Heteropolyanions as Nucleophiles. 1. Synthesis, Characterization, and Reactions of Keggin- and Dawson-Type Tungstostannates(II)[1]

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Abstract: Salts of the following tungstostannate(II) heteropolyanions, $PW_{11}O_{39}Sn^{5-}$, $SiW_{11}O_{39}Sn^{6-}$, $GeW_{11}O_{39}Sn^{6-}$, $BW_{11}O_{39}Sn^{7-}$, $GaW_{11}O_{39}Sn^{7-}$, and α_2-$P_2W_{17}O_{61}Sn^{8-}$, have been prepared and characterized by elemental analysis, electronic and vibrational spectra, cyclic voltammetry, and ^{11}B, ^{31}P, and ^{119}Sn NMR spectroscopy. The corresponding tin(IV) derivatives, $XW_{11}O_{39}SnOH^{n-}$, were also isolated. Treatment of $K_6SiW_{11}O_{39}Sn$ with $IFe(CO)_2(C_5H_5)$ leads to displacement of I^- and the formation of $SiW_{11}O_{39}SnFe(CO)_2(C_5H_5)^{5-}$. The P- and Ga-centered polytungstostannates reacted similarly. Analogous reactions with alkyl halides and cholesteryl *p*-toluenesulfonate yielded the following organotin derivatives, isolated as tetramethylammonium salts: $SiW_{11}O_{39}SnR^{5-}$ (R = $CH_2C_6H_5$, $(CH_2)_3Br$, $(CH_2)_4Cl$, $(CH_2)_{11}CH_3$, $(CH_2)_6Br$, $C_{27}H_{45}$) and α_2-$P_2W_{17}O_{61}Sn(CH_2)_{11}CH_3^{7-}$. The organic derivatives are soluble in aqueous buffer (pH 4.5–5.5) and in dimethyl sulfoxide and have been characterized by elemental analysis, cyclic voltammetry, and vibrational and NMR spectroscopy.

Heteropolyanions and isopolyanions[2] attract current attention in view of their potential applications in catalysis,[3] but recent applications in electron microscopy[4] and as possible antiviral and antitumoral agents[5] are also of interest.

For these and other reasons, several research groups have directed their efforts toward the synthesis of organic and organometallic derivatives of heteropolyanions. Two general routes to such derivatives involve (1) the attachment of organometallic moieties to surface oxygen atoms of the polyanion[6] and (2) the incorporation of an organometallic group RM *into* the polyanion structure, typically by reaction of $RMCl_3$ with a lacunary anion.[7]

In both of the above the polyanion functions as a polydentate ligand, binding through oxygen. The structure of $GaW_{11}PbO_{39}^{7-}$ reported by Tourné et al.[8] suggests a different possible approach. The tunsgtogallate anion has the well-known Keggin structure with one of the W=O terminal groups replaced by Pb and a stereochemically active lone pair of electrons. In view of the extensive chemistry of $SnCl_3^-$ and SnR_3^- as σ donors (or a candidates for oxidative addition reactions depending on one's point of view) we have chosen to explore the chemistry of possible Sn(II) analogues of Tourné's anion. The heteropolytungstostannites described here prove to be easily synthesized complexes that act as nucleophiles toward both organic and organometallic compounds. They offer a direct method of attaching a heavy, electron-dense oxometalate moiety to virtually any desired substrate. The implications for labeling (electron microscopy, etc.) and other applications are under investigation.

Experimental Section

Syntheses of Complexes. The following lacunary anion salts were prepared according to published methods and were identified by infrared spectroscopy and in some cases by polarography: h-$K_9BW_{11}O_{39}\cdot xH_2O$;[9] α-$K_9GaW_{11}O_{39}\cdot xH_2O$;[10] α-$K_8SiW_{11}O_{39}\cdot 12H_2O$;[11] α-$K_8GeW_{11}O_{39}\cdot xH_2O$;[11] α-$K_7PW_{11}O_{39}\cdot xH_2O$;[12] α-$[(n\text{-}C_4H_9)_4N]_4H_3PW_{11}O_{39}$;[13] and α_2-$K_{10}P_2W_{17}O_{61}\cdot 7H_2O$.[14]

Syntheses of Tin-Substituted Polyanions. The preparation of pure tin(II) compounds is complicated by the ease of oxidation of stannous tin in aqueous solutions. The preparations of all tin(II)-substituted polyanions were thus performed under an inert atomsphere and at low pH values (4 to 4.5).

Potassium α-Undecatungstoborostannate(II). Two grams (0.009 mol) of $SnSO_4$ was dissolved in 10 mL of acetic acid and 20 mL of water. The solution was heated to 70–80 °C and the pH was raised to 4.0 with potassium acetate and potassium carbonate; a faint turbidity was seen. The solid $K_9BW_{11}O_{39}$ (19.2 g, 0.006 mol) was added to the above solution. The solution turned bright yellow when addition was complete, the volume was increased to 200 mL by the addition of water (maintaining the pH at 4), and the solution was heated for 1 h under a stream of nitrogen after which time it had become orange. The solution was allowed to cool and a small amount of buff-colored precipitate was filtered off. A threefold excess of methanol was added to the orange filtrate, and the solution left to cool in the refrigerator. A bright yellow solid precipitated out and was isolated by filtration, washed with water, and recrystallized from hot water. Yield 8.3 g. Anal. Calcd for $K_7BW_{11}O_{39}Sn\cdot 8H_2O$: K, 8.55; B, 0.34; W, 63.33; Sn, 3.73. Found: K, 8.37; B, 0.33; W, 63,53; Sn, 3.71. NMR: ^{11}B ($\delta = -16.6$ ppm, $\Delta\nu = 22.1$ Hz in D_2O; $\delta = -16.3$ ppm, $\Delta\nu = 45.6$ Hz in 10 M LiCl in D_2O); ^{119}Sn ($\delta = -11.1$ ppm in 10 M LiCl in D_2O).

