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Registry No. 3-ETSNa, 106681-66-7; 3-BTSNa, 106681-67-8; methyl 3-ETS, 106681-68-9; methyl 3-BTS, 106681-69-0; Br_2, 7726-95-6.

New Oligomeric Tungsten–Selenium Anions: Synthesis and Characterization by ^{77}Se NMR and X-ray Diffraction Techniques

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The synthesis, characterization, and chemistry of soluble transition-metal sulfides is an active area of research.[1] Particular emphasis has been directed toward Mo and W sulfides in connection with the modeling of biological systems[2] and with industrial catalytic processes.[3] The formation of many of the sulfides involves internal redox chemistry[4] and for this reason the reaction solutions often contain a number of different species that are difficult to characterize. The cation, solvent, and pH determine what can be isolated as a solid. We anticipated that because of the differing redox processes involved, the chemistry of the selenides would not parallel directly that of the sulfides. We also believed that NMR techniques (^{77}Se) would prove to be extremely valuable in the study of selenide solutions; no comparable probe exists for the sulfide solutions. Surprisingly, there are very few reports of soluble transition-metal selenides.[1,5] Here we report the syntheses and characterization of four new oligomeric anions in the W–Se system: $W_3Se_9^{2-}$, $W_2Se_9^{2-}$, and $W_2Se_{10}^{2-}$ (two isomers).

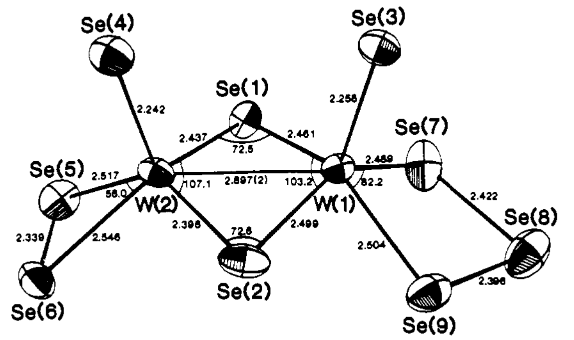

Figure 1. Structure of the $W_2Se_9^{2-}$ ion. Here and in Figures 2 and 3 the 50% probability ellipsoids are shown and the estimated standard deviations in the W–Se and Se–Se bond distances are 0.003–0.004 and 0.005–0.010 Å, respectively, and those in the bond angles are ~0.1°.

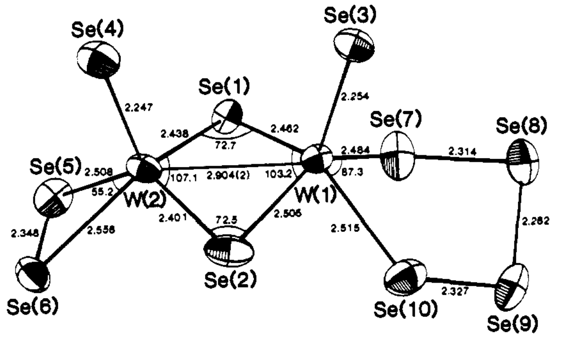

Figure 2. Structure of one isomer of the $W_2Se_{10}^{2-}$ ion.

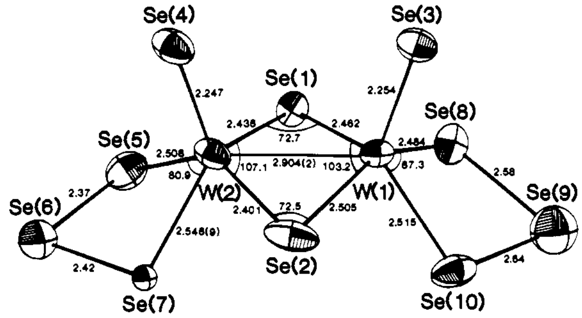

Figure 3. Structure of a second isomer of the $W_2Se_{10}^{2-}$ ion.

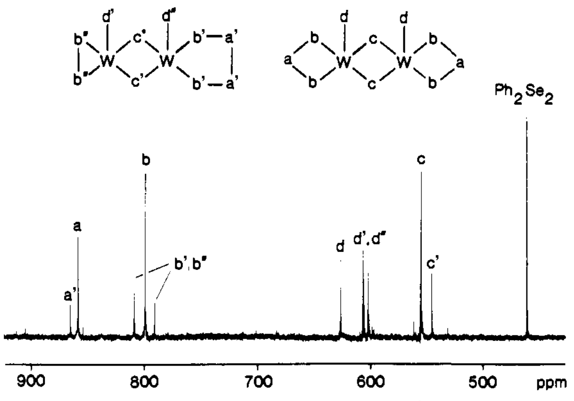

Figure 4. ^{77}Se NMR spectrum for the two $W_2Se_{10}^{2-}$ isomers of Figures 2 and 3 (DMF solvent). The spectrum is referenced relative to Me_2Se at 0 ppm. Ph_2Se_2/C_6D_6 was present as an external standard.

