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New Oligomeric Tungsten–Chalcogenide Anions

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Upon acidification with acetic acid and precipitation from methanol solution with PPh_4^+, the WSe_4^{2-} anion affords $[PPh_4]_2[(W_3Se_9)_{0.46}(W_3Se_8O)_{0.54}]$. This compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.085$ (5) Å, $b = 10.666$ (4) Å, $c = 13.407$ (3) Å, $\alpha = 87.22$ (2)°, $\beta = 86.30$ (3)°, $\gamma = 84.11$ (3)°, and $Z = 1$. The $W_3Se_9^{2-}$ ion shows square-pyramidal coordination of Se atoms about the central W atom and tetrahedral coordination about the outer W atoms. The anion WS_4^{2-} when acidified with H_2SO_4 yields $W_3S_8^{2-}$, which may be isolated as its PPN^+ salt. $[PPN]_2[W_3S_8]$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.548$ (2) Å, $b = 15.175$ (5) Å, $c = 22.181$ (5) Å, $\alpha = 104.90$ (2)°, $\beta = 90.80$ (2)°, $\gamma = 110.31$ (2)°, and $Z = 2$. The central W atom has approximately square-planar coordination of S atoms, and the outer W atoms have tetrahedral coordination. Heating WSe_4^{2-} in acetonitrile yields a complex mixture of anions that includes $W_3Se_9^{2-}$, $W_2Se_9^{2-}$, and $W_2Se_{10}^{2-}$. Addition of elemental Se to the reaction mixture affords two isomers of $W_2Se_{10}^{2-}$ and other dimers in smaller concentrations. $[PPh_4]_2[(W_2Se_9)_{0.66}(W_2Se_{10})_{0.34}]$ ($P\bar{1}$, $a = 10.556$ (5) Å, $b = 11.480$ (6) Å, $c = 22.324$ (11) Å, $\alpha = 76.90$ (2)°, $\beta = 86.58$ (2)°, $\gamma = 79.28$ (2)°, $Z = 2$) and $[PPh_4]_2[W_2Se_{10}]$ (asymmetric/symmetric isomer ratio 0.73/0.27, $P\bar{1}$, $a = 10.678$ (2) Å, $b = 11.492$ (3) Å, $c = 22.392$ (5) Å, $\alpha = 77.20$ (2)°, $\beta = 86.94$ (2)°, $\gamma = 79.81$ (2)°, $Z = 2$) crystallize from these mixtures and have in common the $(W_2(\mu\text{-}Se)_2Se_2)^{2-}$ core. $W_2Se_9^{2-}$ and the two isomeric $W_2Se_{10}^{2-}$ anions differ only in the chain lengths of the chelating polyselenides. In these structures the WSe_3 and WSe_4 rings have conformations similar to cyclobutane and cyclopentane, respectively. Detailed structural data are reported. The ^{77}Se NMR data for the selenides in DMF solution are presented and indicate that the solid-state structures remain intact in solution.

Introduction

In recent years the synthesis and characterization of soluble transition-metal sulfides has become an active area of research.[2] Molybdenum and tungsten sulfides have been studied as models of biological systems[3] and industrial catalytic processes.[4] A number of these compounds are produced in simple internal redox reactions.[5] Species such as $W_2S_{11}H^-$,[6] $W_3S_9^{2-}$,[7] and $W_4S_{12}^{2-}$,[8] for example, have resulted from the acidification or heating reactions of the WS_4^{2-} ion. Yet there are more species to be isolated and characterized, as evidenced by the recent synthesis of the $W_3S_8^{2-}$ ion.[9] We anticipated that the internal redox processes involved in the formation of selenides would be different from those of the sulfides. For this reason we believed that the chemistry of the selenides would not parallel that of the sulfides. Surprisingly, there are very few examples of soluble transition-metal selenides.[2,10] Here we provide details on the synthesis and characterization of four new oligomeric W–Se anions, namely $W_3Se_9^{2-}$, $W_2Se_9^{2-}$, and $W_2Se_{10}^{2-}$ (two isomers),[11] as well as the $W_3S_8^{2-}$ ion.[9]

Experimental Section

All solvents and reagents were used as obtained. Reactions were routinely carried out with the use of standard Schlenk-line procedures under an atmosphere of dry dinitrogen. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. $[NH_4]_2[WS_4]$ was prepared by the method of Corleis,[12] and $[NH_4]_2[WSe_4]$ was purchased from Alfa Products, Danvers, MA.

$[PPh_4]_2[(W_3Se_9)_{0.46}(W_3Se_8O)_{0.54}]$. CH_3CO_2H (1.0 mL, 17.5 mmol) was added rapidly to a stirred solution of $[NH_4]_2[WSe_4]$ (0.10 g, 0.19 mmol) in methanol (10 mL). The resulting dark red solution was stirred for 0.25 h and then filtered. Addition of $[PPh_4]Cl$ (0.20 g, 0.53 mmol) in methanol (2.0 mL) gave $[PPh_4]_2[(W_3Se_9)_{0.46}(W_3Se_8O)_{0.54}]$ (0.03 g, 25%) as a brown solid. Deep red platelike crystals suitable for X-ray crystallographic analysis were grown from a CH_2Cl_2 solution onto which hexane had been layered. Anal. Calcd for $C_{48}H_{40}O_{0.54}P_2Se_{8.46}W_3$ (a 0.46:0.54 mixture of $W_3Se_9^{2-}$ and $W_3Se_8O^{2-}$ as derived from the X-ray crystallographic results): C, 30.2; H, 2.1; P, 3.3; Se, 35.0; W, 28.9. Found: C, 30.7; H, 2.1; P, 3.0; Se, 36.1; W, 27.9. The presence of oxygen was confirmed qualitatively by Auger spectroscopy on a crystalline sample cleaned by argon ion sputtering. Longer reaction times (1–3 h) increased the proportion of $W_3Se_8O^{2-}$ in the mixture.

$[PPh_4]_2[W_3Se_9]$. $[NH_4]_2[WSe_4]$ (0.20 g, 0.37 mmol) and $[PPh_4]Cl$ (0.15 g, 0.40 mmol) were dissolved in acetonitrile (10 mL). This mixture was refluxed with stirring for 0.5 h. During this time the solution darkened and $[PPh_4]_2[W_3Se_9]$ (0.08 g, 35%) was deposited as a dark brown crystalline solid. Anal. Calcd for $C_{48}H_{40}P_2Se_9W_3$: C, 29.7; H, 2.1; P, 3.2; Se, 36.6; W, 28.4. Found: C, 29.5; H, 2.3; P, 3.1; Se, 34.9; W, 27.1.

$[PPh_4]_2[(W_2Se_9)_{0.66}(W_2Se_{10})_{0.34}]$. $[NH_4]_2[WSe_4]$ (0.20 g, 0.37 mmol) and $[PPh_4]Cl$ (0.15 g, 0.40 mmol) were dissolved in DMF (10 mL). This mixture was stirred and heated to 85 °C for 0.5 h. During this time the solution darkened to red-black. The resulting solution was cooled to room temperature, and upon addition of excess diethyl ether $[PPh_4]_2[W_3Se_9]$ (0.08 g, 35%) was deposited as a dark brown crystalline solid. When the supernatant solution was cooled to −15 °C for a period of 8 h, red-black needles of $[PPh_4]_2[(W_2Se_9)_{0.66}(W_2Se_{10})_{0.34}]$ (0.15 g, 45%) were obtained. These crystals were suitable for X-ray structural analysis. Anal. Calcd for $C_{48}H_{40}P_2Se_{9.34}W_2$ (a 0.66:0.34 mixture of $W_2Se_9^{2-}$ and $W_2Se_{10}^{2-}$ as derived from the X-ray crystallographic results): C, 32.3; H, 2.2; P, 3.5; Se, 41.4; W, 20.6. Found: C, 32.5; H, 2.2; P, 3.3; Se, 38.9; W, 20.3. Addition of black selenium (<0.37 mmol) to the reaction mixture increased the yield of $[PPh_4]_2[(W_2Se_9)_{0.66}(W_2Se_{10})_{0.34}]$ relative to $[PPh_4]_2[W_3Se_9]$.

$[PPh_4]_2[W_2Se_{10}]$ (Two Isomers). $[NH_4]_2[WSe_4]$ (0.20 g, 0.37 mmol) and $[PPh_4]Cl$ (0.15 g, 0.40 mmol) were dissolved in acetonitrile (10 mL). Black selenium (0.12 g, 1.52 mmol) was added, and the mixture was stirred under reflux for 0.5 h. $[PPh_4]_2[W_2Se_{10}]$ (two isomers, 0.26 g, 76%) was deposited as a black crystalline solid. Black platelike crystals suitable for X-ray crystallography were obtained by layering diethyl ether on a DMF solution. Anal. Calcd for $C_{48}H_{40}P_2Se_{10}W_2$: C, 31.4; H, 2.2; P, 3.4; Se, 43.0; W, 20.0. Found: C, 31.1; H, 2.1; P, 3.2; Se, 41.4; W, 18.4.

$[PPN]_2[W_3S_8]$ (PPN = Bis(triphenylphosphine)nitrogen(1+)). $[NH_4]_2[WS_4]$ (0.60 g, 1.72 mmol) was stirred with H_2SO_4 (0.20 g, 2.04 mmol) in methanol (50 mL) for 4 h. The color of the solution turned from yellow to dark red. The solution was filtered through Celite, and

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(2) (a) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934–955. (b) Hadjikyriacou, A. I.; Coucouvanis, D. *Inorg. Chem.* **1987**, *26*, 2400–2408.

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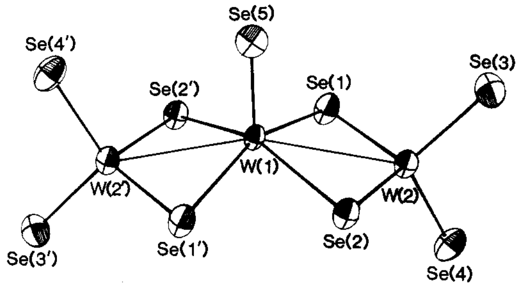

Figure 1. Structure of the $W_3Se_9^{2-}$ ion. In Figures 1–5 the 50% probability vibrational ellipsoids are shown.

a methanol (5 mL) solution of [PPN]Cl (0.60 g, 1.05 mmol) was added to the filtrate. Crude $[PPN]_2[W_3S_8]$ was precipitated as a red-brown solid. This solid was dissolved in CH_2Cl_2 (2 mL), and the solution was subjected to thin-layer chromatography with CH_3CN/CH_2Cl_2 (130 mL/40 mL) as the eluent. Two bands, an orange followed by a purple one, were obtained. The former band was selected; the material was extracted in CH_2Cl_2 and crystallized by the addition of Et_2O. Crystals suitable for X-ray diffraction were grown by layering hexane on a CH_2Cl_2 solution. Anal. Calcd for $C_{72}H_{60}N_2P_4S_8W_3$: C, 45.9; H, 3.2; S, 13.6; W, 29.3. Found: C, 44.5; H, 3.1; S, 16.5; W, 28.3. From the intensity of the IR band at 440 cm^{-1}, the amount of $W_3S_8^{2-}$ in the crude product was probably less than 10%.