The following salts were prepared analogously and were precipitated from the reaction mixture by addition of a saturated solution of KOAc in methanol. The yellow products were recrystallized from hot water.

Potassium α-Undecatungstogallostannate(II). Yield 15.8 g. Anal. Calcd for $K_6NaGaW_{11}O_{39}Sn\cdot 8H_2O$: K, 7.23; Na, 0.71; Ga, 2.15; W, 62.49; Sn, 3.68. Found: K, 7.18; Na, 0.76; Ga, 2.04; W, 62.79; Sn, 3.75. NMR: ^{119}Sn ($\delta = -162.6$ ppm, in 10 M LiCl in D_2O).

Potassium α-Undecatungstosilicostannate(II). Yield 17.7 g. Anal. Calcd for $K_5NaSiW_{11}O_{39}Sn\cdot 8H_2O$: K, 6.18; Na, 0.73; Si, 0.89; W, 64.09; Sn, 3.77. Found: K, 5.96; Na, 0.71; Si, 0.92; W, 64.99; Sn, 3.86. NMR: ^{119}Sn ($\delta = -153$ ppm in D_2O; $\delta = -178$ ppm in 10 M LiCl in D_2O).

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Potassium α-Undecatunsgtogermanostannate(II). Yield: 12.4 g. Anal. Calcd for $K_6GeW_{11}O_{39}Sn{\cdot}20H_2O$: K, 6.82; Ge, 2.12; W, 58.93; Sn, 3.47. Found: K, 7.12; Ge, 2.04; W, 60.14; Sn, 3.52. NMR: ^{119}Sn ($\delta = -185.6$ ppm in D_2O; $\delta = -207.1$ ppm in 10 M LiCl in D_2O).

Potassium α-Undecatungstophosphostannate(II). Yield: 16.5 g. Anal. Calcd for $K_5PW_{11}O_{39}Sn{\cdot}5H_2O$: K, 6.33; P, 1.01; W, 65.63; Sn, 3.86. Found: K, 6.78; P, 0.98; W, 65.83; Sn, 3.92. NMR: ^{31}P ($\delta = -11.6$ ppm in D_2O; $\delta = -11.4$ ppm in 10 M LiCl in D_2O); ^{119}Sn ($\delta = -43.9$ ppm in D_2O; $\delta = -45.7$ ppm in 10 M LiCl in D_2O).

Tetramethylammonium α-Undecatungstophosphostannate(II). Addition of excess $(CH_3)_4NCl$ to an aqueous buffered solution of $K_5PW_{11}Sn^{II}$ afforded a light yellow solid, which was recrystallized from hot water. NMR: ^{31}P ($\delta = -11.2$ ppm in D_2O).

Potassium α₂-Heptadecatungstodiphosphostannate(II). A solution of 1.72 g (0.008 mol) of $SnSO_4$ in 30 mL of 1:2 acetic acid–water (pH 4.0 and at 70–80 °C) was treated with 18.8 g (0.004 mol) of α_2-$K_{10}P_2W_{17}O_{61}$ and the volume increased to 200 mL. The resulting yellow solution was heated for an hour under nitrogen, cooled, and treated with an excess of methanol to produce a yellow solid, which was washed with methanol and water and recrystallized from hot water. Yield 14.5 g. Anal. Calcd for $K_8P_2W_{17}O_{61}Sn{\cdot}8H_2O$: K, 6.49; P, 1.29; W, 64.97; Sn, 2.47. Found: K, 6.57; P, 1.30; W, 64.22; Sn, 2.38. NMR: ^{31}P ($\delta = -6.98$ and -12.8 ppm in D_2O); ^{119}Sn ($\delta = -148.8$ ppm in D_2O; $\delta = -177.3$ ppm in 10 M LiCl in D_2O).

Potasssium α-Undecatungstoborohydroxostannate(IV). A dilute solution of bromine in water was added dropwise with stirring to a buffered (pH 4.7) solution of the α-$BW_{11}Sn^{II}$ compound, until the color (golden yellow) had faded. The potassium salt was isolated by the addition of a threefold excess of methanol and was recrystallized from hot water. Alternatively the compound was prepared following the procedure described by Schouten.[15] The pH of an aqueous solution of $SnCl_4{\cdot}5H_2O$ was adjusted to 4.0 with potassium bicarbonate. The solution was heated to 60–70 °C and solid $K_9BW_{11}O_{39}$ was added. After 30 min, excess reagent was filtered off, and on cooling a white precipitate of the potassium salt of α-$BW_{11}O_{39}SnOH^{6-}$ separated. Addition of KCl or a saturated solution of potassium acetate in methanol to the reagent mixture precipitated the heteropolyanion completely. It was recrystallized from hot water. The IR spectra and the cyclic voltammograms of the solids obtained by the two different methods were identical. The IR spectra exhibited well-resolved absorptions in the W–O region and resembled that of the α-BW_{12} anion. NMR: ^{11}B ($\delta = -16.96$ ppm, $\Delta\nu = 20.6$ Hz in D_2O; $\delta = -16.5$ ppm; $\Delta\nu = 22.1$ Hz in 10 M LiCl in D_2O).

Tetramethylammonium α-Undecatungstoborohydroxostannate(IV). Five grams of $K_7BW_{11}Sn^{II}$ was dissolved in acetate buffer (pH 4.7) and excess $(CH_3)_4NCl$ (10 g) was added. A pale yellow solid precipitated out and was filtered off and washed withh cold water and methanol. Recrystallization from hot water yielded white crystals of the tetramethylammonium salt of $BW_{11}Sn^{IV}OH$. Addition of excess $(CH_3)_4NCl$ to a buffered solution of $K_6BW_{11}Sn^{IV}OH$ also afforded the same compound. The IR spectrum of this compound exhibited strong, characteristic, and well-resolved absorptions in the W–O region and resembled that of the α-BW_{12} anion.

