide anions of W and Mo, the closest similarities are between the W/Se and Mo/S systems, the chemistry reported here differs from that found in the Mo/S system. Thus, the starting symmetrical $W_2Se_{10}^{2-}$ anion has no known Mo/S counterpart and the reaction of the unsymmetrical $Mo_2S_{10}^{2-}$ anion with BH_4^- affords the $Mo_2S_9^{2-}$ ion and not the $Mo_2S_6^{2-}$ ion.[1]

Experimental Section

$[PPh_4]_2[W_2Se_{10}]$ was prepared by the literature method.[3] All reactions were carried out with the use of standard Schlenk-line techniques under a dry dinitrogen atmosphere. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The IR spectra were recorded on a Perkin-Elmer 283 spectrometer. Electronic spectra were obtained on a Perkin-Elmer 330 UV-vis spectrophotometer. The ^{77}Se NMR spectra of DMF solutions were recorded on a Varian XLA-400 spectrometer with use of a 10-mm tunable probe

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(1) Hadjikyriacou, A. I.; Coucouvanis, D. *Inorg. Chem.* **1987**, *26*, 2400–2408 and references therein.
(2) For a recent review see: Müller, A. *Polyhedron* **1986**, *5*, 323–340.
(3) Wardle, R. W. M.; Bhaduri, S.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 1747–1755.

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Table I. Crystallographic Data for $[P(C_6H_5)_4]_2[W_2Se_6]$

$C_{48}H_{40}P_2Se_6W_2$	mol wt = 1520.26
a = 10.228 (4) Å	$C_i^1 - P\bar{1}$
b = 9.903 (2) Å	t = −155 °C
c = 13.027 (5) Å	λ = 1.540 562 Å
α = 72.01 (3)°	ρ_{calcd} = 2.160 g/cm^3
β = 76.09 (3)°	μ = 155 cm^{-1}
γ = 70.38 (2)°	trans coeff = 0.387–0.478
V = 1168 (1) Å^3	$R(F_o)$ = 0.044
Z = 1	$R_w(F_o)$ = 0.055

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[PPh_4]_2[W_2Se_6]$

atom	x	y	z	B, Å^2
W(1)	−0.061134 (44)	0.151620 (45)	−0.057003 (35)	2.32 (1)
Se(1)	−0.09888 (12)	0.35318 (11)	0.007485 (91)	3.26 (3)
Se(2)	−0.13448 (11)	0.21555 (11)	−0.222993 (84)	2.91 (3)
Se(3)	−0.186073 (97)	−0.01510 (11)	0.072407 (80)	2.61 (3)
P	0.45755 (24)	0.34892 (25)	0.32730 (19)	2.40 (7)
C(11)	0.50393 (95)	0.5043 (10)	0.23040 (78)	2.5 (3)
C(12)	0.4606 (10)	0.5609 (11)	0.12754 (74)	2.7 (3)
C(13)	0.5036 (11)	0.6789 (11)	0.05493 (81)	3.1 (3)
C(14)	0.5903 (12)	0.7378 (12)	0.08265 (88)	3.6 (4)
C(15)	0.6353 (12)	0.6811 (13)	0.18274 (94)	4.1 (4)
C(16)	0.5907 (12)	0.5666 (12)	0.25708 (89)	3.8 (4)
C(21)	0.33305 (94)	0.4008 (10)	0.44148 (75)	2.5 (3)
C(22)	0.2855 (10)	0.5463 (11)	0.45221 (84)	3.0 (3)
C(23)	0.1813 (11)	0.5789 (11)	0.53950 (87)	3.3 (3)
C(24)	0.1273 (10)	0.4723 (13)	0.61355 (91)	3.6 (4)
C(25)	0.1747 (12)	0.3277 (13)	0.60492 (97)	3.9 (4)
C(26)	0.2774 (11)	0.2927 (12)	0.51820 (89)	3.4 (3)
C(31)	0.37624 (94)	0.26293 (98)	0.26813 (76)	2.5 (3)
C(32)	0.4420 (10)	0.1227 (10)	0.24981 (80)	2.9 (3)
C(33)	0.3700 (12)	0.0602 (11)	0.20604 (87)	3.5 (4)
C(34)	0.2379 (11)	0.1360 (11)	0.18034 (80)	3.0 (3)
C(35)	0.1744 (11)	0.2756 (12)	0.19732 (85)	3.4 (3)
C(36)	0.2423 (10)	0.3398 (10)	0.24136 (85)	3.0 (3)
C(41)	0.6174 (10)	0.22148 (98)	0.37089 (80)	2.7 (3)
C(42)	0.7312 (10)	0.1911 (11)	0.28864 (82)	3.0 (3)
C(43)	0.85652 (97)	0.0898 (11)	0.31543 (85)	3.1 (3)
C(44)	0.8693 (11)	0.0190 (11)	0.42370 (92)	3.4 (3)
C(45)	0.7581 (11)	0.0521 (11)	0.50524 (85)	3.3 (3)
C(46)	0.63210 (98)	0.1512 (10)	0.47915 (74)	2.6 (3)