Physical Measurements. IR spectra were obtained as KBr pellets on a Perkin-Elmer 283 spectrophotometer. The qualitative oxygen analysis by Auger spectroscopy was made with the use of a Physical Electronics 590 scanning Auger microprobe.

The ^{77}Se NMR spectra were recorded, ^2H-locked, with the use of a Varian XLA-400 spectrometer (VXR-4000 data system with VAX software, version 6.1d) at room temperature. Saturated solutions (0.05–0.15 g in 2 mL DMF) were prepared in 10 mm o.d. precision glass, round-bottom NMR tubes (Wilmad) with the use of 4 mm o.d. inserts containing the external standard (Ph_2Se_2/C_6D_6, δ 460 ppm). The operating frequency was 76.28 MHz, and the spectra were referenced to Me_2Se at 0 ppm. For $[NH_4]_2[WSe_4]$/DMF the pulse width for a 90° pulse angle was 80 μs and T_1 was measured as 0.6 s with the FIRFT pulse sequence. The delay time was set to 0 s since it was assumed that the primary mechanism for relaxation was chemical shift anisotropy. A pulse width of 25 μs and an acquisition time of 0.146 s were chosen to be the optimum parameters for acquisition. It was thus assumed that all of the compounds have similar T_1 values.

Crystallographic Studies. Intensity data were collected from single crystals with the use of Picker FACS-1 and Enraf-Nonius CAD4 diffractometers equipped with graphite-monochromated Mo Kα ($\lambda(K\alpha_1)$ = 0.7093 Å) radiation sources. The data collection parameters are given in Table I. All data were collected at −150 °C.

In the solution and refinement of these structures, procedures standard in this laboratory were employed.[13] The structures were solved by Patterson and Fourier techniques and refined by full-matrix least-squares methods. For $[PPh_4]_2[(W_3Se_9)_{0.46}(W_3Se_8O)_{0.54}]$ the occupancies of Se(5) and O(1) were estimated as 0.5 and 0.5. They were then refined with the restriction that their sum be equal to unity. This refinement resulted in occupancies of 0.46 (2) and 0.54 (2), respectively. In the final stages of refinement of $[PPh_4]_2[(W_2Se_9)_{0.66}(W_2Se_{10})_{0.34}]$ the occupancies of atoms Se(9A), Se(9B), and Se(10B) were refined. The sum of the occupancies of atoms Se(9A) and Se(9B) was set to unity and the occupancies of atoms Se(9B) and Se(10B) were linked. This refinement resulted in occupancies of 0.66 (1), 0.34 (1), and 0.34 (1), respectively. The disorder in the metal–selenide rings in the $[PPh_4]_2[W_2Se_{10}]$ (two isomers) system was treated in a similar way, resulting in occupancies of 0.73 (1) and 0.27 (1) for the asymmetric and symmetric isomers, respectively. The final cycles of refinement for all of the structural analyses were carried out on F_o^2. Prior to these final cycles H atoms were included at calculated positions (C–H = 0.95 Å). The results of the refinements are given in Table I. The final positional parameters and equivalent isotropic thermal parameters of all non-hydrogen atoms are given in Tables II–V. Additional crystallographic data are available as supplementary material.

Results

Structures. The compound $[PPh_4]_2[(W_3Se_9)_{0.46}(W_3Se_8O)_{0.54}]$ may be considered as the cocrystallization of the $W_3Se_9^{2-}$ (Figure 1) and $W_3Se_8O^{2-}$ ions with occupancies of 0.46 (2) and 0.54 (2), respectively. The material has a crystallographically imposed center of symmetry. Accordingly, the W(1)Se(5)/O(1) moiety (O(1) not shown) is distributed equally over two sites. It is similar to the analogous C_{2v} sulfide structure ($W_3S_9^{2-}/W_3S_8O^{2-}$) reported by Sĕcheresse et al.[14] The $W_3Se_9^{2-}$ ion has square-pyramidal coordination about the central W atom and tetrahedral coordination around the terminal W atoms.

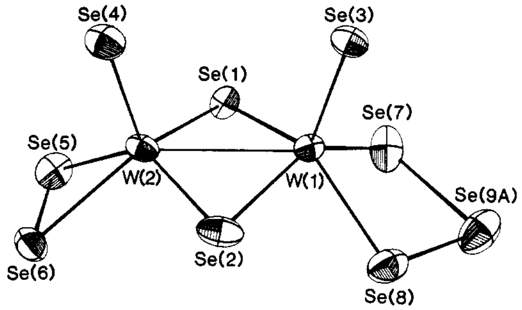

Figure 2. Structure of the $W_2Se_9^{2-}$ ion.

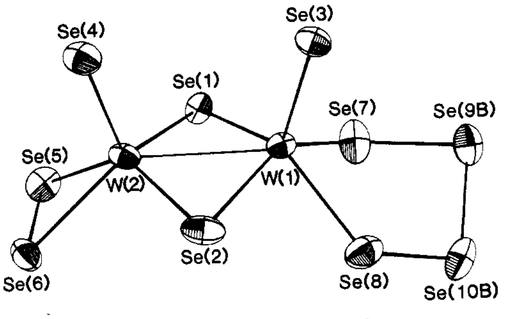

Figure 3. Structure of the asymmetric $W_2Se_{10}^{2-}$ ion.

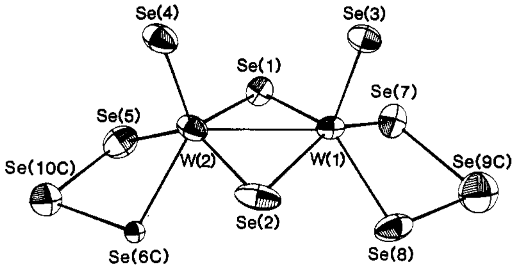

Figure 4. Structure of the symmetric $W_2Se_{10}^{2-}$ ion.

The structure of $[PPh_4]_2[(W_2Se_9)_{0.66}(W_2Se_{10})_{0.34}]$ has $W_2Se_9^{2-}$ and $W_2Se_{10}^{2-}$ ions present in the same triclinic cell with occupancies of 0.66 (1) and 0.34 (1), respectively. The $W_2Se_9^{2-}$ ion (Figure 2) has approximate C_s symmetry with square-pyramidal coordination about the W atoms. In addition to the (Se)W(μ-Se)$_2$W(Se) core that has bridging selenide ions, Se_2^{2-} and Se_3^{2-} groups are also coordinated to the W atoms to give three- and four-membered rings. The analogous sulfide ion $W_2S_9^{2-}$ is unknown. The minor isomer, having three- and five-membered metal–selenium rings, in $[PPh_4]_2[(W_2Se_9)_{0.66}(W_2Se_{10})_{0.34}]$ is identical with the unsymmetrical, major isomer in the $[PPh_4]_2[W_2Se_{10}]$ structure (Figure 3), and its structure closely resembles that of the analogous sulfide ion $W_2S_{10}^{2-}$.[15] The minor isomer of $W_2Se_{10}^{2-}$ (Figure 4, 27%), which contains two four-membered metal–selenium rings, has no known sulfide analogue. Thus, in the $W_2Se_{10-x}^{2-}$ (x = 0, 1) ions the core atoms, (Se)W(μ-Se)$_2$W(Se), have almost identical fractional coordinates in similar triclinic cells. The structures differ only in their ring sizes. During the

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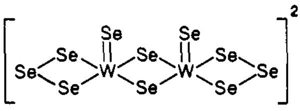
Table I. Crystal Data and Experimental Details

compd	$[PPN]_2[W_3S_8]$	$[PPh_4]_2[(W_3Se_9)_{0.46}(W_3Se_8O)_{0.54}]$	$[PPh_4]_2[(W_2Se_9)_{0.66}(W_2Se_{10})_{0.34}]$	$[PPh_4]_2[W_2Se_{10}]$ (2 isomers, 0.73/0.27)
formula	$C_{72}H_{60}N_2P_4S_8W_3$	$C_{48}H_{40}O_{0.54}P_2Se_{8.46}W_3$	$C_{48}H_{40}P_2Se_{9.34}W_2$	$C_{48}H_{40}P_2Se_{10}W_2$
machine	CAD4	CAD4	FACS-1	CAD4
fw	1884	1907	1784	1836
a, Å	11.548 (2)	9.085 (5)	10.556 (5)	10.678 (2)
b, Å	15.175 (5)	10.666 (4)	11.480 (6)	11.492 (3)
c, Å	22.181 (5)	13.407 (3)	22.324 (11)	22.392 (5)
α, deg	104.90 (2)	87.22 (2)	76.90 (2)	77.20 (2)
β, deg	90.80 (2)	86.30 (3)	86.58 (2)	86.94 (2)
γ, deg	110.31 (2)	84.11 (3)	79.28 (2)	79.81 (2)
V, Å^3	3500	1288	2588	2637
Z	2	1	2	2
d_{calcd}, g/cm^3	1.788	2.420	2.254	2.312
space group	C_i^1–$P\bar{1}$	C_i^1–$P\bar{1}$	C_i^1–$P\bar{1}$	C_i^1–$P\bar{1}$
cryst shape	needle bounded by $\{10\bar{1}\}$, $\{001\}$, $\{010\}$	irregular plate bounded mainly by $\{110\}$, $(1\bar{1}\bar{1})^a$	parallelepiped bounded by $\{001\}$, $\{011\}$, $\{100\}$	plate bounded by $\{011\}$, $\{001\}$, $\{\bar{1}02\}$, (100)
cryst dimens, mm	0.45 × 0.06 × 0.04	0.23 × 0.22 × 0.04	0.25 × 0.13 × 0.09	0.60 × 0.27 × 0.06
cryst vol, mm^3	0.0013	0.0015	0.0031	0.0098
μ, cm^{-1}	53.9	125.1	108.9	113.8
transmission factors (analytical method)	0.700–0.819	0.139–0.608	0.244–0.425	0.093–0.487
takeoff angle, deg	3.0	2.5	2.0	3.0
receiving aperture, mm (horizontal slit × vertical slit)	3.0 × 1.8	3.0 × 3.0	5.0 × 4.5	3.0 × 3.0
scan type	ω–2θ	ω–2θ	2θ	ω
scan speed, deg/min^b	4.12	2.06	1.0	2.06
scan range, deg	0.7	1.0	1.8^c	1.0
data collected	$\pm h,\pm k,\pm l$; $1.2 \le \theta \le 20.0°$	$\pm h,\pm k,\pm l$; $1.0 \le \theta \le 25.0°$	$+h,\pm k,\pm l$; $1.0 \le \theta \le 23.0°$	$+h,\pm k,\pm l$; $1.0 \le \theta \le 23.0°$
p factor	0.05	0.04	0.04	0.04
no. of unique data	6512	4522	7324	7280
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	4060	2912	4700	5132
no. of variables	802	289	348	317
R on F_o^2	0.064	0.082	0.117	0.122
R_w on F_o^2	0.106	0.102	0.159	0.169
R on F_o ($F_o^2 > 3\sigma(F_o^2)$)	0.037	0.046	0.067	0.074
R_w on F_o ($F_o^2 > 3\sigma(F_o^2)$)	0.050	0.047	0.075	0.081
error in observn of unit wt, e^2	0.92	1.14	1.55	2.31

[a] Other smaller faces were estimated as $(1\bar{2}\bar{3})$, $(\bar{2}3\bar{5})$, $(\bar{7},11,5)$, $(\bar{1},6,24)$, and $(2,\bar{3},10)$. [b] Reflections with $\sigma(I)/I > 0.33\underset{\smile}{3}$ were rescanned. [c] 1.0° below Kα_1 to 0.8° above Kα_2.

final stages of refinement of $[PPh_4]_2[(W_2Se_9)_{0.66}(W_2Se_{10})_{0.34}]$, two additional peaks were found close to atom Se(6). These peaks form a four-membered ring with atoms W(2) and Se(5). This suggests the possible presence of the ions $W_2Se_{10}^{2-}$ (symmetric isomer, **1**) and $W_2Se_{11}^{2-}$ (**2**) (≈11% and ≈5%, respectively) as additional cocrystallates.