Potassium α-Undecatungstogallohydroxostannate(IV). Oxidation of a solution of the $GaW_{11}Sn^{II}$ compound with bromine water produced this compound. Alternatively, it was prepared following the procedure described by Schouten.[15] The IR spectrum exhibited well-resolved absorptions in the W–O region.

Tetramethyl- and Tetrabutylammonium α-Undecatungstogallohydroxostannate. The tetramethylammonium salt (white solid) was precipitated by the addition of excess $(CH_3)_4NCl$ to buffered solutions of the $GaW_{11}Sn^{II}$ or the $GaW_{11}Sn^{IV}OH$ compounds and recrystallized from hot water. Anal. Calcd for $[(CH_3)_4N]_6GaW_{11}O_{39}SnOH{\cdot}6H_2O$: C, 8.46; H, 2.50; N, 2.47; W, 59.41. Found: C, 8.24; H, 2.65; N, 2.35; W, 60.06. The tetrabutylammonium salt was precipitated by the addition of $(n\text{-}C_4H_9)_4NBr$ to aqueous buffered solutions of the $GaW_{11}Sn^{II}$ or $GaW_{11}Sn^{IV}OH$ compounds and recrystallized from acetonitrile. The IR spectra exhibited well-resolved W–O absorptions.

Potassium α-Undecatungstosilicohydroxostannate(IV). This compound was prepared by the oxidation with bromine water of an aqueous buffered solution of the $SiW_{11}Sn^{II}$ compound. Alternatively, it was prepared by reacting the lacunary $SiW_{11}O_{39}^{8-}$ anion with $SnCl_4{\cdot}5H_2O$, following the procedure of Schouten.[15] The cyclic voltammogram of this compound obtained by the two different methods was identical.

Tetramethyl- and Tetrabutylammonium α-Undecatungstosilicohydroxostannate(IV). These salts were precipitated by the addition of excess $(CH_3)_4NCl$ or $(n\text{-}C_4H_9)_4NBr$, respectively, to buffered aqueous solutions of the $SiW_{11}Sn^{II}$ or $SiW_{11}Sn^{IV}OH$ compounds. These white solids were recrystallized from hot water or acetonitrile. The IR spectra exhibited well-resolved W–O absorptions and were indistinguishable from that of the corresponding $SiW_{12}O_{40}^{4-}$ anion. Anal. Calcd for $[(CH_3)_4N]_5SiW_{11}O_{39}Sn\text{–}OH{\cdot}5H_2O$: C, 7.34; H, 1.87; N, 2.14; Si, 0.86; W, 61.84; Sn, 3.64. Found: C, 7.30; H, 2.04; N, 2.30; Si, 0.88; W, 61.41; Sn, 3.54. NMR: ^{119}Sn ($\delta = -666$ ppm in D_2O for the Me_4N^+ salt of $SiW_{11}Sn^{IV}\text{–}OH$).

Potassium and Tetramethyl- and Tetrabutylammonium α-Undecatugstogermanohydroxostannate(IV). The potassium salt was prepared by bromine water oxidation of an aqueous buffered solution of $GeW_{11}O_{39}Sn^{6-}$ compound and isolated by addition of a saturated solution of KCl or a saturated solution of KOAc in methanol. The white solid was recrystallized from hot water. The alkylammonium salts were unstable with respect to the tin(II) oxidation state and could be isolated only as the stannic compounds by the addition of the corresponding tetraalkylammonium halide to aqueous buffered solutions of $GeW_{11}Sn^{II}$ or $GeW_{11}Sn^{IV}\text{–}OH$ compounds. Recrystallization was done in hot water or in acetonitrile. The IR spectra exhibited strong, characteristic W–O absorptions and resembled that of the α-$GeW_{12}O_{40}^{4-}$ anion. Anal. Calcd for $[(CH_3)_4N]_5GeW_{11}O_{39}Sn^{IV}\text{–}OH{\cdot}5H_2O$: C, 7.24; H, 2.14; N, 2.11; W, 61.01. Found: C, 7.36; H, 2.19; N, 2.06; W, 61.79.

Tetramethylammonium α-Undecatungstophosphohydroxostannate(IV). A solution of the $PW_{11}Sn^{II}$ compound was oxidized by bromine water to produce this compound.

Tetrabutylammonium α-Undecatungstophosphohydroxostannate(IV). $[(n\text{-}C_4H_9)_4N]_4H_3PW_{11}O_{39}$ (6.4 g, 0.02 mol) was dissolved in 20 mL of DMF and 0.678 g (0.003 mol) of $SnCl_2{\cdot}2H_2O$ dissolved in HCl was added. The resulting bright yellow solution was heated for about 30 min at 60 °C, under a stream of nitrogen. The solution turned blue as a result of partial reduction, probably of traces of $PW_{12}O_{40}^{3-}$ present. Addition of ethyl acetate precipitated a pale yellow solid (5.3 g). From the IR and ^{31}P NMR ($\delta = -13.1$ and -13.9 ppm in CD_3CN) it was evident that this was a mixture of the stannate(II) and hydroxostannate(IV) compounds. The material was redissolved in acetonitrile and oxidized completely by bromine water to produce the pure hydroxostannate(IV) compound (^{31}P NMR $\delta = -13.1$ ppm in CD_3CN). Anal. Calcd for $[(n\text{-}C_4H_9)_4N]_4PW_{11}O_{39}Sn\text{–}OH$: C, 20.31; H, 3.81; N, 1.48; W, 53.48. Found: C, 20.32; H, 3.92; N, 1.42; W, 54.01.

Potassium α₂-Heptadecatungstodiphosphohydroxostannate(IV). Oxidation of a solution of the $P_2W_{17}Sn$ compound with bromine water produced this compound. NMR: ^{31}P ($\delta = -10.0$ and -12.3 ppm in D_2O).