and a deuterium lock. All chemical shifts are referenced to Me_2Se at δ 0 ppm. The detailed experimental procedures are described elsewhere.[3]

$[PPh_4]_2[W_2Se_6]$. $[PPh_4]_2[W_2Se_{10}]$ (0.50 g, 0.27 mmol) and $NaBH_4$ (0.25 g, 6.60 mmol) were dissolved in DMF (10 mL), and the mixture was stirred at 20 °C for 24 h. During this time the solution changed in color from black to red-brown. This solution was filtered, and methanol (20 mL) was added. $[PPh_4]_2[W_2Se_6]$ was deposited overnight as deep brown crystals in 50% yield. These crystals were suitable for X-ray structural analysis. IR (KBr): 320, 295 cm^{-1}. UV-vis (DMF): 320 (16 000), 340 (sh), 415 (6840), 480 (11 040), 520 (sh) nm. ^{77}Se NMR (DMF): δ 1559, 591 ppm (J_{W-Se} = 99 Hz). Anal. Calcd for $C_{48}H_{40}P_2Se_6W_2$: C, 37.92; H, 2.65; P, 4.08; Se, 31.16; W, 24.19. Found: C, 36.96; H, 2.66; P, 4.18; Se, 30.73; W, 21.26.

The crystal structure of $[PPh_4]_2[W_2Se_6]$ was determined by methods standard in this laboratory.[4] Crystal data and experimental details are given in Table I. Final positional parameters of all non-hydrogen atoms are given in Table II. Selected bond distances and bond angles for the $W_2Se_6^{2-}$ anion are given in Table III.[5] Additional data are given in the supplementary material.

Results and Discussion

Reactions of the BH_4^- ion with an approximately 1:1 mixture of the symmetrical and unsymmetrical isomers of $W_2Se_{10}^{2-}$ in DMF affords the $W_2Se_6^{2-}$ ion in about 50% yield. Under diverse conditions, which include change of cation, recrystallization, warming, or refluxing, the two isomers of $W_2Se_{10}^{2-}$ have failed to interconvert. Thus, we presume that in the present instance each has reacted with the BH_4^- ion to afford the $W_2Se_6^{2-}$ ion. This chemistry differs from that of the Mo/S system where the unsymmetrical $Mo_2S_{10}^{2-}$ ion reacts with BH_4^- to afford $Mo_2S_9^{2-}$.[1] Indeed, $Mo_2S_6^{2-}$ is prepared by the reaction of PPh_3 with Mo_2S_{10}/S_{12}^{2-} or $Mo_2S_8^{2-}$.[1]

Table III. Bond Distances (Å) and Bond Angles (deg) in the $W_2Se_6^{2-}$ Anion

W(1)-Se(1)	2.281 (1)	Se(1)-W(1)-Se(2)	112.11 (4)
W(1)-Se(2)	2.292 (1)	Se(1)-W(1)-Se(3)	109.38 (4)
W(1)-Se(3)	2.421 (1)	Se(1)-W(1)-Se(3′)	110.28 (4)
W(1)-Se(3′)	2.427 (1)	Se(2)-W(1)-Se(3)	108.87 (4)
W(1)-W(1′)	2.899 (1)	Se(2)-W(1)-Se(3′)	109.49 (4)
		Se(3)-W(1)-Se(3′)	106.55 (3)
		W(1)-Se(3)-W(1′)	73.45 (3)