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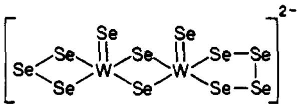

2

The $W_3S_8^{2-}$ ion (Figure 5) has pseudo-D_{2h} symmetry with tetrahedral coordination around the terminal W atoms. The central W atom has square-planar coordination of S atoms with a very slight tetrahedral distortion. Deviations (Å) from the best weighted least-squares plane: W(2), −0.0032 (6); S(3), −0.179 (4); S(4), 0.188 (4); S(5), 0.167 (4); S(6), −0.210 (4).

The W–W bond lengths for the di- and trimeric chalcogenide anions[16,17] and $W_2Cl_8Se_3^{2-}$[18] are compared in Table VI. In $W_2Se_9^{2-}$ and $W_2Se_{10}^{2-}$ this distance is significantly shorter than in $W_3S_9^{2-}$ or $W_3Se_9^{2-}$ since there are two d electrons available for W–W bonding rather than one. This trend has been noted previously.[9] For anions with the same number of d electrons per bond, the selenides show a slightly increased W–W bond length over the sulfides and the anion $W_2Cl_8Se_3^{2-}$, which has both Se^{2-} and η^2-Se_2^{2-} bridging ligands.

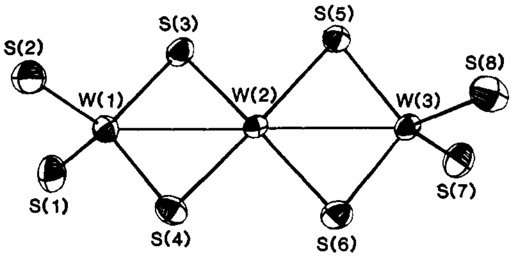

Figure 5. Structure of the $W_3S_8^{2-}$ ion.

In $W_3S_8^{2-}$ (Table VII) three different types of W–S bonds, those around the central W atom, those involving terminal W and bridging S atoms, and the terminal ones, with average values of 2.344 (3), 2.237 (3), and 2.152 (6) Å, respectively, are observed. The last two values are very close to the corresponding distances in bis(tetrathiotungstato) complexes, such as $Ni(WS_4)_2^{2-}$ (2.232 (4) and 2.151 (3) Å)[2], and in the WS_4^{2-} anion (2.177 Å).[2] A similar trend is seen in the bond lengths in $W_3Se_9^{2-}$ (Table VIII; 2.52 (4), 2.370 (7), and 2.274 (4) Å). The distances around atom W(2) are similar to the average W–Se distance in WSe_4^{2-} (2.317 (7) Å).[19] The bond from the central W atom, W(1), to the unique

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(17) $W_2S_{12}^{2-}$: Cohen, S. A.; Stiefel, E. I. *Inorg. Chem.* **1985**, *24*, 4657–4662.

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Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for $[PPN]_2[W_3S_8]$

atom	*x*	*y*	*z*	B_{eq},[a] Å^2	atom	*x*	*y*	*z*	B_{eq},[a] Å^2
W(1)	0.075318 (57)	0.231214 (46)	−0.279680 (29)	2.32 (2)	C(225)	0.7309 (12)	0.3120 (11)	0.73369 (64)	2.1 (6)
W(2)	0.069590 (52)	0.423865 (44)	−0.262037 (28)	1.62 (2)	C(226)	0.6821 (12)	0.3500 (10)	0.69254 (72)	2.6 (5)
W(3)	0.050677 (54)	0.612461 (45)	−0.243269 (28)	2.09 (2)	C(231)	0.5216 (12)	0.4506 (10)	0.62885 (63)	1.9 (5)
S(1)	−0.07981 (41)	0.09786 (31)	−0.29056 (21)	3.7 (2)	C(232)	0.4074 (13)	0.4517 (10)	0.64636 (63)	2.1 (5)
S(2)	0.24508 (38)	0.20154 (33)	−0.28183 (20)	3.7 (2)	C(233)	0.3943 (13)	0.5359 (11)	0.68177 (65)	2.2 (6)
S(3)	0.08064 (35)	0.34005 (29)	−0.18852 (18)	2.6 (1)	C(234)	0.4991 (13)	0.62384 (97)	0.70125 (58)	1.9 (5)
S(4)	0.06151 (35)	0.30310 (29)	−0.35471 (18)	2.7 (1)	C(235)	0.6166 (13)	0.6230 (11)	0.68378 (63)	2.2 (6)
S(5)	0.11058 (34)	0.55387 (28)	−0.17081 (17)	2.4 (1)	C(236)	0.6277 (13)	0.5378 (11)	0.64829 (69)	2.4 (6)
S(6)	0.02342 (37)	0.49891 (29)	−0.33451 (18)	2.9 (1)	C(311)	−0.2604 (13)	0.17955 (95)	0.00611 (70)	2.1 (5)
S(7)	−0.12055 (40)	0.63378 (33)	−0.22368 (21)	3.9 (2)	C(312)	−0.2242 (14)	0.1218 (11)	−0.04376 (68)	2.7 (6)
S(8)	0.19187 (41)	0.75042 (31)	−0.24392 (20)	4.0 (2)	C(313)	−0.1285 (13)	0.0888 (11)	−0.03338 (71)	2.6 (6)
P(1)	0.34954 (32)	0.18603 (27)	0.48523 (18)	1.9 (1)	C(314)	−0.0717 (12)	0.1143 (10)	0.02635 (73)	2.2 (6)
P(2)	0.53623 (32)	0.33864 (28)	0.58806 (17)	1.9 (1)	C(315)	−0.1079 (13)	0.1694 (11)	0.07686 (69)	2.5 (6)
P(3)	−0.36769 (34)	0.23658 (29)	−0.00810 (18)	2.2 (1)	C(316)	−0.2011 (13)	0.2024 (10)	0.06647 (67)	2.2 (6)
P(4)	−0.56452 (35)	0.27020 (29)	0.06748 (18)	2.2 (1)	C(321)	−0.4680 (13)	0.1578 (11)	−0.07938 (73)	2.6 (6)
N(1)	0.40900 (94)	0.26843 (77)	0.54930 (48)	1.9 (4)	C(322)	−0.4858 (13)	0.1879 (11)	−0.13056 (70)	2.3 (6)
N(2)	−0.43723 (93)	0.25602 (83)	0.05232 (47)	1.9 (4)	C(323)	−0.5664 (15)	0.1232 (13)	−0.18295 (70)	3.5 (7)
C(111)	0.2470 (12)	0.2205 (11)	0.44169 (67)	1.8 (5)	C(324)	−0.6309 (14)	0.0283 (11)	−0.18372 (72)	2.7 (6)
C(112)	0.1787 (12)	0.1585 (10)	0.38715 (67)	2.0 (6)	C(325)	−0.6138 (14)	−0.0030 (11)	−0.13200 (76)	2.8 (6)
C(113)	0.0952 (13)	0.1808 (12)	0.35505 (71)	2.8 (6)	C(326)	−0.5331 (15)	0.0597 (13)	−0.08095 (75)	3.3 (7)
C(114)	0.0768 (13)	0.2683 (12)	0.38004 (71)	2.5 (6)	C(331)	−0.2713 (12)	0.3480 (10)	−0.02548 (64)	1.8 (5)
C(115)	0.1482 (13)	0.3355 (11)	0.43495 (74)	2.4 (6)	C(332)	−0.2587 (14)	0.4357 (12)	0.01516 (68)	2.8 (6)
C(116)	0.2329 (12)	0.3097 (10)	0.46663 (60)	1.6 (5)	C(333)	−0.1780 (13)	0.5228 (11)	0.00410 (75)	2.6 (6)
C(121)	0.4592 (12)	0.1574 (10)	0.43506 (64)	1.7 (5)	C(334)	−0.1063 (12)	0.5207 (11)	−0.04423 (76)	2.5 (6)
C(122)	0.5306 (13)	0.1106 (11)	0.45285 (65)	2.3 (6)	C(335)	−0.1199 (13)	0.4304 (12)	−0.08392 (72)	2.8 (6)
C(123)	0.6245 (13)	0.0955 (11)	0.41896 (79)	3.1 (6)	C(336)	−0.1999 (13)	0.3452 (11)	−0.07572 (70)	2.5 (6)
C(124)	0.6427 (13)	0.1233 (11)	0.36343 (73)	2.8 (6)	C(411)	−0.6720 (12)	0.2365 (10)	−0.00119 (63)	1.8 (5)
C(125)	0.5715 (15)	0.1669 (12)	0.34504 (74)	3.5 (7)	C(412)	−0.6573 (13)	0.3002 (11)	−0.03794 (74)	2.8 (6)
C(126)	0.4777 (13)	0.1860 (10)	0.38169 (74)	2.4 (6)	C(413)	−0.7318 (13)	0.2713 (12)	−0.09330 (70)	2.2 (6)
C(131)	0.2535 (12)	0.07333 (95)	0.50023 (64)	1.5 (5)	C(414)	−0.8190 (15)	0.1772 (13)	−0.11557 (67)	3.0 (7)
C(132)	0.1908 (12)	0.0814 (10)	0.55235 (69)	2.1 (5)	C(415)	−0.8319 (13)	0.1135 (11)	−0.08048 (78)	2.9 (6)
C(133)	0.1051 (13)	−0.0035 (12)	0.56309 (72)	2.6 (6)	C(416)	−0.7566 (13)	0.1424 (11)	−0.02339 (65)	2.1 (6)
C(134)	0.0832 (12)	−0.0923 (11)	0.52049 (74)	2.4 (6)	C(421)	−0.5431 (13)	0.3927 (10)	0.11148 (66)	2.0 (5)
C(135)	0.1450 (13)	−0.1002 (11)	0.46758 (73)	2.8 (6)	C(422)	−0.6335 (13)	0.4302 (10)	0.10920 (66)	2.5 (6)
C(136)	0.2291 (13)	−0.0159 (11)	0.45739 (65)	2.1 (6)	C(423)	−0.6184 (14)	0.5220 (11)	0.14685 (78)	3.0 (6)
C(211)	0.6619 (13)	0.3657 (10)	0.54086 (65)	2.1 (5)	C(424)	−0.5105 (15)	0.5758 (12)	0.18806 (75)	3.3 (6)
C(212)	0.7654 (15)	0.3413 (10)	0.54816 (67)	2.7 (6)	C(425)	−0.4193 (14)	0.5366 (11)	0.18879 (66)	2.6 (6)
C(213)	0.8603 (12)	0.3591 (11)	0.50985 (67)	2.5 (6)	C(426)	−0.4329 (13)	0.4464 (11)	0.15253 (72)	2.6 (6)
C(214)	0.8461 (13)	0.3978 (10)	0.46103 (66)	2.4 (6)	C(431)	−0.6368 (12)	0.19662 (97)	0.11731 (67)	2.0 (5)
C(215)	0.7431 (13)	0.4240 (11)	0.45304 (72)	2.9 (6)	C(432)	−0.7484 (14)	0.1972 (10)	0.13734 (64)	2.3 (6)
C(216)	0.6523 (12)	0.4059 (11)	0.49198 (70)	2.6 (6)	C(433)	−0.8008 (15)	0.1411 (12)	0.17830 (73)	3.4 (7)
C(221)	0.5846 (12)	0.2904 (10)	0.64489 (60)	1.7 (5)	C(434)	−0.7441 (16)	0.0901 (12)	0.20133 (74)	3.5 (7)
C(222)	0.5364 (13)	0.1881 (11)	0.64003 (71)	2.8 (6)	C(435)	−0.6295 (16)	0.0917 (11)	0.18207 (70)	3.2 (6)
C(223)	0.5822 (15)	0.1507 (11)	0.67985 (72)	2.8 (6)	C(436)	−0.5775 (14)	0.1429 (10)	0.13911 (65)	2.5 (6)
C(224)	0.6806 (14)	0.2117 (14)	0.72645 (71)	3.4 (7)					