Tetramethylammonium α-Undecatungstosilico(cyclopentadienyldicarbonyliron)stannate. $K_6SiW_{11}O_{39}Sn$ (3.4 g, 0.001 mol) was dissolved in 50 mL of hot water to form a yellow solution. A solution of $IFe(CO)_2Cp$ (0.456 g, 0.0015 mol) in methanol was added, and the mixture was refluxed overnight in an inert atmosphere. After the solution was cooled and excess $(CH_3)_4NCl$ added a pale yellow solid precipitated out. It was recrystallized from hot water. Yield 3.0 g. Anal. Calcd for $[(CH_3)_4N]_5SiW_{11}O_{39}SnFe(CO)_2Cp{\cdot}5H_2O$: C, 9.53; H, 2.21; N, 2.06; W, 59.51; Sn, 3.50; Fe, 1.65. Found: C, 9.35; H, 2.27; N, 2.09; W, 59.64; Sn, 3.56; Fe, 1.55.

The IR spectrum of $[(CH_3)_4N]_5SiW_{11}O_{39}SnFe(CO)_2Cp$[16] showed characteristic and well-resolved W–O stretch frequencies and two carbonyl absorptions at 2013 and 1961 cm⁻¹. ^1H NMR showed resonances for the C_5H_5 ($\delta = 5.35$ ppm) and for the $(CH_3)_4N^+$ ($\delta = 3.17$ ppm) with an integrated ratio of 1:11.3 (expected ratio = 1:12). The cyclic voltammogram was similar to that of the $SiW_{11}Sn^{IV}\text{–}OH$ compound. The reaction given above is analogous to that reported for $SnCl_2{\cdot}2H_2O$.[17]

The $PW_{11}Sn^{II}$ and $GaW_{11}Sn^{II}$ compounds reacted analogously but less completely, even on refluxing for longer periods. Unreacted starting material was removed by recrystallization. Yields were 2.1 and 1.6 g, respectively. IR and ^1H NMR spectra were satisfactory.[18]

Tetramethylammonium α-Undecatungstosilico(organo)stannates. A slurry of 3.2 g (0.001 mol) of $K_8SiW_{11}O_{39}$ in 30 mL of Me_2SO was heated to 60 °C and then treated with an excess (fivefold) of the organic reagent, RX, in a nitrogen atmosphere. After 40–50 min, the solution had clarified and became colorless as the organic derivative of the polyanion was soluble in Me_2SO. The stannic compound, $SiW_{11}SnOH$, was not soluble in Me_2SO and could be easily separated by filtration. A methanolic solution of $(CH_3)_4NCl$ was added to the Me_2SO solution to precipitate the tetramethylammonium salt of the polyanion. The product was washed with large volumes of methanol, ether, and water. Yields varied from 1.0 to 1.5 g for the smaller R groups and 0.5 to 1.0 g for the

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[15] Schouten, A.; Cros, B. *Polyhedron* **1982**, *1*, 283.

[16] Knoth[7b] first prepared this compound by reacting $Cl_3SnFe(CO)_2Cp$ with $SiW_{11}O_{39}^{8-}$. The IR spectra of tetramethylammonium salts prepared by both methods were identical.

[17] Mays, M. J.; Pearson, S. M. *J. Chem. Soc. A* **1969**, 136.

[18] Carbonyl stretching frequencies for $XW_{11}O_{39}SnFe(CO)_2Cp^{n-}$ (in cm⁻¹: X = P, 2021, 1971; X = Si, 2013, 1961; X = Ga, 2000, 1950) diminish with decreasing electronegativity of X.

bulkier groups. The resulting white solids were soluble in acetate buffer solutions (pH 4.0–5.5) and very soluble in Me_2SO. The different groups that were successfully introduced were the following: R = $CH_2C_6H_5$ (starting with both benzyl bromide and benzyl chloride), $(CH_2)_3Br$ (from 1,3-dibromopropane), $(CH_2)_4Cl$ (from 1,4-dichlorobutane), $(CH_2)_{11}CH_3$ (from 1-bromododecane) $(CH_2)_6Br$ (from 1,6-dibromohexane), and $C_{27}H_{45}$ (cholesteryl, from the tosylate).

Analysis. (1) $[(CH_3)_4N]_5SiW_{11}O_{39}Sn(CH_2)_{11}CH_3 \cdot 7H_2O$. Integration of the alkyl protons of the organic group (δ = 1.89–1.25 and 0.9 ppm) with N–CH_3 (δ = 3.17 ppm) gave a ratio of 1:2.9 (expected, 1:2.4). Anal. Calcd: C, 11.10; H, 2.86; N, 2.02; W, 58.48. Found: C, 12.03; H, 3.16; N, 2.12; W, 58.16.

(2) $[(CH_3)_4N]_5SiW_{11}O_{39}SnC_{27}H_{45} \cdot 6H_2O$. Integrated ratios of the cholesteryl group protons to the N–CH_3 group protons was found to be 1:1.8 (expected, 1:1.4). Anal. Calcd: C, 15.49; H, 3.21; N, 1.92; W, 55.55. Found: C, 16.06; H, 3.49; N, 2.05; W, 55.39.

(3) $[(CH_3)_4N]_5SiW_{11}O_{39}SnCH_2Ph \cdot 7H_2O$. In the ^1H NMR the integrated ratio observed was 1:12.4 (expected, 1:12). Anal. Calcd: C, 9.58; H, 2.40; N, 2.07; W, 59.83. Found: C, 10.41; H, 2.69; N, 2.14; W, 60.42.

(4) $[(CH_3)_4N]_5SiW_{11}O_{39}Sn(CH_2)_3Br \cdot 4H_2O$. Expected integrated ratio in the ^1H NMR is 1:30 while the observed value is 1:29.1. Anal. Calcd: C, 8.22; H, 2.20; N, 2.08; W, 60.24; Br, 2.38. Found: C, 7.85; H, 2.30; N, 2.13; W, 60.95; Br, 2.21.

