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Polyoxometalate Derivatives with Multiple Organic Groups. 2. Synthesis and Structures of Tris(organotin) α, *β*-Keggin Tungstosilicates

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Eight tris(organotin)-substituted Keggin tungstosilicate heteropolyanions have been synthesized and characterized by elemental analysis, infrared and Mössbauer spectroscopy, multinuclear NMR, and X-ray crystallography. The new anions contain α- or *β*-$SiW_9O_{34}^{10-}$ moieties and are of two structural types, $[(RSn)_3(SiW_9O_{37})]^{7-}$ (R, isomer: Ph, α-, **1**; *n*-Bu, α-, **2**; Ph, *β*-, **3**; *n*-Bu, *β*-, **4**) and $[(RSnOH)_3(SiW_9O_{34})_2]^{14-}$ (Ph, α-, **5**; *n*-Bu, α-, **6**; Ph, *β*-, **7**; *n*-Bu, *β*-, **8**). Crystals of $Cs_4H_3[(PhSn)_3(SiW_9O_{37})]\cdot 8H_2O$ (anion **3**) are monoclinic, space group C2/c, with lattice constants $a = 48.91(2)$ Å, $b = 12.111(3)$ Å, $c = 20.334(9)$ Å, $\beta = 102.30°$, and $Z = 8$. The anion has nominal C_{3v} symmetry and has a structure with three corner-shared WO_6 octahedra of the *β*-Keggin anion replaced by three $PhSnO_5$ groups. Crystals of $Cs_9H_5[(BuSnOH)_3(SiW_9O_{34})_2]\cdot 36H_2O$ (anion **6**) are tetragonal, space group $P\bar{4}2_1m$, with lattice constants $a = b = 29.005(4)$ Å, $c = 13.412(4)$ Å, and $Z = 4$. The anion has the anticipated D_{3h} symmetry and contains three BuSnOH groups sandwiched between A,α-$SiW_9O_{34}^{10-}$ anions.

Introduction

The chemistry of the polyoxometalate anions of the early transition elements is of considerable current interest with respect to the applications of these complexes in many fields.[1] Particular attention is being focused on their potential roles in environmentally benign catalytic processes,[2] and in antiviral and antitumoral chemotherapy.[3] The versatility of polyoxometalates for these and other applications has not yet been fully demonstrated, and the synthesis of new types of such complexes remains an important research objective.

We have long been interested in developing the chemistry of robust hydrolytically-stable organic derivatives of polyoxometalates.[4] Such complexes could have many possible important applications; e.g. they could be incorporated into polymer matrices to yield anchored catalytic or ion-exchange sites, or they could be designed for binding to, or passage through cell membranes, leading to improved delivery of possible polyoxometalate pharmaceuticals. Organotin derivatives of polyoxoanions are particularly attractive in this context because of the stability of the tin−carbon bond and the size compatibility of WO^{4+} and SnR^{3+} moieties. Earlier work has demonstrated that SnR^{3+} can be incorporated into Keggin and Dawson structures.[4,5] We report here the structural characterization of complexes derived from the lacunary anions $SiW_9O_{34}^{10-}$.

Experimental Section

Synthesis. Sodium A,α-9-tungstosilicate ($Na_{10}[\alpha\text{-}SiW_9O_{34}]\cdot xH_2O$) and sodium A,*β*-9-tungstosilicate ($Na_{10}[\beta\text{-}SiW_9O_{34}]\cdot 23H_2O$) were prepared following published methods[6] and were confirmed by infrared spectroscopy. Phenyltin trichloride and butyltin trichloride were obtained from Aldrich and used without further purification.

$Cs_{4.25}H_{2.75}[(PhSn)_3(\alpha\text{-}SiW_9O_{37})]\cdot 12.5H_2O$ (1). To a solution of 0.6 mL of $PhSnCl_3$ (3 mmol) in 40 mL of water at room temperature was added quickly 2.7 g (1 mmol) of powdered $Na_{10}[\alpha\text{-}SiW_9O_{34}]\cdot xH_2O$. After 10 min of vigorous stirring, any undissolved white residue was filtered off. Cesium chloride was added to the filtrate in small portions

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until no more precipitation was observed. The precipitate was collected on a medium-porosity sintered glass frit and dried under suction overnight. The resulting solid was recrystallized from hot water and dried under suction, giving a yield of 2.7 g. Anal. Calcd for $Cs_{4.25}H_{2.75}[(PhSn)_3(\alpha\text{-}SiW_9O_{37})]\cdot 12.5H_2O$: Cs, 15.45; C, 5.92; Sn, 9.74; Si, 0.77; W, 45.27. Found: Cs, 15.57; C, 5.92; Sn, 10.19; Si, 0.75; W, 45.26. NMR: ^1H, δ 7.68 (d, 2H, $J_{H-Sn} = 116$ Hz), 7.48 (m, 3H); $^{13}C\{H\}$, δ 133.2, 133.0, 128.1, 127.4; ^{119}Sn and ^{183}W, see Table 6.