[a] In this and in ensuing tables $B_{eq} = {}^{8}/_{3}\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

apical Se atom, Se(5), is exceptionally short (2.154 (9) Å), as is the equivalent W–S bond (2.070 (10) Å) in the analogous sulfide, $W_3S_9^{2-}$.[16]

The W–Se distances (Table IX) from the W atoms to the bridging Se^{2-} ligands in $W_2Se_9^{2-}$ and $W_2Se_{10}^{2-}$ have average values of 2.45 (5) and 2.45 (4) Å, respectively, and are slightly longer than those distances in $W_2Cl_8Se_3^{2-}$ (mean 2.40 (2) Å).[18] The average W–Se (terminal) distances of 2.25 (1) and 2.251 (4) Å for $W_2Se_9^{2-}$ and $W_2Se_{10}^{2-}$, respectively, are comparable to that involving the terminal W atoms in $W_3Se_9^{2-}$ (2.274 (4) Å). The Se–Se distances in the Se_2^{2-} ligands (2.340 (4) Å in $W_2Se_9^{2-}$ and 2.348 (4) Å in $W_2Se_{10}^{2-}$) are very similar to this distance in $Ir(Se_2)(dppe)_2^+$ (2.312 (3) Å),[20] $Os(Se_2)(CO)_2(PPh_3)_2$ (2.321 (1) Å),[21] and Na_2Se_2 (2.38 (5) Å).[22] The mean Se–Se distance in the Se_3^{2-} ligand is 2.42 (2) Å in $W_2Se_9^{2-}$. This distance is similar to that for uncomplexed Se_3^{2-} (2.383 (2) Å) in K_2Se_3.[23] For the Se_4^{2-} ligand, bonding to W gives rise to a reversal in the alternation of the bond lengths. For Se_4^{2-},[24] Se(external)–Se(internal) is 2.312 (3) Å and Se(internal)–Se(internal) is 2.397 (4) Å, but for the WSe_4 ring, these distances are 2.322 (9) Å (mean) and 2.281 (5) Å, respectively. Block and Allmann have proposed that M(dπ)–S(dπ) interactions cause this effect in the Mo–S system.[25] The puckered nature of the WSe_3 and WSe_4 rings is similar to that of their organic counterparts cyclobutane and cyclopentane. The geometry of the four-membered rings in $W_2Se_9^{2-}$ and $W_2Se_{10}^{2-}$ (minor isomer) is similar to that in $TiS_3(C_5Me_5)_2$[26] although their ring-puckering angles differ ($W_2Se_9^{2-}$, 23°; $W_2Se_{10}^{2-}$, 25 and 35°; $TiS_3(C_5Me_5)_2$, 49°).

The striking difference between the chemistry of metal sulfides and metal selenides highlighted here in the structure of the four-membered rings possibly results from the difference in the atomic radii of S and Se atoms. The larger Se atom more readily supports the smaller bond angles needed to form three- and four-membered rings.

Synthesis. Oligomeric tungsten–chalcogenide anions are produced on acidifying or heating the simple tetrathio- or tetraselenidotungstates according to the following schemes. The ratios

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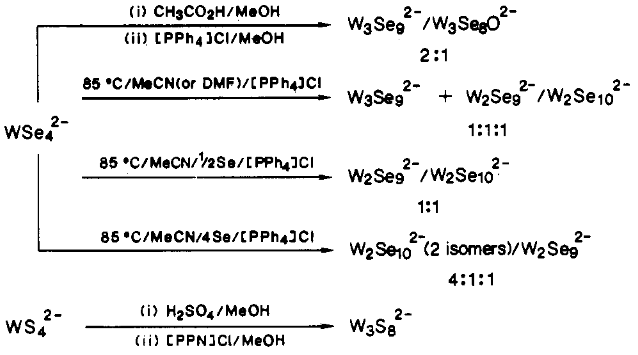
Table III. Positional Parameters and Equivalent Isotropic Thermal Parameters for $[PPh_4]_2[(W_3Se_9)_{0.46}(W_3Se_8O)_{0.54}]$

atom	x	y	z	B_{eq}, Å^2
W(1)	−0.03938 (11)	−0.019234 (86)	−0.026705 (62)	1.72 (3)
W(2)	0.200393 (61)	−0.007871 (46)	−0.185259 (36)	2.10 (1)
Se(1)	0.03631 (15)	0.16554 (11)	−0.131258 (84)	2.33 (3)
Se(2)	0.18895 (16)	−0.16602 (12)	−0.054877 (86)	2.81 (3)
Se(3)	0.12188 (17)	−0.08061 (12)	−0.327615 (92)	3.22 (4)
Se(4)	0.43377 (17)	0.05031 (15)	−0.21183 (11)	3.81 (4)
Se(5)	−0.19678 (82)	−0.09034 (62)	−0.11748 (56)	3.2 (2)
O(1)	−0.1578 (66)	−0.0756 (48)	−0.0763 (48)	7 (1)
P(1)	0.41977 (34)	0.45721 (28)	0.28344 (21)	1.88 (8)
C(10)	0.3984 (14)	0.3156 (11)	0.36348 (85)	2.3 (3)
C(11)	0.4988 (13)	0.2796 (12)	0.43190 (83)	2.4 (3)
C(12)	0.4787 (15)	0.1817 (11)	0.49836 (92)	2.8 (4)
C(13)	0.3515 (16)	0.1221 (12)	0.49360 (97)	3.3 (4)
C(14)	0.2491 (15)	0.1561 (11)	0.42398 (98)	2.9 (4)
C(15)	0.2716 (14)	0.2538 (11)	0.35784 (91)	2.7 (3)
C(20)	0.3011 (12)	0.5877 (10)	0.33387 (78)	1.8 (3)
C(21)	0.2956 (13)	0.7056 (11)	0.28584 (79)	2.3 (3)
C(22)	0.2073 (14)	0.8092 (11)	0.32592 (90)	2.6 (3)
C(23)	0.1239 (14)	0.7886 (12)	0.41431 (87)	2.8 (4)
C(24)	0.1306 (13)	0.6725 (12)	0.46524 (77)	2.5 (3)
C(25)	0.2225 (13)	0.5692 (11)	0.42393 (78)	2.1 (3)
C(30)	0.3668 (14)	0.4256 (12)	0.16031 (88)	2.6 (3)
C(31)	0.2709 (15)	0.5065 (12)	0.10777 (83)	2.9 (4)
C(32)	0.2386 (19)	0.4743 (13)	0.01295 (98)	4.1 (5)
C(33)	0.2980 (17)	0.3639 (15)	−0.02943 (92)	3.9 (4)
C(34)	0.3906 (15)	0.2844 (15)	0.0246 (10)	4.1 (4)
C(35)	0.4237 (17)	0.3099 (15)	0.1214 (10)	4.6 (5)
C(40)	0.6095 (12)	0.4916 (11)	0.28183 (71)	1.7 (3)
C(41)	0.6493 (14)	0.6018 (11)	0.31945 (83)	2.4 (3)
C(42)	0.7950 (14)	0.6262 (10)	0.31736 (83)	2.3 (3)
C(43)	0.9044 (13)	0.5357 (12)	0.27963 (84)	2.5 (3)
C(44)	0.8688 (14)	0.4269 (13)	0.24325 (89)	2.9 (4)
C(45)	0.7224 (14)	0.4035 (11)	0.24546 (83)	2.4 (3)

were estimated from approximate line intensities in the ^{77}Se NMR spectra.



The acidification reactions are considered to follow the stoichiometry

$$3WQ_4^{2-} + 4H^+ \rightarrow W_3Q_{9-x}^{2-} + 2H_2Q + (1 + x)Q\downarrow \quad (1)$$

$$Q = S,\ x = 1;\ Q = Se,\ x = 0$$

IR data[9] suggest that several products are formed in the synthesis of $W_3S_8^{2-}$ although, by following the stoichiometry in (1), one finds that the formation of other anions such as $W_3S_9^{2-}$, $W_3S_8O^{2-}$, and $W_4S_{12}^{2-}$ is minimized. Attempts to precipitate one of these thiotungstate anions selectively with the use of different tetraalkylammonium salts have not been successful. However, pure $[PPN]_2[W_3S_8]$ may be obtained by chromatographic separation followed by fractional crystallization by slow diffusion. The acidification reaction of WSe_4^{2-} to give $W_3Se_9^{2-}$ occurs more rapidly, although the product is contaminated with $W_3Se_8O^{2-}$. The oxygen may originate from slow hydrolysis; no attempt was made to dry the solvents. In contrast, other acidification reactions of WS_4^{2-} have yielded a variety of dimeric ($W_2S_8OH_3^-$ (**3**),[27] $W_2S_{11}H^-$ (**4**),[6] and $W_2S_{11}^{2-}$ (**5**)),[28] trimeric ($W_3S_9^{2-}$ [7] and $W_3S_8O^{2-}$ [14]), and tetrameric ($W_4S_{12}^{2-}$ [8]) sulfido anions.