(5) $[(CH_3)_4N]_5SiW_{11}O_{39}Sn(CH_2)_4Cl \cdot 5H_2O$. The proton integration ratio observed was 1:15.3 (expected, 1:15). Anal. Calcd: C, 8.61; H, 2.33; N, 2.09; W, 60.46; Cl, 1.06. Found: C, 8.57; H, 2.37; N, 2.14; W, 60.86; Cl, 1.18.

(6) $[(CH_3)_4N]_5SiW_{11}O_{39}Sn(CH_2)_6Br \cdot 7H_2O$. The integrated proton ratio observed was 1:5.6 (expected, 1:5). Anal. Calcd: C, 9.03; H, 2.55; N, 2.03; W, 58.56. Found: C, 9.34; H, 2.34; N, 2.03; W, 58.67.

Reaction of α_2-$K_8P_2W_{17}O_{61}Sn$ with 1-bromododecane proceeded in an analogous fashion.

Analyses. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, TN.

Physical Measurements. Optical and vibrational spectra and electrochemical measurements were made as described earlier.[19] All NMR spectra were obtained in pulse mode with a wide-band multinuclear probe on a Bruker WH/HFX-90 Fourier Transform spectrometer with an internal deuterium lock at 13.82 MHz. The spectrometer was equipped with a quadraphase detector. The spectra were recorded at the normal probe temperature (~30 °C) of the spectrometer. Spinning 10-mm NMR tubes containing the samples in deuteriated solvents were used. All spectra were referenced externally by the sample replacement method and chemical shifts at higher frequencies than the reference are recorded as positive.

Boron-11 Spectra. The spectra were obtained at 28.88 MHz with use of a 13.5-μs pulse. All spectra were digitized with 4096 data points and recorded by using a sweep width of 6000 Hz with a frequency offset of 2400 Hz and a repetition rate of 2.0 s. Chemical shifts were referenced to 0.1 M H_3BO_3 in D_2O.

Phosphorus-31 Spectra. The spectra were obtained at 36.44 MHz, using a 5.0-μs pulse, repetition rate of 3.0 s, SW 2000 Hz, and an offset of 1630 Hz. All spectra were digitized with 4096 data points and were referenced to 85% H_3PO_4.

Tin-119 Spectra. The ^{119}Sn NMR signal for a 60% (v/v) solution of $Sn(CH_3)_4$ in C_6D_6 (99.5%) at room temperature was located at a frequency of exactly 33.57 MHz. The ^{119}Sn NMR signal for a 20% (v/v) solution of $Sn(CH_3)_4$ in C_6D_6 at room temperature was located at the same frequency, since the reference does not change on dilution with noncoordinating solvents like benzene. A series of experiments was carried out on a 60% solution of $Sn(CH_3)_4$ in C_6D_6 to determine the exact value for a 90° pulse. The value was determined to be 12.3 μs. The ^{119}Sn spectra were recorded with a SW of 20000 Hz, a 12.3-μs pulse, and a repetition rate of 2.0 s, and the offset was varied depending on the compound under study. All spectra were digitized with 8192 data points and were referenced to $Sn(CH_3)_4$ in C_6D_6.

Results and Discussion

Inorganic Derivatives. Preparation and isolation of the Sn(II) and Sn(IV) heteropolyanions is straightforward. The Sn(IV) complexes can be prepared directly from the lacunary polyanion and $SnCl_4$ as reported by Schouten[15] or by oxidation of the preformed tungstostannate(II) anion, e.g., by aqueous Br_2.

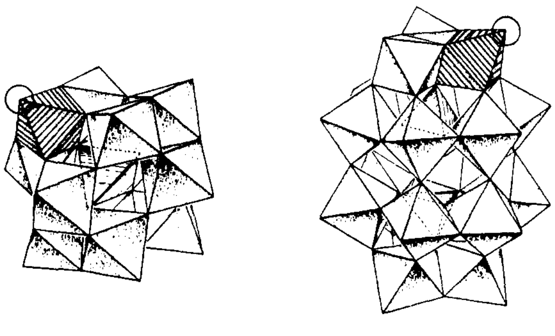

Figure 1. Polyhedral representations of (a) $XW_{11}O_{39}Sn^{n-}$ (Keggin) and (b) α_2-$P_2W_{17}O_{61}Sn^{8-}$ (Dawson) structures. The Sn(II) atoms occupy the hatched octahedra with lone-pair electrons directed toward the circled apices.

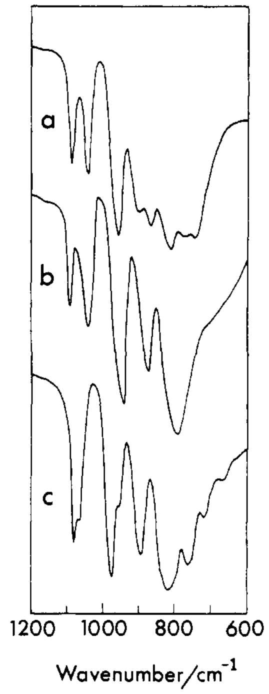

Figure 2. Infrared spectra (KBr disks) of tetramethylammonium salts of (a) $PW_{11}O_{39}^{7-}$, (b) $PW_{11}O_{39}Sn^{5-}$, and (c) $PW_{11}O_{39}SnOH^{4-}$.

Table I. Voltammetric Reduction Potentials of Tungstostannate(II) Anions[a]

anion	*E*, V vs. SCE
$PW_{11}O_{39}Sn^{5-}$	-1.04
$SiW_{11}O_{39}Sn^{6-}$	-0.89 (-0.97)[b]
$GeW_{11}O_{39}Sn^{6-}$	-0.89 (-0.97)[b]
$BW_{11}O_{39}Sn^{7-}$	-1.05
$GaW_{11}O_{39}Sn^{7-}$	-1.05 (-1.14)[b]
α_2-$P_2W_{17}O_{61}Sn^{8-}$	-0.56,[c] -0.81[c]

[a] Glassy carbon electrode; 2 V min^{-1}. 0.50 M acetate buffer, pH 4.7. [b] pH 5.5. [c] pH 4.3.