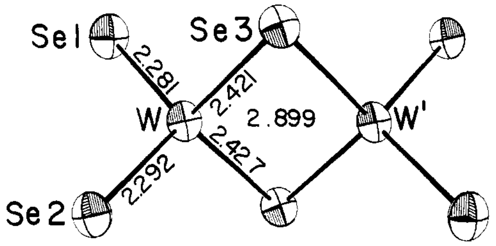

Figure 1. Drawing of the $W_2Se_6^{2-}$ anion showing the labeling scheme, important bond distances, and vibrational ellipsoids at the 50% probability level. Estimated standard deviations on the bond distances are 0.001 Å.

The spectroscopy of the $W_2Se_6^{2-}$ ion is fully compatible with the X-ray structure. Thus, the ^{77}Se NMR resonance at 1559 ppm is well within the range expected for a terminal Se atom bound to a W center while the resonance at 591 ppm is near the range of 1000–600 ppm expected for "W-bound" Se atoms.[3,6,7] The observation of W–Se coupling (J = 99 Hz) is consistent with this resonance being from a bridging Se atom. Although the oligomeric W/Se anions show no characteristic UV–vis bands, the $W_2Se_6^{2-}$ ion does. These bands are presumably of the charge-transfer type ($\pi(Se) \rightarrow d(W)$) and arise from the WSe_4 moiety.

The $W_2Se_6^{2-}$ anion (Figure 1) is very similar in structure to the $Mo_2S_6^{2-}$ ion. The W–Se distances are about 0.13 Å longer than the corresponding Mo–S distances. The $W_2Se_6^{2-}$ ion has a crystallographically imposed center of symmetry and may be thought of as made up of two edge-sharing WSe_4 tetrahedra. The dihedral angle between the W–Se(1)–Se(2) and W–Se(3)–Se(3′) planes is 89.91°.

The W–W distances in $W_2Se_9^{2-}$,[3] $W_2Se_{10}^{2-}$,[3] and $W_2Se_6^{2-}$ (all formally W^V anions) are the same at 2.897 (2), 2.903 (2), and 2.899 (1) Å, being characteristic of W–W bonds containing two d electrons. Direct comparisons of the W–Se bond lengths within these three ions is made difficult by the cocrystallization of $W_2Se_9^{2-}/W_2Se_{10}^{2-}$ and of $W_2Se_{10}^{2-}$ (two isomers). The W–Se terminal distances of 2.281 (1) and 2.292 (1) Å are comparable with those of 2.281 (1) and 2.288 (1) Å in $Ni(Se_2)(WSe_4)^{2-}$,[7] an anion of W^{VI}.

In the series $Mo_2Q_6^{2-}$ (M = Mo, W.; Q = S, Se, Te), only the $Mo_2S_6^{2-}$ and $W_2Se_6^{2-}$ ions are known. These are formed in rather different reactions, and we anticipate that the reaction chemistry of these ions themselves will show interesting differences.

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Supplementary Material Available: Tables of crystallographic data, H atom positions, and anisotropic thermal parameters (2 pages); a table of observed and calculated structure amplitudes (16 pages). Ordering information is given on any current masthead page.

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(4) See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

(5) The geometry of the PPh_4 cation is normal. The P–C distances range from 1.786 (10) to 1.794 (10) Å and average 1.793 (5) Å. The C–C distances range from 1.362 (15) to 1.405 (12) Å and average 1.389 (3) Å. The standard deviation of a single observation, as estimated from the 24 C–C values averaged, is 0.011 Å, less than that for a single observation estimated from the inverse matrix. Thus, the estimated standard deviations in this structure determination are reliable.

(6) Wardle, R. W. M.; Mahler, C. H.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 2790–2795.

(7) Ansari, M. A.; Chau, C.-N.; Mahler, C. H.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 650–654.