Table IV. Positional Parameters and Equivalent Isotropic Thermal Parameters for $[PPh_4]_2[(W_2Se_9)_{0.66}(W_2Se_{10})_{0.34}]$

atom	x	y	z	B_{eq}, Å^2
W(1)	0.003382 (77)	0.113810 (80)	0.232819 (37)	1.97 (3)
W(2)	−0.069596 (79)	0.308869 (78)	0.297568 (40)	2.24 (3)
Se(1)	−0.07102 (19)	0.09387 (18)	0.340602 (91)	2.29 (6)
Se(2)	0.06014 (21)	0.32181 (21)	0.20545 (10)	3.07 (7)
Se(3)	−0.16792 (19)	0.11942 (20)	0.175615 (96)	2.62 (7)
Se(4)	−0.27014 (21)	0.39501 (21)	0.26638 (11)	3.16 (7)
Se(5)	−0.03763 (22)	0.32484 (22)	0.40614 (11)	3.57 (8)
Se(6)	0.02804 (28)	0.47469 (27)	0.32710 (15)	3.4 (1)
Se(7)	0.08501 (25)	−0.10622 (22)	0.27764 (11)	3.95 (8)
Se(8)	0.20544 (21)	0.09161 (24)	0.16975 (11)	3.66 (8)
Se(9A)	0.23591 (49)	−0.12637 (48)	0.19245 (21)	4.6 (2)
Se(9B)	0.14102 (78)	−0.20152 (66)	0.19997 (32)	3.9 (3)
Se(10B)	0.30933 (91)	−0.10493 (84)	0.17440 (41)	3.6 (3)
P(1)	0.47996 (45)	0.27883 (44)	0.44502 (23)	1.7 (1)
P(2)	0.62777 (49)	0.60725 (48)	0.08446 (24)	2.1 (2)
C(110)	0.4833 (16)	0.4291 (16)	0.40125 (79)	1.4 (3)
C(111)	0.5912 (17)	0.4829 (17)	0.39807 (83)	1.7 (4)
C(112)	0.5893 (19)	0.5972 (19)	0.36165 (93)	2.8 (4)
C(113)	0.4800 (21)	0.6554 (21)	0.3280 (10)	3.9 (5)
C(114)	0.3739 (19)	0.6057 (19)	0.33004 (93)	3.2 (4)
C(115)	0.3746 (17)	0.4871 (17)	0.36566 (84)	1.9 (4)
C(120)	0.4552 (17)	0.1853 (17)	0.39390 (84)	1.6 (4)
C(121)	0.5497 (17)	0.1675 (16)	0.34821 (82)	1.8 (4)
C(122)	0.5294 (19)	0.0959 (18)	0.30847 (91)	2.8 (4)
C(123)	0.4189 (19)	0.0454 (18)	0.31267 (91)	2.5 (4)
C(124)	0.3259 (18)	0.0691 (18)	0.35514 (90)	2.5 (4)
C(125)	0.3429 (18)	0.1380 (18)	0.39610 (89)	2.3 (4)
C(130)	0.6299 (16)	0.2199 (16)	0.48498 (78)	1.4 (3)
C(131)	0.7080 (16)	0.1212 (16)	0.47341 (78)	1.5 (3)
C(132)	0.8238 (17)	0.0799 (17)	0.50528 (86)	2.4 (4)
C(133)	0.8597 (17)	0.1423 (17)	0.54657 (85)	1.8 (4)
C(134)	0.7748 (19)	0.2433 (18)	0.55693 (92)	2.7 (4)
C(135)	0.6580 (18)	0.2834 (18)	0.52677 (91)	2.4 (4)
C(140)	0.3559 (17)	0.2752 (17)	0.50446 (84)	1.9 (4)
C(141)	0.2489 (19)	0.3727 (19)	0.50067 (93)	2.7 (4)
C(142)	0.1534 (21)	0.3636 (20)	0.5450 (10)	3.7 (5)
C(143)	0.1565 (21)	0.2571 (21)	0.5923 (11)	3.7 (5)
C(144)	0.2654 (18)	0.1654 (17)	0.59270 (87)	2.4 (4)
C(145)	0.3616 (17)	0.1761 (17)	0.55029 (85)	2.0 (4)
C(210)	0.5289 (17)	0.5055 (17)	0.13071 (82)	1.6 (4)
C(211)	0.5463 (18)	0.3869 (18)	0.12279 (88)	2.1 (4)
C(212)	0.4722 (18)	0.3067 (17)	0.15924 (88)	2.4 (4)
C(213)	0.3885 (18)	0.3468 (18)	0.20107 (88)	2.4 (4)
C(214)	0.3662 (19)	0.4663 (19)	0.20801 (93)	3.0 (4)
C(215)	0.4406 (19)	0.5466 (18)	0.17225 (92)	2.6 (4)
C(220)	0.5260 (18)	0.7246 (17)	0.03142 (86)	2.1 (4)
C(221)	0.5838 (19)	0.8169 (18)	−0.00564 (92)	2.7 (4)
C(222)	0.5087 (19)	0.9058 (18)	−0.04818 (92)	3.0 (4)
C(223)	0.3805 (21)	0.9057 (20)	−0.0526 (10)	3.8 (5)
C(224)	0.3233 (18)	0.8191 (18)	−0.01486 (90)	2.5 (4)
C(225)	0.3970 (17)	0.7211 (17)	0.02734 (83)	1.8 (4)
C(230)	0.7500 (17)	0.5224 (16)	0.04377 (83)	1.8 (4)
C(231)	0.8349 (18)	0.4280 (17)	0.07641 (86)	2.0 (4)
C(232)	0.9190 (19)	0.3630 (18)	0.04403 (93)	2.8 (4)
C(233)	0.9291 (19)	0.3876 (18)	−0.02058 (94)	2.8 (4)
C(234)	0.8418 (18)	0.4828 (18)	−0.05298 (89)	2.6 (4)
C(235)	0.7526 (17)	0.5527 (17)	−0.02125 (83)	2.1 (4)
C(240)	0.6956 (18)	0.6827 (18)	0.13445 (89)	2.5 (4)
C(241)	0.6167 (20)	0.7790 (20)	0.1523 (10)	3.5 (5)
C(242)	0.6670 (23)	0.8353 (22)	0.1930 (11)	4.8 (6)
C(243)	0.7906 (23)	0.7958 (22)	0.2120 (11)	4.4 (5)
C(244)	0.8632 (28)	0.7084 (27)	0.1930 (13)	6.3 (7)
C(245)	0.8251 (21)	0.6423 (21)	0.1521 (10)	3.8 (5)

The thermal reactions lead to a complex mixture of selenotungstates. The use of tetraphenylphosphonium as a counterion was investigated in detail, as it gives the most crystalline products. In addition to the anions indicated in the scheme, ^{77}Se NMR spectroscopy suggests that a variety of other dimeric products differing only in ring size are also obtained in low yield. The

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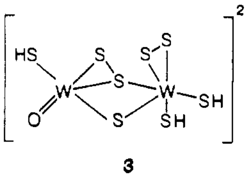
(28) Manoli, J. M.; Potvin, C.; Sécheresse, F. *Inorg. Chem.* **1987**, *26*, 340–341.



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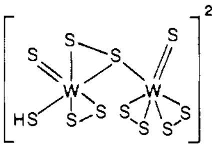
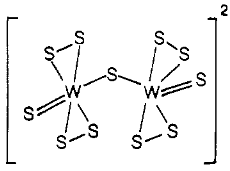


4



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product distribution is profoundly affected by the reaction conditions. In particular, the presence of additional elemental selenium affords products with a higher Se content. The use of triphenylbenzylphosphonium, NEt_4, or PPN as the counterion gives somewhat less of the other low-yield species, but the products are less crystalline.

In refluxing acetonitrile, $W_3Se_9^{2-}$ is the major product although it is not as crystalline as when it is cocrystallized with $W_3Se_8O^{2-}$. A similar reaction occurs in DMF, and $W_3Se_9^{2-}$ may be precipitated from solution with diethyl ether. If the supernatant solution is cooled overnight, the $W_2Se_9^{2-}/W_2Se_{10}^{2-}$ cocrystallate is obtained. Selenide anions and selenium are probable byproducts in reactions of the form shown in (2) and (3). Indeed, addition of small

$$3WSe_4^{2-} \xrightarrow{\Delta} W_3Se_9^{2-} + Se + 2Se^{2-} \quad (2)$$

$$2WSe_4^{2-} + (3 - x)Se \xrightarrow{\Delta} W_2Se_{10-x}^{2-} + Se^{2-}\ (x = 0, 1) \quad (3)$$

quantities of elemental selenium (<1 mol of Se/mol of WSe_4^{2-}) significantly increases the yield of $W_2Se_{10-x}^{2-}$ (x = 0, 1). When excess elemental selenium (>1 mol of Se/mol of WSe_4^{2-}) is added to the reaction mixture in acetonitrile, $W_2Se_{10}^{2-}$ is obtained as the major product in a reaction of the form shown in (4).

$$2WSe_4^{2-} + 8Se \xrightarrow{\Delta} W_2Se_{10}^{2-} + Se_6^{2-} \quad (4)$$

Attempts at separation of the mixtures have been unsuccessful although repeated recrystallization from acetone of the $P(CH_2Ph)Ph_3^+$ salt of the $W_2Se_9^{2-}/W_2Se_{10}^{2-}$ system leads to some fractionation. This did not appear to be a viable method of separation owing to the small change in the ratio of the products. Separation by chromatography was also investigated. Again, some fractionation was evident, but decomposition of the compounds occurred (on silica or alumina) presumably owing to the intrinsic instability of this class of compounds. It is thought that a mixture of ring sizes was produced for the following reason. Ordinary commercial vitreous black Se is comprised of long chain spirals of selenium atoms up to high molecular weights. When heated or dissolved, these chains cleave into a mixture of smaller fragments. These become attached to the W_2Se_4 core to produce the mixtures observed. Indeed, the use of red Se[29] (composed of Se_8 rings) leads to somewhat less of the low-yield species in the mixtures.