There are a number of lines of evidence to indicate that in these heteropolyanions the Sn(II) is too large to fit into the "octahedral" vacancy (ionic radius $W^{6+} \sim Sn^{4+} \sim 0.74$ Å, Sn^{2+} 1.12 Å) but is attached to the exterior of the vacancy as seen in the structure of the Pb(II) derivative, $GaW_{11}O_{39}Pb^{7-}$ (Figure 1).[8] (1) The IR spectra of the $XW_{11}O_{39}Sn^{II}$ anions in the 700–1000-cm^{-1} region more closely resemble those of lacunary $XW_{11}O_{39}^{n-}$, whereas the spectra of Sn(IV) derivatives are similar to those of $XW_{12}O_{40}^{n-}$. (See Figure 2, for example.) (2) The P–O stretching vibration at 1080 cm^{-1} in the spectrum of $PW_{12}O_{40}^{3-}$ is split by 45 cm^{-1} in $PW_{11}O_{39}^{7-}$. A similar splitting (50 cm^{-1} for K^+, Me_4N^+, and Bu_4N^+ salts) is observed for $PW_{11}O_{39}Sn^{5-}$ whereas for $PW_{11}O_{39}SnOH^{4-}$ it has been reduced to 15 and 20 cm^{-1} (Me_4N^+ and Bu_4N^+ salts). Weakley[20a] and Rocchiccioli-Deltcheff[20b] have

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[19] (a) Varga, G. M., Jr.; Papaconstantinou, E.; Pope, M. T. *Inorg. Chem.* **1970**, *9*, 662. (b) Prados, R. A.; Pope, M. T. *Ibid.* **1976**, *15*, 2547.

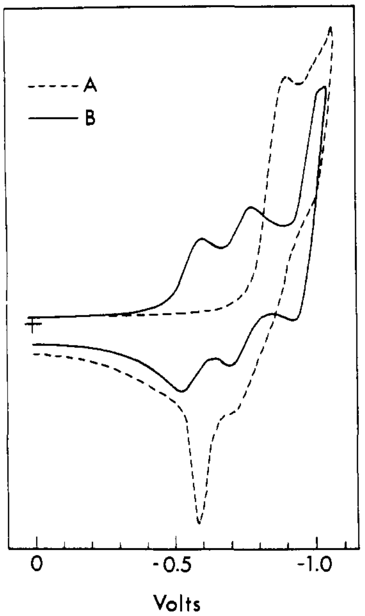

Figure 3. Cyclic voltammograms of (a) $SiW_{11}O_{39}Sn^{6-}$ and (b) $SiW_{11}O_{39}SnOH^{5-}$ at pH 4.7. Glassy carbon electrode. Sweep rate: 2.0 V/min.

Table II. Voltammetric Reduction Potentials of Tungstostannate(IV) Anions in Aqueous and Nonaqueous Solution[a]

anion	*E*, V vs. SCE (no. of electrons) aqueous[b]	*E*, V vs. SCE (no. of electrons) acetonitrile[c]
$PW_{11}O_{39}SnOH^{4-}$	-0.44 (1)	-0.95 (1)
	-0.68 (1)	-1.43 (1)
	-0.95 (2)	
$SiW_{11}O_{39}SnOH^{5-}$	-0.63 (1)	-1.35 (1)
	-0.76 (1)	-1.75 (1)
	-0.98 (2)	-1.95 (1)
$GeW_{11}O_{39}SnOH^{5-}$	-0.61 (1)	-1.28 (1)
	-0.74 (1)	-1.50 (1)
	-0.98 (2)	-1.80 (1)
$BW_{11}O_{39}SnOH^{6-}$	-0.82 (1)	
	-1.09 (?)	
$GaW_{11}O_{39}SnOH^{6-}$[d]	-0.74 (1)	-1.15 (1)
	-0.97 (1)	-1.60 (1)
	-1.15	-1.78 (1)
α_2-$P_2W_{17}O_{61}SnOH^{7-}$[e]	-0.29 (1)	
	-0.41 (1)	
	-0.66	
	-0.89	

[a] Glassy carbon electrode, 2 V min^{-1}. All reductions were reversible with $\Delta E \sim$ 60–80 mV. [b] 0.5 M acetate buffer, pH 4.7. [c] Tetrabutylammonium salts. 0.1 M Bu_4NClO_4. [d] pH 5.0. [e] pH 4.3.

argued that the magnitude of such splittings can be taken as a measure of the (lack of) interaction of the phosphate oxygen with the substituent metal cation. (3) Cyclic voltammograms of $XW_{11}O_{39}Sn^{II}$ (Table I) all show a large poorly resolved (?4-electron) reduction at about −1.0 V vs SCE. This behavior is similar to that of the corresponding lacunary species. On the other hand the cyclic voltammograms of the Sn(IV) derivatives show well-defined one- or two-electron W(VI→V) processes (Figure 3 and Table II) that parallel those of $XW_{12}O_{40}^{n-}$. Like the latter the reduction potentials become more negative as the anion charge increases (ca. 150 mV per unit charge) but for anions of the same charge, e.g., $PW_{11}O_{39}SnOH^{4-}$ and $SiW_{12}O_{40}^{4-}$, the tungstostannite is reduced at a more negative potential (by about 250 mV). Note that reduction of Sn(IV) to Sn(II) or oxidation of Sn(II) to Sn(IV) in the heteropolyanions is not observed in the cyclic voltammograms.[21] Furthermore, controlled potential reduction of a solution of $SiW_{11}O_{39}SnOH^{5-}$ (2.0 mM; pH 5.5) at −0.66 V consumed one faraday/mol and produced a dark blue solution. The ESR spectrum of the solution (aqueous glycerol glass at 77 K) showed an isotropic signal at g = 1.785, width 160 G (cf. $SiW^{V}W_{11}O_{40}^{5-}$ at g = 1.821; width ca. 100 G[19]). (4) Phosphorus-31 NMR spectra of $PW_{11}O_{39}SnOH^{4-}$ and α_2-$P_2W_{17}O_{61}SnOH^{7-}$ (Figure 4) show ^{31}P-O-^{119}Sn coupling of 18 ± 0.5 and 19.0 ± 0.5 Hz, respectively,[22] whereas the corresponding Sn(II) complexes show no coupling. Further, the ^{31}P chemical shifts for $P_2W_{17}O_{61}Sn^{8-}$ (−6.98 and −12.8 ppm) are close to those of the lacunary anion (−7.1 and −13.6 ppm[23]).