The $W_3S_9^{2-}$,[6] $W_3S_8^{2-}$,[7] and $W_4S_{12}^{2-}$ [8] ions have been isolated from acidified solutions of $[NH_4]_2[WS_4]$. Acidification of $[NH_4]_2[WSe_4]$ (0.10 g) with CH_3COOH (1.0 mL) in methanol (10 mL), followed by addition of $[PPh_4]Cl$ (0.20 g) in methanolic solution (2 mL), afforded $[PPh_4]_2[W_3Se_9]$ in 25% yield.[9] The ion closely resembles the analogous $W_3S_9^{2-}$ species. The W–W distances are approximately 0.06 Å longer than in the sulfide, while the W–Se distances are about 0.12 Å longer than the W–S distances. $[PPh_4]_2[W_3Se_9]$ may also be produced in 35% yield by heating $[NH_4]_2[WSe_4]$ (0.20 g) with $[PPh_4]Cl$ (0.15 g) in refluxing acetonitrile (10 mL) or by heating the same mixture in DMF (10 mL) to 85 °C for 0.5 h followed by addition of excess diethyl ether. When the supernatant solution was cooled to −15 °C for a period of 8 h red-black crystals of $[PPh_4]_2[W_2Se_9]/[PPh_4]_2[W_2Se_{10}]$ were obtained in 45% yield.[10] The $W_2Se_9^{2-}$ and

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[9] Crystal data for $[PPh_4]_2[W_3Se_9]/[PPh_4]_2[W_3Se_8O]$ (ratio 0.46/0.54). $C_{48}H_{40}O_{0.54}P_2Se_{8.46}W_3$, triclinic, C_i^1-$P\bar{1}$, $Z = 1$, $a = 9.085$ (5) Å, $b = 10.666$ (4) Å, $c = 13.407$ (3) Å, $\alpha = 87.22$ (2)°, $\beta = 86.30$ (3)°, $\gamma = 84.11$ (3)°. $V = 1288$ Å^3 at −150 °C, 9599 reflections measured out to 2θ(Mo Kα_1) = 50°, $R = 0.046$ on 2912 reflections having $F_o^2 > 3\sigma(F_o^2)$. The anions have crystallographically imposed symmetry $\bar{1}$ and are disordered at the central W–Se/O moiety. Similar contamination of S with O and disorder occur in the analogous sulfide.[6] ν(W–Se) = 325, 310 cm^{-1}; ν(W–O) = 962 cm^{-1}. It is thought that oxygen was incorporated from the acetic acid. Its presence was confirmed by Auger spectroscopy.

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$W_2Se_{10}^{2-}$ ions are present in the same cell with occupancies of 0.66 and 0.34, respectively. The $W_2Se_9^{2-}$ ion (Figure 1) has approximate C_s symmetry with square-pyramidal coordination about the W atoms. The analogous sulfide ion $W_2S_9^{2-}$ is unknown. The thermal reaction of WSe_4^{2-} in refluxing acetonitrile in the presence of $[PPh_4]Cl$ (in similar quantities to those described above) and 0.12 g of black selenium afforded two isomers of $[PPh_4]_2[W_2Se_{10}]$[11] in the ratio of 7:3 in 75% yield. The major isomer (Figure 2) is identical with that found in the mixed $[PPh_4]_2[W_2Se_9]/[PPh_4]_2[W_2Se_{10}]$ crystals and its structure closely resembles the analogous sulfide ion $W_2S_{10}^{2-}$.[12] The minor isomer of $W_2Se_{10}^{2-}$ (Figure 3) has no known sulfide analogue. The four-membered MSe_3 rings reported here have no counterparts in the literature; indeed, there appears to be a single example known of an MS_3 ring, that in $TiS_3(Me_5C_5)_2$.[13] The geometries of these rings are similar, although the ring-puckering angles differ ($W_2Se_9^{2-}$, 23°; $W_2Se_{10}^{2-}$, 25 and 35°; $TiS_3(Me_5C_5)_2$, 49°).