The thermal reactions of WS_4^{2-} have been shown to yield dimeric sulfido anions although the metal–polysulfide ring size is limited to three or five. Some control of the stoichiometry of the product is possible by addition of elemental sulfur. For example, in the absence of S_8, $W_2S_{10}^{2-}$ is the minor product in a reaction yielding $W_3S_9^{2-}$,[15] whereas upon addition of $^5/_8$ equiv of S_8, $W_2S_{12}^{2-}$[17] is produced. Cocrystallization is not as prevalent here as it is for the selenides. However, it has been observed for $Mo_2S_{10}^{2-}$ and $Mo_2S_{12}^{2-}$ in the analogous molybdenum system.[30]

Table V. Positional Parameters and Equivalent Isotropic Thermal Parameters for $[PPh_4]_2[W_2Se_{10}]$ Isomers

atom	x	y	z	B_{eq}, Å^2
W(1)	0.005892 (75)	0.109396 (81)	0.233081 (36)	2.28 (3)
W(2)	−0.064088 (81)	0.307468 (83)	0.295918 (43)	2.96 (3)
Se(1)	−0.06653 (20)	0.09397 (20)	0.340375 (93)	2.85 (6)
Se(2)	0.06374 (21)	0.31693 (23)	0.20407 (11)	4.06 (8)
Se(3)	−0.16366 (19)	0.11728 (20)	0.175675 (96)	3.01 (7)
Se(4)	−0.26276 (20)	0.39311 (21)	0.26537 (11)	3.61 (7)
Se(5)	−0.04119 (23)	0.32187 (25)	0.40491 (11)	4.44 (8)
Se(6)	0.03347 (33)	0.47108 (33)	0.32899 (16)	4.38 (8)
Se(6C)	0.08058 (57)	0.46644 (59)	0.27840 (29)	1.8 (1)
Se(7)	0.06937 (22)	−0.11166 (21)	0.281438 (94)	3.48 (7)
Se(8)	0.20692 (21)	0.09209 (25)	0.17207 (10)	4.17 (8)
Se(9B)	0.14319 (30)	−0.20615 (30)	0.20206 (14)	3.4 (1)
Se(10B)	0.31077 (32)	−0.10544 (32)	0.17618 (15)	3.78 (7)
Se(9C)	0.2287 (11)	−0.1463 (11)	0.19462 (50)	5.8 (4)
Se(10C)	0.00225 (78)	0.52211 (81)	0.37434 (39)	4.0 (2)
P(1)	0.48304 (47)	0.27654 (47)	0.44393 (23)	2.2 (2)
P(2)	0.63163 (49)	0.60481 (49)	0.08228 (24)	2.4 (2)
C(110)	0.4867 (17)	0.4269 (17)	0.40010 (84)	2.0 (4)
C(111)	0.5966 (18)	0.4782 (18)	0.39746 (88)	2.8 (4)
C(112)	0.5960 (21)	0.5909 (21)	0.3631 (10)	4.2 (5)
C(113)	0.4892 (21)	0.6538 (21)	0.3293 (10)	3.9 (5)
C(114)	0.3871 (20)	0.6030 (20)	0.33185 (98)	3.7 (5)
C(115)	0.3842 (19)	0.4856 (19)	0.36614 (91)	3.0 (4)
C(120)	0.4625 (17)	0.1833 (17)	0.39213 (82)	2.0 (4)
C(121)	0.5504 (19)	0.1706 (19)	0.34805 (92)	2.9 (4)
C(122)	0.5355 (19)	0.0969 (19)	0.30676 (94)	3.0 (4)
C(123)	0.4249 (20)	0.0447 (20)	0.31079 (98)	3.5 (5)
C(124)	0.3355 (21)	0.0641 (22)	0.3531 (11)	4.0 (5)
C(125)	0.3501 (20)	0.1338 (20)	0.39382 (97)	3.4 (5)
C(130)	0.6317 (17)	0.2187 (17)	0.48429 (82)	2.1 (4)
C(131)	0.7088 (16)	0.1179 (17)	0.47288 (79)	2.1 (4)
C(132)	0.8208 (20)	0.0765 (20)	0.50543 (96)	3.6 (5)
C(133)	0.8565 (18)	0.1383 (18)	0.54785 (89)	2.8 (4)
C(134)	0.7723 (18)	0.2406 (18)	0.55818 (85)	2.6 (4)
C(135)	0.6599 (18)	0.2802 (18)	0.52776 (87)	2.8 (4)
C(140)	0.3602 (17)	0.2724 (18)	0.50110 (85)	2.5 (4)
C(141)	0.2583 (23)	0.3645 (23)	0.4989 (11)	5.1 (6)
C(142)	0.1565 (29)	0.3586 (29)	0.5422 (14)	7.8 (8)
C(143)	0.1624 (23)	0.2503 (24)	0.5884 (11)	4.8 (6)
C(144)	0.2668 (21)	0.1633 (21)	0.59262 (98)	3.5 (5)
C(145)	0.3644 (19)	0.1754 (19)	0.54978 (94)	3.2 (4)
C(210)	0.5387 (16)	0.5025 (17)	0.12750 (81)	2.3 (4)
C(211)	0.5457 (18)	0.3860 (19)	0.12189 (88)	2.7 (4)
C(212)	0.4744 (17)	0.3078 (18)	0.15780 (85)	2.5 (4)
C(213)	0.3901 (18)	0.3492 (19)	0.20038 (90)	2.8 (4)
C(214)	0.3814 (18)	0.4638 (19)	0.20690 (90)	2.7 (4)
C(215)	0.4544 (19)	0.5407 (20)	0.17218 (94)	3.1 (4)
C(220)	0.5327 (18)	0.7167 (18)	0.02986 (87)	2.6 (4)
C(221)	0.5917 (19)	0.8086 (19)	−0.00718 (92)	2.9 (4)
C(222)	0.5117 (19)	0.8981 (19)	−0.04777 (92)	3.2 (4)
C(223)	0.3788 (20)	0.9014 (21)	−0.0500 (10)	3.8 (5)
C(224)	0.3235 (20)	0.8103 (20)	−0.01214 (97)	3.3 (5)
C(225)	0.4009 (17)	0.7167 (18)	0.02783 (85)	2.6 (4)
C(230)	0.7525 (17)	0.5236 (17)	0.04286 (82)	2.3 (4)
C(231)	0.8350 (17)	0.4248 (18)	0.07411 (83)	2.1 (4)
C(232)	0.9263 (20)	0.3615 (20)	0.04138 (98)	3.6 (5)
C(233)	0.9294 (19)	0.3871 (19)	−0.02228 (92)	2.9 (4)
C(234)	0.8438 (19)	0.4787 (20)	−0.05355 (92)	3.0 (4)
C(235)	0.7550 (17)	0.5489 (18)	−0.02239 (85)	2.5 (4)
C(240)	0.7019 (19)	0.6796 (19)	0.12952 (92)	3.0 (4)
C(241)	0.6276 (20)	0.7815 (20)	0.14449 (97)	3.7 (5)
C(242)	0.6738 (23)	0.8389 (23)	0.1858 (11)	4.6 (5)
C(243)	0.7891 (25)	0.7961 (25)	0.2135 (12)	5.3 (6)
C(244)	0.8558 (27)	0.7032 (28)	0.1970 (13)	6.2 (7)
C(245)	0.8229 (22)	0.6341 (22)	0.1539 (11)	4.8 (5)

Spectroscopy. The infrared spectra for the oligomeric tungsten chalcogenides, $[NH_4]_2[WSe_4]$,[31] and $Cs_2[WSe_4]$[32] are summarized in Table X. In addition to the peaks below 500 cm^{-1} that arise from metal–chalcogenide vibrations, $W_3Se_8O^{2-}$ shows a single sharp peak at 962 cm^{-1} from the W=O stretching mode. The IR spectrum of the product from the thermal reaction is identical with that from the acidification reaction except that the ν(W–O) band at 962 cm^{-1} is absent. In this way the product of the thermal reaction was identified as $[PPh_4]_2[W_3Se_9]$. The anions $W_2Se_9^{2-}/W_2Se_{10}^{2-}$ (isomers) show common features in the low-

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[29] Prepared by the method of: Foss, O.; Janickis, V. *J. Chem. Soc., Chem. Commun.* **1977**, 834–835.

[30] Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321–3332.

[31] Müller, A.; Krebs, B.; Kebabcioglu, R.; Stockburger, M.; Glemser, O. *Spectrochim. Acta, Part A* **1968**, *A24*, 1831–1837.

[32] Müller, A.; Schmidt, K. H.; Tytko, K. H.; Bouwma, J.; Jellinek, F. *Spectrochim. Acta, Part A* **1972**, *A28*, 381–391.

Table VI. Comparison of W–W Distances in Thio- and Selenotungstate Anions

anion	mean W–W, Å	no. of d electrons/ W–W bond	ref
$W_3S_8O^{2-}$	2.975	1	14
$W_3S_9^{2-}$	2.965	1	16
$W_3S_8^{2-}$	2.871 (1)[a]	2	this work
$W_3Se_9^{2-}/W_3Se_8O^{2-}$	3.037	1	this work
$W_2S_{12}^{2-}$	2.836 (2)	2	17
$W_2S_{10}^{2-}$	2.840 (2)	2	15
$W_2Se_9^{2-}$	2.897 (2)	2	this work
$W_2Se_{10}^{2-}$	2.903 (2)	2	this work
$W_2Cl_8Se_3^{2-}$	2.862 (3)	2	18

[a] Estimated standard deviation of the mean is given where equivalent distances were averaged; i.e., in $W_3S_8O^{2-}$, $W_3S_9^{2-}$, and $W_3Se_9^{2-}/W_3Se_8O^{2-}$ the central W atom is asymmetrically bound to the bridging Se atoms.

Table VII

(a) Selected Bond Distances (Å) in $W_3S_8^{2-}$

W(1)–W(2)	2.872 (1)	W(2)–S(4)	2.352 (4)
W(2)–W(3)	2.870 (1)	W(2)–S(5)	2.341 (4)
W(1)–S(1)	2.141 (4)	W(2)–S(6)	2.346 (4)
W(1)–S(2)	2.157 (4)	W(3)–S(5)	2.232 (4)
W(1)–S(3)	2.242 (4)	W(3)–S(6)	2.231 (4)
W(1)–S(4)	2.243 (4)	W(3)–S(7)	2.144 (4)
W(2)–S(3)	2.338 (4)	W(3)–S(8)	2.165 (4)
C–C (mean)[a]	1.38 (2)		

(b) Selected Bond Angles (deg) in $W_3S_8^{2-}$

W(1)–W(2)–W(3)	177.04 (3)	S(3)–W(2)–S(6)	170.6 (1)
W(1)–S(3)–W(2)	77.6 (1)	S(4)–W(2)–S(5)	171.2 (1)
W(1)–S(4)–W(2)	77.3 (1)	S(4)–W(2)–S(6)	81.7 (1)
W(2)–S(5)–W(3)	77.7 (1)	S(5)–W(2)–S(6)	98.7 (1)
W(2)–S(6)–W(3)	77.6 (1)	S(5)–W(3)–S(6)	105.7 (1)
S(1)–W(1)–S(2)	109.5 (2)	S(5)–W(3)–S(7)	110.0 (2)
S(1)–W(1)–S(3)	110.3 (2)	S(5)–W(3)–S(8)	110.1 (2)
S(1)–W(1)–S(4)	111.9 (2)	S(6)–W(3)–S(7)	110.2 (2)
S(2)–W(1)–S(3)	109.8 (2)	S(6)–W(3)–S(8)	111.3 (2)
S(2)–W(1)–S(4)	109.6 (2)	S(7)–W(3)–S(8)	109.4 (2)
S(3)–W(1)–S(4)	105.7 (1)	P(1)–N(1)–P(2)	142.6 (7)
S(3)–W(2)–S(4)	99.3 (1)	P(3)–N(2)–P(4)	136.8 (7)
S(3)–W(2)–S(5)	81.7 (1)		

[a] 1.38 (2) Å in $[PPh_4]_2[(W_3Se_9)_{0.46}(W_3Se_8O)_{0.54}]$, 1.38 (3) Å in $[PPh_4]_2[(W_2Se_9)_{0.66}(W_2Se_{10})_{0.34}]$, and 1.38 (3) Å in $[PPh_4]_2[W_2Se_{10}]$ isomers. That these standard deviations, as calculated on the assumption of equivalent C–C distances, are near those estimated from the inverse matrices suggests that the estimated standard deviations given for other metrical results are reliable.