$Cs_{4.5}H_{2.5}[(BuSn)_3(\alpha\text{-}SiW_9O_{37})]\cdot 2H_2O$ (2) was prepared analogously using the same quantities as above (0.6 mL of $BuSnCl_3$). Yield: 2.5 g. Anal. Calcd $Cs_{4.5}H_{2.5}[(BuSn)_3(\alpha\text{-}SiW_9O_{37})]\cdot 2H_2O$: Cs, 17.50; C, 4.22; Sn, 10.44; Si, 0.83; W, 48.51. Found: Cs, 18.00; C, 4.23; Sn, 10.41; Si, 0.93; W, 48.17. NMR: ^1H, δ 1.63 (t, 2H), 1.39 (m, 2H), 1.24 (m, 2H), 0.91 (t, 3H); ^{13}C, δ 28.1, 25.3, 23.3, 11.2; ^{29}Si, −83.8 (s, 1Si); ^{119}Sn and ^{183}W, see Table 6.

$Cs_4H_3[(PhSn)_3(\beta\text{-}SiW_9O_{37})]\cdot 8H_2O$ (3) and $Cs_xH_{7-x}[(BuSn)_3(\beta\text{-}SiW_9O_{37})]\cdot nH_2O$ (4) were prepared analogously. Powdered $Na_{10}[\beta\text{-}SiW_9O_{34}]$ (2.7 g, 1 mmol) was added to a solution of 0.6 mL of $RSnCl_3$ (R = Ph, Bu). Then CsCl was used to precipitate out **3** and **4**. Recrystallization of **3** from warm water gave long needle-like crystals, which were used for X-ray crystallography.

3. Yield: 2.5 g. Anal. Calcd for $Cs_4H_3[(PhSn)_3(\beta\text{-}SiW_9O_{37})]\cdot 8H_2O$: Cs, 14.98; C, 6.09; Sn, 10.03; Si, 0.79; W, 46.61. Found: Cs, 14.89; C, 6.05; Sn, 8.90; Si, 0.73; W, 46.58. NMR: ^1H, δ 7.70 (d, 2H, $J_{H-Sn} = 126$ Hz), 7.47 (m, 3H); ^{119}Sn and ^{183}W, see Table 6.

4. Yield: 1.7 g. NMR for $Cs_xH_{7-x}[(BuSn)_3(\beta\text{-}SiW_9O_{37})]\cdot nH_2O$: ^{119}Sn and ^{183}W, see Table 6.

$Cs_8H_6[(PhSnOH)_3(\alpha\text{-}SiW_9O_{34})_2]\cdot 23H_2O$ (5) was prepared by quickly adding excess $Na_{10}[\alpha\text{-}SiW_9O_{34}]$ (8 g, 3 mmol) to 40 mL of a solution containing 0.6 mL of $PhSnCl_3$ with stirring. Within a few seconds, the solution become clear. Cesium chloride was added to this solution in small portions after 10 min, until no more precipitation was observed. The precipitate was collected on a medium porosity sintered glass frit and dried overnight under suction. Recrystallization from hot water gave a yield of 3.2 g. Anal. Calcd for $Cs_8H_6[(PhSnOH)_3(\alpha\text{-}SiW_9O_{34})_2]\cdot 23H_2O$: Cs, 16.17; C, 3.29; Sn, 5.41; Si, 0.85; W, 50.33. Found: Cs, 15.68; C, 3.28; Sn, 4.63; Si, 0.79; W, 50.27. NMR: ^{29}Si, −83.2 (s, 2Si); ^{119}Sn and ^{183}W, see Table 6.

$Cs_9H_5[(BuSnOH)_3(\alpha\text{-}SiW_9O_{34})_2]\cdot 36H_2O$ (6), $Cs_xH_{14-x}[(PhSnOH)_3(\beta\text{-}SiW_9O_{34})_2]\cdot yH_2O$ (7) and $Cs_xH_{14-x}[(BuSnOH)_3(\beta\text{-}SiW_9O_{34})_2]\cdot yH_2O$ (8) were prepared analogously. Powdered $Na_{10}[\alpha\text{-}SiW_9O_{34}]$ or $Na_{10}[\beta\text{-}SiW_9O_{34}]$ (8 g, 3 mmol) was added to a solution of $RSnCl_3$ (R = Ph, Bu). Addition of CsCl yielded white precipitates which were filtered off and recrystallized from hot water. Single crystals of **6** were obtained by the method of vapor diffusion with ethanol.