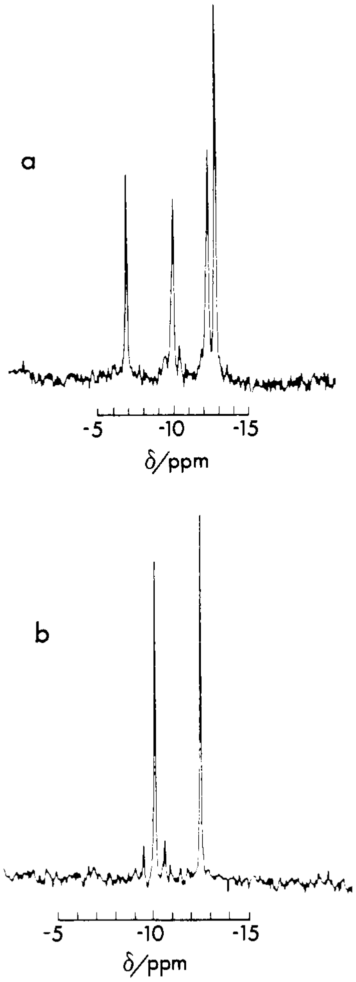

Figure 4. Phosphorus-31 NMR spectra of (a) a mixture of α_2-$P_2W_{17}O_{61}Sn^{8-}$ and α_2-$P_2W_{17}O_{61}SnOH^{7-}$ and (b) pure α_2-$P_2W_{17}O_{61}SnOH^{7-}$ showing Sn–P coupling of 19 Hz.

Organic and Organometallic Derivatives. The Sn(II) heteropolyanions react analogously to $SnCl_3^-$ as expected. Our synthesis of α-$SiW_{11}O_{39}SnFe(CO)_2Cp^{5-}$ can be compared with the following sequence of reactions reported by Knoth[7b]

$$SnCl_3^- + IFe(CO)_2Cp \rightarrow Cl_3SnFe(CO)_2Cp + I^-$$

$$Cl_3SnFe(CO)_2Cp + SiW_{11}O_{39}^{8-} \rightarrow SiW_{11}O_{39}SnFe(CO)_2Cp^{5-} + 3Cl^-$$

For the organic derivatives the displacement of bromide, chloride, or tosylate proceeds with moderate ease from aliphatic carbon

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(20) (a) Peacock, R. D.; Weakley, T. J. R. *J. Chem. Soc. A* **1971**, 1836. (b) Rocchiccioli-Deltcheff, C.; Thouvenot, R. *J. Chem. Res., Synop.* **1977**, 46. (c) Zonneville, F.; Tourné, C. M.; Tourné, G. F. *Inorg. Chem.* **1982**, *21*, 2742.

(21) This is of course to be expected since Sn(II) ↔ Sn(IV) involves atom as well as electron transfer.

(22) The coupling constant observed for the stannic compound is in good agreement with that reported by Knoth[7b] for $PW_{11}O_{39}SnPh^{4-}$ and $PW_{10}O_{38}(SnPh)^{5-}$ (16–20 Hz). No such coupling was observed in the ^{31}P NMR spectrum of $(PhSnOH_2)_3W_{18}P_2O_{68}^{9-}$, an anion with no Sn–O–P linkages.[7f]

(23) Harmalker, S. P.; Leparulo, M. A.; Pope, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 4286.

Table III. Voltammetric Reduction Potentials of $SiW_{11}O_{39}SnR^{5-}$ Derivatives[a]

R	E, V vs. SCE (no. of electrons)	R	E, V vs. SCE (no. of electrons)
$Fe(CO)_2Cp$	−0.60 (1)	$CH_2C_6H_5$	−0.63 (1)
	−0.82 (1)		−0.76 (1)
	−1.0 (2)		−0.98 (2)
$(CH_2)_4Cl$	−0.64 (1)	$C_{27}H_{45}$	−0.65 (1)
	−0.77 (1)		−0.82 (1)
	−0.98 (2)		−1.0 (2)
$(CH_2)_{11}CH_3$	−0.73 (1)	$(CH_2)_6Br$	−0.64 (1)
	−0.94 (1)		−0.77 (1)
			−1.0 (2)

[a] Glassy carbon electrode, 2 V min^{-1}. 0.5 M acetate buffer. pH 4.7.