Table VIII

(a) Selected Bond Distances (Å) in $W_3Se_9^{2-}/W_3Se_8O^{2-}$

W(1)–W(2)	2.951 (2)	W(1)–Se(5)	2.154 (9)
W(1)–W(2′)[a]	3.123 (1)	W(1)–O(1)	1.49 (7)
W(1)–Se(1)	2.492 (2)	W(2)–Se(1)	2.365 (2)
W(1)–Se(2)	2.487 (2)	W(2)–Se(2)	2.375 (2)
W(1)–Se(1′)[a]	2.569 (2)	W(2)–Se(3)	2.277 (2)
W(1)–Se(2′)[a]	2.533 (2)	W(2)–Se(4)	2.271 (2)

(b) Selected Bond Angles (deg) in $W_3Se_9^{2-}/W_3Se_8O^{2-}$

W(2)–W(1)–W(2′)	158.20 (4)	Se(2)–W(1)–O(1)	106 (2)
W(1)–Se(1)–W(2)	74.80 (5)	Se(1′)–W(1)–Se(2′)	95.69 (5)
W(1)–Se(2)–W(2)	74.71 (5)	Se(1′)–W(1)–Se(5)	104.6 (2)
W(1)–Se(1′)–W(2′)	78.44 (5)	Se(1′)–W(1)–O(1)	97 (2)
W(1)–Se(2′)–W(2′)	78.99 (5)	Se(2′)–W(1)–Se(5)	103.0 (2)
Se(1)–W(1)–Se(1′)	153.53 (5)	Se(2′)–W(1)–O(1)	101 (2)
Se(1)–W(1)–Se(2)	98.86 (6)	Se(1)–W(2)–Se(2)	105.88 (5)
Se(1)–W(1)–Se(2′)	76.87 (5)	Se(1)–W(2)–Se(3)	109.74 (6)
Se(1)–W(1)–Se(5)	101.9 (2)	Se(1)–W(2)–Se(4)	110.04 (6)
Se(1)–W(1)–O(1)	109 (2)	Se(2)–W(2)–Se(3)	109.43 (6)
Se(2)–W(1)–Se(1′)	76.28 (5)	Se(2)–W(2)–Se(4)	111.09 (6)
Se(2)–W(1)–Se(2′)	153.27 (5)	Se(3)–W(2)–Se(4)	110.56 (6)
Se(2)–W(1)–Se(5)	103.7 (2)		

[a] Atoms W(2′), Se(1′), and Se(2′) are generated by the crystallographic inversion center.

Table IX

(a) Selected Bond Distances (Å) in the Dimeric Selenotungstates

	$W_2Se_9^{2-}/W_2Se_{10}^{2-}$	$W_2Se_{10}^{2-}$ isomers
W(1)–W(2)	2.897 (2)	2.903 (2)
W(1)–Se(1)	2.460 (3)	2.462 (2)
W(1)–Se(2)	2.502 (3)	2.507 (3)
W(2)–Se(1)	2.440 (3)	2.439 (2)
W(2)–Se(2)	2.393 (3)	2.400 (3)
W(1)–Se(3)	2.258 (2)	2.253 (2)
W(2)–Se(4)	2.242 (2)	2.248 (2)
W(1)–Se(7)	2.504 (3)	2.517 (3)
W(1)–Se(8)	2.490 (3)	2.484 (2)
W(2)–Se(5)	2.519 (3)	2.510 (3)
W(2)–Se(6)	2.550 (3)	2.561 (4)
W(2)–Se(6C)		2.458 (6)
Se(5)–Se(6)	2.340 (4)	2.348 (4)
Se(7)–Se(9A)	2.431 (6)	
Se(8)–Se(9A)	2.402 (6)	
Se(7)–Se(9B)	2.247 (8)	2.316 (4)
Se(8)–Se(10B)	2.300 (9)	2.328 (5)
Se(9B)–Se(10B)	2.24 (1)	2.281 (5)
Se(7)–Se(9C)		2.57 (1)
Se(8)–Se(9C)		2.64 (1)
Se(5)–Se(10C)		2.372 (9)
Se(6C)–Se(10C)		2.44 (1)

(b) Selected Bond Angles (deg) in the Dimeric Selenotungstates

	$W_2Se_9^{2-}/W_2Se_{10}^{2-}$	$W_2Se_{10}^{2-}$ isomers
W(1)–Se(1)–W(2)	72.48 (7)	72.62 (6)
W(1)–Se(2)–W(2)	72.51 (7)	72.50 (7)
Se(1)–W(1)–Se(2)	103.28 (8)	103.17 (9)
Se(1)–W(1)–Se(3)	107.80 (9)	108.28 (8)
Se(1)–W(1)–Se(7)	77.93 (8)	75.98 (8)
Se(1)–W(1)–Se(8)	140.89 (8)	139.74 (8)
Se(2)–W(1)–Se(3)	106.71 (8)	105.32 (8)
Se(2)–W(1)–Se(7)	144.95 (9)	148.59 (8)
Se(2)–W(1)–Se(8)	75.18 (9)	73.10 (9)
Se(3)–W(1)–Se(7)	106.08 (9)	104.61 (9)
Se(3)–W(1)–Se(8)	109.98 (9)	111.33 (9)
Se(7)–W(1)–Se(8)	82.32 (9)	87.36 (9)
Se(1)–W(2)–Se(2)	107.22 (9)	107.14 (9)
Se(1)–W(2)–Se(4)	107.27 (8)	107.48 (8)
Se(1)–W(2)–Se(5)	86.11 (8)	84.09 (9)
Se(1)–W(2)–Se(6)	135.75 (9)	133.5 (1)
Se(2)–W(2)–Se(4)	105.21 (9)	105.77 (9)
Se(2)–W(2)–Se(5)	135.32 (8)	138.18 (9)
Se(2)–W(2)–Se(6)	90.8 (1)	93.0 (1)
Se(4)–W(2)–Se(5)	111.13 (9)	108.8 (1)
Se(4)–W(2)–Se(6)	106.2 (1)	106.5 (1)
Se(5)–W(2)–Se(6)	54.99 (9)	55.1 (1)
Se(1)–W(2)–Se(6C)		141.9 (2)
Se(2)–W(2)–Se(6C)		65.4 (2)
Se(4)–W(2)–Se(6C)		110.4 (2)
Se(5)–W(2)–Se(6C)		80.9 (2)
W(1)–Se(7)–Se(9A)	92.8 (1)	
W(1)–Se(8)–Se(9A)	93.9 (1)	
Se(7)–Se(9A)–Se(8)	85.7 (2)	
W(2)–Se(5)–Se(6)	63.2 (1)	63.5 (1)
W(2)–Se(6)–Se(5)	61.8 (1)	61.3 (1)
W(1)–Se(7)–Se(9B)	108.4 (2)	106.0 (1)
W(1)–Se(8)–Se(10B)	115.4 (3)	114.7 (1)
Se(7)–Se(9B)–Se(10B)	91.0 (4)	95.3 (2)
Se(8)–Se(10B)–Se(9B)	99.4 (4)	99.7 (2)
W(1)–Se(7)–Se(9C)		92.4 (3)
W(1)–Se(8)–Se(9C)		91.3 (3)
Se(7)–Se(9C)–Se(8)		83.1 (3)
W(2)–Se(5)–Se(10C)		92.0 (2)
W(2)–Se(6C)–Se(10C)		89.5 (3)
Se(5)–Se(10C)–Se(6C)		86.0 (3)

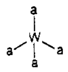
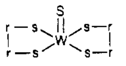
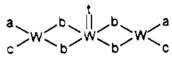
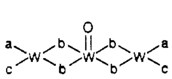
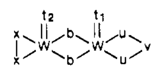
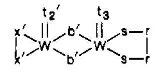
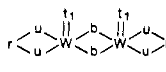
frequency region of their IR spectra with bands at 330 cm^{-1} and around 280 cm^{-1}. The former band in the $W_2Se_{10}^{2-}$ (isomers) spectrum is more intense relative to the latter than it is in the $W_2Se_9^{2-}/W_2Se_{10}^{2-}$ mixture. In this way the band at 330 cm^{-1} may be tentatively assigned to ν(Se–Se) and the weaker bands around 280 cm^{-1} to ν(W–Se) since there are more Se–Se bonds in $W_2Se_{10}^{2-}$ (isomers). By comparison, $[PPh_4]_2[WSe_4]$ has a strong

Table X Infrared Spectroscopic Data

compd	IR,[a] cm^{-1}
$[PPh_4]_2[(W_3Se_9)_{0.46}(W_3Se_8O)_{0.54}]$	962 (m), 325 (m), 310 (m)
$[PPh_4]_2[W_3Se_9]$	325 (m), 310 (m)
$[PPh_4]_2[(W_2Se_9)_{0.66}(W_2Se_{10})_{0.34}]$	330 (m), 288 (w), 273 (w)
$[PPh_4]_2[W_2Se_{10}]$ (two isomers)	330 (m), 286 (w), 270 (w)
$[PPh_4]_2[WSe_4]$	298 (s)
$[NH_4]_2[WSe_4]$	310 (s)[b]
$Cs_2[WSe_4]$	309 (s)[c]
$[PPN]_2[W_3S_8]$	495 (m), 490 (m), 440 (w)

[a] KBr pellets. [b] Reference 31. [c] Reference 32.

Table XI. ^{77}Se NMR Spectroscopic Data Measured in DMF Solvent, Ph_2Se_2/C_6D_6 External Standard: δ ($^1J_{Se-W}$, Hz)

$[NH_4]_2[WSe_4]$		a 1235 (52)
$[AsPh_4]_2[WS(Se_4)_2]$		s 993 (106) r 313
$[PPh_4]_2[W_3Se_9]$		t 2262 a, c 1739, 1618 b 889 (112, 90; $^3J_{Se-W}$ = 18 Hz; $^2J_{Se-Se}$ = 34 Hz)
$[PPh_4]_2[W_3Se_8O]$		a, c 1653, 1540 b 731 (113, 66; $^3J_{Se-W}$ = 18 Hz; $^2J_{Se-Se}$ = 33 Hz)
$[PPh_4]_2[W_2Se_9]$		t_2 1926 t_1 1787 b 859 (85) u 625 (47) v 152 x 132 (70)
$[PPh_4]_2[W_2Se_{10}]$		t_3 2086 t_2' 1940 b′ 858 (83) s 799 (89) r 554 x′ 131 (69)
$[PPh_4]_2[W_2Se_{10}]$		t_1 1847 b 864 (92) u 605 (48) r 190

ν(W–Se) vibration at 298 cm^{-1}. For $[PPN]_2[W_3S_8]$ the bands at 495 and 490 cm^{-1} may be assigned to $\nu(W-S_{term})$ and that at 440 cm^{-1} to $\nu(W-S_{bridge})$.

While electronic spectroscopy has been of some utility in the study of sulfide solutions, solutions of the tungsten–selenide anions exhibit no characteristic bands. For the selenide solutions, NMR spectroscopy provides a convenient probe that is not applicable to the sulfides. The NMR receptivity of sulfur is low (^{33}S, I = $^3/_2$, abundance 0.8%), but selenium, on the other hand, is relatively easy to observe, as its ^{77}Se isotope (I = $^1/_2$) is moderately abundant (7.6%).