The generation of multiple components in solution and subsequent coprecipitation of different species are prevalent here as they are in the sulfides.[14] While electronic spectra have been of some utility in the study of sulfide solutions, selenide solutions of the present red-black materials exhibit no characteristic bands. But, as opposed to the sulfide solutions, NMR spectroscopy provides a convenient probe of these selenide solutions. In Figure 4 we show the ^{77}Se NMR spectrum for the solution from which the two $W_2Se_{10}^{2-}$ ions were isolated as their PPh_4 salts. While there is an extensive literature on ^{77}Se NMR spectra of organoselenium compounds,[15,16] no corresponding data base for inorganic selenides exists. Consequently the assignment in Figure 4 is based on comparisons with other spectra and on shielding arguments; it is not based on intensities as T_1 values have not been obtained. Successive preparations yielded spectra that have slightly differing a:a′, b:b′, b″, etc. ratios and so it was possible to link the four lines, a, b, c, and d, to the symmetrical isomer. The remaining six lines were assigned to the six unique Se sites in the unsymmetrical isomer. The ten lines lie in a range between that of WSe_4^{2-} (δ 1235, not shown) at the low-field end and that of Ph_2Se_2 (δ 460) at the high-field end. The resonance for the W^{VI} ion, WSe_4^{2-} would be expected to lie at the low-field end of resonances from the formally W^V $W_2Se_{10}^{2-}$ ions. Shielding arguments suggest the relative placement of the different types of Se sites.[17] Type "a" ring sites are least shielded, being furthest from W nuclei. Type "b" sites are less shielded than type "d" sites, as the latter are involved in stronger W–Se bonding; type "c" sites are highly shielded, being in close proximity to two W nuclei. Evidence to support this assignment is provided by the ^{77}Se NMR spectrum of $WS(Se_4)_2^{2-}$,[18] which contains WSe_4 five-membered rings and exhibits resonances at δ 824 and 988 from Se atoms in "b"- and "a"-type environments, and by the ^{77}Se NMR spectrum of $Rh_2Se_5(Me_5C_5)_2$,[19] which contains an Se_4 bridge between two Rh sites and has resonances at δ 485 and 783 for sites that are approximately type "c" and type "b". Complete confirmation of the assignment in Figure 4 must await the isolation of pure materials, a process that can now be followed by ^{77}Se NMR techniques. Indeed, we anticipate that ^{77}Se NMR spectroscopy will prove to be as valuable in the chemistry of soluble transition-metal selenides as have ^{17}O NMR techniques in the chemistry of the polyoxoanions.[20] On the basis of the preliminary work reported here the details of the selenide chemistry will be easier to delineate and will differ significantly from those of the sulfide chemistry.

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(10) Crystal data for $[PPh_4]_2[W_2Se_9]/[PPh_4]_2[W_2Se_{10}]$ (ratio 0.66/0.34). $C_{48}H_{40}P_2Se_{9.34}W_2$, triclinic, C_i^1-$P\bar{1}$, $Z = 2$, $a = 10.556$ (5) Å, $b = 11.480$ (6) Å, $c = 22.324$ (11) Å, $\alpha = 76.90$ (2) °, $\beta = 86.58$ (2)°, $\gamma = 79.28$ (2)°. $V = 2588$ Å^3 at −150 °C, 8941 reflections measured out to $2\theta(\text{Mo K}\alpha_1) = 46°$, $R = 0.068$ on 4700 reflections having $F_o^2 > 3\sigma(F_o^2)$. ν(Se–Se) = 330 cm^{-1}; ν(W–Se) = 288, 273 cm^{-1}.

(11) Crystal data for $[PPh_4]_2[W_2Se_{10}]$ (two isomers, ratio 0.70/0.30). $C_{48}H_{40}P_2Se_{10}W_2$, triclinic, C_i^1-$P\bar{1}$, $Z = 2$, $a = 10.678$ (2) Å, $b = 11.492$ (3) Å, $c = 22.392$ (5) Å, $\alpha = 77.20$ (2)°, $\beta = 86.94$ (2)°, $\gamma = 79.81$ (2)°. $V = 2637$ Å^3 at −150 °C, 10376 reflections measured out to $2\theta(\text{Mo K}\alpha_1) = 46°$, $R = 0.075$ on 5132 reflections having $F_o^2 > 3\sigma(F_o^2)$. ν(Se–Se) = 330 cm^{-1}; ν(W–Se) = 286, 270 cm^{-1}.

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Borane–THF as a Dual Reagent. Preparation and Characterization of the Metal-Rich Cobaltaborane $(\mu_3\text{-H})_2[(\eta^5\text{-}C_5H_5)Co]_4B_2H_2$

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The range of metallaboranes synthesized continues to increase as does the number of synthetic methods.[1-3] The great majority of metallaboranes have low metal to boron ratios and only a few metal-rich systems (M/B ratio >1, unbridged M–B interactions) are known. The latter systems present an unusual environment to the borane fragment as well as offering useful comparisons to metal-rich, transition-metal hydrocarbyl clusters.[4,5] Here we present a new route to a metal-rich metallaborane based on well-known, but not fully appreciated, properties of BH_3·THF. Borane coordinates Lewis bases just like a transition metal,[6] and, hence, BH_3 can be used to remove ligands from a transition-metal complex.[7,8] With excess BH_3 present further reaction with the transition-metal fragments is possible.[9] We show below that when BH_3 can be induced to remove two ligands from $CpCoL_2$, the highly unsaturated CpCo fragments condense with themselves and borane to produce the metal-rich cluster $(CpCo)_4B_2H_4$ in useful (16% based on cobalt) yield. This strategry constitutes an alternative to using complexes with weakly coordinating ligands, e.g., $CpCo(C_2H_4)_4$.[10]

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