Table IV. ^{119}Sn NMR Data for Tungstosilicostannates

compound	δ, ppm	$^2J(^{119}Sn-^1H)$, Hz
$(CH_3)_4Sn$	0.0	54.4
$SiW_{11}O_{39}Sn^{6-}$	−153	
$SiW_{11}O_{39}SnOH^{5-}$	−666	
$Si_{11}O_{39}SnCH_3{}^{5-}$	−493	114.8

atoms (typically 1 h at 50 °C). However, no reaction was observed, even on heating overnight, with the aryl halides 1-bromonaphthalene and 4,4′-dibromobiphenyl. Attempts to prepare "dumbell"-type derivatives with α,ω-dihalides lead to displacement of one halide ion only and recovery of excess unreacted tungstostannite. We have no immediate explanation for the aparent lack of reactivity of the second halide function. The analytical data show that the halide is still present in the products. Although most reactions with alkyl halides were made with $SiW_{11}O_{39}Sn^{6-}$, reaction of α_2-$P_2W_{17}O_{61}Sn^{8-}$ with 1-bromododecane proceeded analogously.[24]

The tetramethylammonium salts are water soluble and hydrolytically stable to pH 5.5–6.5 depending upon the polyanion moiety and charge. Cyclic voltammograms of the organo- and organometallic derivatives showed redox patterns analogous to those of the corresponding "inorganic" Sn(IV) complexes, and at virtually identical potentials (see Table III). This implies that the Sn atom is six-coordinate and nominally in oxidation state IV. A similar conclusion is provided by the following. The IR spectrum of $P_2W_{18}O_{62}{}^{6-}$ shows two P–O stretching bands at 1100 and 1022 cm^{-1}. The first of these is split in the spectra of the lacunary (1090, 1050 cm^{-1}) and Sn(II) (1092, 1062 cm^{-1}) anions, but not in the $Sn^{IV}OH$ (1098 cm^{-1}) and SnR (1100 cm^{-1}) species.[25]

Tin-119 NMR Spectroscopy. Chemical shifts and couplings provide a further insight into the electronic structure of the tin atoms in these complexes. All resonances were observed upfield from $Sn(CH_3)_4$ and this can be attributed mainly to the change in coordination around the tin atom. The paramagnetic contribution to nuclear shielding can be written[26]

$$\sigma_{(p)} = -(\Delta E)^{-1}\{A\langle r^{-3}\rangle_{5p}W_{5p} + B\langle r^{-3}\rangle_{5d}Q_{5d}\} \tag{1}$$

where ΔE is a mean excitation energy, A and B are positive constants, and the Q's represent electon imbalances in the respective orbitals. Both $\langle r^{-3}\rangle$ and Q_{5d} decrease as the tin atom is oxidized and the d orbitals are utilized for sp^3d (5-coordinate Sn(II)) and sp^3d^2 hybridization. The data in Table IV illustrate this effect. Note that the chemical shift of the heteropoly methyltin derivative lies between that of the Sn(II) and Sn(IV) polyanions but is closer to the latter. Note also that the coupling to the methyl protons is greater in the heterpolyanion than in tetramethyltin. The customary explanation of variations in such J values invokes isovalent hybridization arguments to account for the different degree of s character in the Sn–C(H$_3$) bond. Since J = 96.9 Hz for CH_3SnCl_3[27] we conclude that the s character in the Sn–C bond in this compound is similar to that in the heteropolyanion in spite of the differences in hybridization.

The chemical shifts for the tungstostannites range from −11.1 ppm for $BW_{11}O_{39}Sn^{7-}$ to −207.1 ppm for $GeW_{11}O_{39}Sn^{6-}$ (both measured in 10 M LiCl to enhance solubility, see Experimental Section). The large range cannot be attributed to differences in excitation energies (the ΔE term in eq 1) since the UV spectra vary very little, and we consider that the differences are due to electron imbalances (Q terms). There is a good correlation of δ(Sn) with Sn-Mössbauer data, and we discuss these effects elsewhere.[28] Coupling to ^{183}W was observed for $SiW_{11}O_{39}Sn^{6-}$ (124.5, 61.0 ± 2.5 Hz) and $GaW_{11}O_{39}Sn^{7-}$ (112.3 ± 2.5 Hz). The larger value is presumed to involve the corner-shared W–O–Sn connection and the smaller the edge-shared connection, as generally observed for $^{183}W-^{183}W$ and $^{183}W-^{51}V$ couplings.[7d,e,10,25,29] Knoth has reported Sn–W corner-shared cupling of 40 Hz in the ^{183}W NMR spectrum of $P_2W_{18}(PhSnOH_2)_3O_{68}{}^{9-}$.[7g]

The chemical shifts of the Sn(II) complexes were also found to be dependent upon the concentration of LiCl added to enhance the solubility. In those cases studied[30] the resonances moved upfield as [Li$^+$] increased. For example, for $SiW_{11}O_{39}Sn^{6-}$: M LiCl, δ; 0, −153; 2, −160; 5, −166; 8, −175; 10, −178.[31] Comparably large shifts were observed for $GeW_{11}O_{39}Sn^{6-}$ and α_2-$P_2W_{17}O_{61}Sn^{8-}$, but for $PW_{11}O_{39}Sn^{5-}$ the change was much smaller: −43.9 ppm in D_2O and −45.7 ppm in 10 M LiCl. Such shifts are in a direction consistent with the formation of ion-paired complexes in which Li$^+$ is associated with lone-pair electrons of the tin atom.

Acknowledgment. We thank Professor C. F. Hammer for advice and discussion on NMR and the National Science Foundation for support through Grant No. 8306736.

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[24] An attempt to react $PW_{11}O_{39}Sn^{5-}$ with 1-bromododecane was unsuccessful.

[25] Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677 and references therein.

[26] Gutowsky, H. S.; Juan, C. *J. Am. Chem. Phys.* **1962**, *37*, 2198.

[27] Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: New York, 1978; p 309.

[28] Chorghade, G. S.; Long, G. A.; Pope, M. T., in preparation.

[29] (a) Lefebvre, J.; Chauveau, F.; Doppelt, P.; Brĕvard, C. *J. Am. Chem. Soc.* **1981**, *103*, 4589. (b) Leparulo, M. A. Ph.D. Thesis, Georgetown University, 1984.

[30] With the 90-MHz spectrometer available, spectra of $BW_{11}O_{39}Sn^{7-}$ and the $GaW_{11}O_{39}Sn^{7-}$ could only be recorded in LiCl solutions.

[31] The ^2J(Sn–W) values also decreased as [LiCl] increased.