In Table XI the chemical shift and coupling constant data for the tungsten selenides are summarized. We have reported preliminary results of this investigation for the isomeric anions of $W_2Se_{10}^{2-}$.[11] We originally believed that there are only two species (the symmetric and asymmetric isomers of $W_2Se_{10}^{2-}$) in solutions from which the $W_2Se_{10}^{2-}$ isomers were isolated. We assigned the 10 lines, in the absence of coupling constant data, to the 10 different Se sites in these species. From a combination of the X-ray crystallographic data described above and the ^{77}Se NMR data, we now know that there are at least four species in these solutions, viz., $W_2Se_9^{2-}$, $W_2Se_{10}^{2-}$ (two isomers), and $W_2Se_{11}^{2-}$. A more thorough survey of the extensive chemical shift range for ^{77}Se in the compounds has revealed a very much wider chemical shift dispersion than was first anticipated. Assignments are not based on intensities, as T_1 values have not been measured in detail. The results have been rationalized in terms of shielding arguments in a manner similar to that for the ^{17}O NMR spectra of transition-metal oxoanions.[33] Additional data for assignment are available in the low-intensity tungsten satellites (^{183}W, I = $^1/_2$, abundance 14.3%).

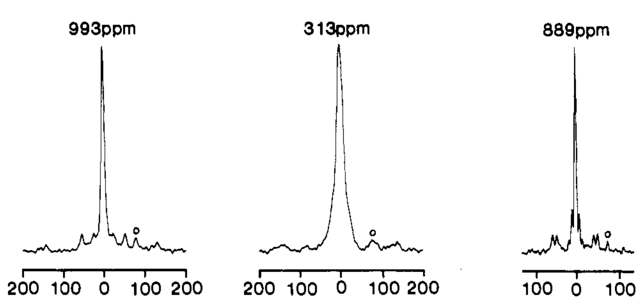


Figure 6. Expansions of selected ^{77}Se NMR lines (abscissas in hertz): (a, left) "W-bound Se" in $WS(Se_4)_2^{2-}$; (b, center) "ring Se" in $WS(Se_4)_2^{2-}$; (c, right) "bridging Se" in $W_3Se_9^{2-}$. The peaks marked "o" lying at ca. 80 Hz to the high field of the main peaks are fourth-order spinning sidebands (sample spinning rate ca. 20 Hz).

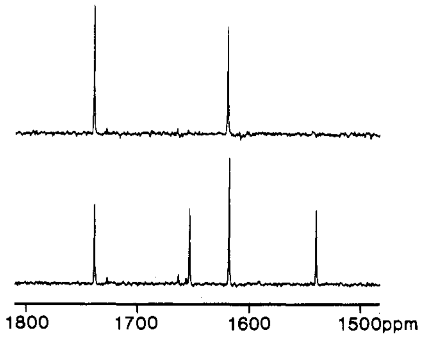


Figure 7. Comparison of the "terminal Se" regions: (a, top) $W_3Se_9^{2-}$ (the apical Se resonance at δ 2262 is not shown); (b, bottom) $W_3Se_9^{2-}$/$W_3Se_8O^{2-}$ mixture.

As an aid to the interpretation of the NMR spectroscopic results, data were obtained on the compound $[AsPh_4]_2[WS(Se_4)_2]$,[34] which contains WSe_4 five-membered rings. The ^{77}Se NMR spectrum of a solution of this material exhibits resonances at δ 993 and 313 (see Figure 6a,b). The line at δ 993 shows W satellites ($^1J_{Se-W}$ = 106 Hz) whereas the line at δ 313 has very much weaker Se satellites ($^1J_{Se-Se}$ = 276 Hz). In this way we may assign the line at δ 993 to Se atoms directly bound to W ("W-bound Se") and the δ 313 line to Se atoms not directly bound to W ("ring Se"). Originally,[11] we assigned a line at δ 824 to $WS(Se_4)_2^{2-}$, but further experiments revealed that the sample was contaminated with $WO(Se_4)_2^{2-}$. This resonance may be assigned to the W-bound Se atoms in $WO(Se_4)_2^{2-}$ on the basis of its satellite structure ($^1J_{Se-W}$ = 98 Hz). An additional line at δ 280 from the ring Se atoms in $WO(Se_4)_2^{2-}$ is also found. In the solid state the ring Se atoms in $WS(Se_4)_2^{2-}$ are inequivalent, as the WSe_4 ring is nonplanar. The present data suggest that on the NMR time scale these sites are equivalent in solution. The single resonance at δ 1235 in the spectrum of WSe_4^{2-} also exhibits W satellites ($^1J_{Se-W}$ = 52 Hz), and its low-field shift relative to $WS(Se_4)_2^{2-}$ is due to an increase in bond order ("terminal Se"). This is similar to the effect noted by Kidd[35] in the ^{17}O NMR spectra of some chromium–oxygen compounds. A third type of Se site ("bridging Se") is present in $W_3Se_9^{2-}$. Its resonance at δ 889 may be distinguished from the others because it is in the high-field region of the spectrum relative to the other lines and it is strongly coupled to two W atoms ($^1J_{Se-W}$ = 112 and 90 Hz) and weakly coupled to a third ($^3J_{Se-W}$ = 18 Hz) (see Figure 6c). For $W_3Se_9^{2-}$/$W_3S_8O^{2-}$, in addition to the two resonances at δ 1739 and 1618 for $W_3Se_9^{2-}$ (Figure 7a), there are also two additional lines at 1653

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(33) Day, V. W.; Klemperer, W. G. *Science (Washington, D.C.)* **1985**, *228*, 533–541.

(34) Wardle, R. W. M.; Mahler, C. H.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.*, in press.

(35) Kidd, R. G. *Can. J. Chem.* **1967**, *45*, 605–608.

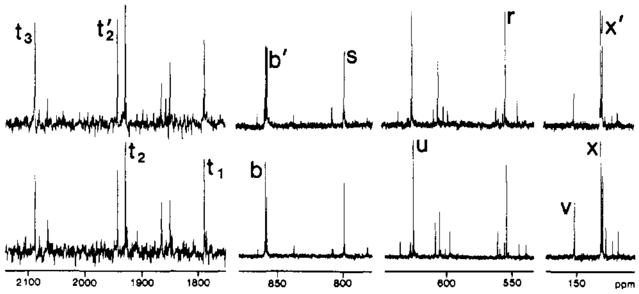
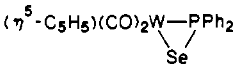


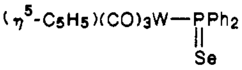
Figure 8. ^{77}Se NMR spectra for $W_2Se_9^{2-}/W_2Se_{10}^{2-}$: (a, top) crude reaction product; (b, bottom) product after two recrystallizations from acetone/ether.

and 1540 ppm (Figure 7b). All these resonances belong to the terminal Se atoms bonded to the outer W atoms. There are two resonances for each of the $W_3Se_9^{2-}$ and $W_3Se_8O^{2-}$ ions owing to the tetrahedral coordination of Se atoms about the outer W atoms. The central apical terminal Se atom in $W_3Se_9^{2-}$ resonates at δ 2262 since the W–Se bond is strong (2.154 (9) Å). No W satellites are resolved for the terminal Se atoms.

Assignment of the $W_2Se_9^{2-}/W_2Se_{10}^{2-}$ spectra was made by comparing spectra of solutions from the reaction in acetonitrile in the presence of $^1/_2$ mol of elemental Se. Preparations using different countercations (PPh_4^+, $P(CH_2Ph)Ph_3^+$, and PPN^+) yielded spectra having slightly differing $W_2Se_9^{2-}$: $W_2Se_{10}^{2-}$ ratios. Two sets of such spectra are shown in Figure 8 for the $P(CH_2Ph)Ph_3^+$ salt. In Figure 8a the ratio is approximately 1:1. Several recrystallizations from acetone/ether increased the proportion of $W_2Se_9^{2-}$ in the mixture (Figure 8b). Lines b, b′, s, u, x, and x′ show W satellites (see Table XI). Lines b and b′ lie in a chemical shift range similar to that of the bridging Se atoms in $W_3Se_9^{2-}$ and are therefore associated with the bridging Se atoms in $W_2Se_9^{2-}/W_2Se_{10}^{2-}$. The W-bound Se atoms in the WSe_3 and WSe_4 rings give rise to lines u and s, respectively. Lines v and r exhibit no W satellites and may be assigned to ring Se atoms. Resonances x and x′ are associated with the Se atoms in the WSe_2 three-membered rings. A similar high-field shift for strained three-membered rings has also been noted by McFarlane and McFarlane[36] in the compound **6** whereas the uncomplexed Se atom in compound **7** resonates at a much lower field. Lines t_3, t_2', t_2, and t_1 at low field are considered to arise from the four different terminal Se sites in the mixture. The assignment of the symmetrical $W_2Se_{10}^{2-}$ isomer is tentative and was made by comparing these spectra with those obtained from the heating reaction in the presence of 4 mol of elemental Se.



6 (δ -910)



$(\eta^5\text{-}C_5H_5)(CO)_3W{-}\underset{\overset{\|}{Se}}{P}Ph_2$

7 (δ 160)

From the data presented here it is not possible to make any quantitative chemical shift vs bond order correlations. We do note, however, that terminal Se atoms in the compounds under investigation resonate in the 2500–1000 ppm region, bridging Se and "W-bound" Se atoms lie in the range of 1000–600 ppm, lines from ring Se atoms occur around 600–200 ppm, and ring strain (i.e., in three- and possibly four-membered rings) causes a high-field shift (<200 ppm).

Summary

The tungsten–selenide chemistry described here does not parallel that of the tungsten–sulfide chemistry. To date, the WS_3 ring does not exist nor have we produced a selenium analogue of $W_3S_8^{2-}$. As a rule, the selenide chemistry is more complex and the compounds are less stable. Although ^{77}Se NMR spectroscopy is an excellent method for monitoring solutions of reactions and the chemical shift of selenium may be linked to its bonding mode, we do not yet have a method of separating species from the complex mixtures generated.

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Registry No. $[PPh_4]_2[W_3Se_9]$, 106905-73-1; $[PPh_4]_2[W_2Se_{10}]$ (isomer I), 106905-79-7; $[PPh_4]_2[W_2Se_{10}]$ (isomer II), 106905-81-1; $[PPh_4]_2[WSe_4]$, 112988-67-7; $[PPh_4]_2[W_3Se_8O]$, 106905-75-3; $[PPh_4]_2[W_2Se_9]$, 106905-77-5; $[PPN]_2[W_3S_8]$, 99572-95-9; $[NH_4]_2[WSe_4]$, 22474-80-2; $[AsPh_4][WS(Se_4)_2]$, 113584-94-4; $[NH_4]_2[WS_4]$, 13862-78-7; Se, 7782-49-2; ^{77}Se, 14681-72-2.

Supplementary Material Available: Listings of thermal parameters for non-hydrogen atoms and hydrogen atom positions (8 pages); listings of structure amplitudes (106 pages). Ordering information is given on any current masthead page.

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(36) McFarlane, H. C. E.; McFarlane, W. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic: London, 1983; pp 275–299.