6. Yield: 5.7 g. Anal. Calcd for $Cs_9H_5[(BuSnOH)_3(\alpha\text{-}SiW_9O_{34})_2]\cdot 36H_2O$: Cs, 17.39; C, 2.09; Sn, 5.18; Si, 0.82; W, 48.11. Found: Cs, 17.52; C, 2.01; Sn, 5.43; Si, 0.69; W, 48.23. NMR: ^1H, δ 1.91 (t, 2H, $J_{H-Sn} = 144$ Hz), 1.45 (m, 4H), 0.95 (t, 3H); ^{29}Si, −82.3 (s, 2Si); ^{119}Sn and ^{183}W, see Table 6.

7. Yield: 3.3 g. NMR for $Cs_xH_{14-x}[(PhSnOH)_3(\beta\text{-}SiW_9O_{34})_2]\cdot yH_2O$: ^1H, δ 8.14 (m, 2H, $J_{H-Sn} = 120$ Hz), 7.53 (m, 3H); ^{29}Si, −82.4 (s, 2Si); ^{119}Sn and ^{183}W, see Table 6.

8. Yield: 6.5 g. NMR for $Cs_xH_{14-x}[(BuSnOH)_3(\beta\text{-}SiW_9O_{34})_2]\cdot yH_2O$: ^{119}Sn and ^{183}W, see Table 6.

Physical Measurements. Elemental analyses were performed by E&R Microanalytical Laboratory Inc., Corona, NY. Infrared spectra were recorded on a MIDAC FTIR instrument. All NMR data were obtained on a Bruker AM-300WB spectrometer. Resonance frequencies were 300.113 MHz for ^1H and 75.469 MHz for ^{13}C in 5 mm tubes and 111.925 MHz for ^{119}Sn, 59.628 MHz for ^{29}Si, and 12.505 MHz for ^{183}W in 10 mm tubes. Pulse widths (90°) were 2.1 μs for ^{13}C, 11 μs for ^{119}Sn, 13.8 μs for ^{29}Si, and 40 μs for ^{183}W. Chemical shifts are reported with respect to 70% tetramethylsilane in acetonitrile for ^{29}Si and 2 M Na_2WO_4 for ^{183}W. For ^{119}Sn NMR, a solution of $SnCl_2$ in 12 M HCl (Chemical shift −388.1 vs tetramethyltin)[7] was used as an external standard, but the chemical shifts are reported with respect to $(CH_3)_4Sn$. All chemical shifts downfield of the references are reported as positive. Most of the NMR experiments were carried out in aqueous unbuffered solutions. To achieve sufficiently concentrated solutions for ^{183}W NMR (ca. 1 g/2 mL), the potassium and cesium salts were treated with $LiClO_4$.

Table 1. Crystallographic Data for $Cs_4H_3[(PhSn)_3(SiW_9O_{37})]\cdot 8H_2O$ and $Cs_9H_5[(BuSnOH)_3(SiW_9O_{34})_2]\cdot 36H_2O$

	3	**6**
chem formula	$Cs_4H_3[(PhSn)_3(SiW_9O_{37})]\cdot 8H_2O$	$Cs_9H_5[(BuSnOH)_3(SiW_9O_{34})_2]\cdot 36H_2O$
fw	3506.64	6209.35
T, °C	−100	25
λ, Å	0.710 73	0.710 73
space group	$C2/c$ (No. 15)	$P\bar{4}2_1m$ (No. 113)
unit cell dimens		
a, Å	48.91(2)	29.005(4)
b, Å	12.111(3)	29.005(4)
c, Å	20.334(9)	13.412(4)
β, deg	102.30(0)	
V, Å^3	11769(7)	11283(4)
Z	8	4
ρ_{calcd}, g cm^{-3}	3.958	3.655
μ, mm^{-1}	21.318	21.894
final R $[I > 2\sigma(I)]^a$		0.0957
final R $[I > 3\sigma(I)]^a$	0.0907	

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.

Mössbauer Spectroscopy. The tin-119 Mössbauer spectra were measured at 78 K on a conventional constant acceleration spectrometer which utilized a room-temperature $BaSnO_3$ matrix tin-119m source and was calibrated at room temperature with $BaSnO_3$. The spectra were fit with Lorentzian line shape doublets with equal component line widths and equal or close to equal component areas. The error limits on the resulting hyperfine parameters are estimated to be ±0.01 mm/s or better.

Crystallography. Crystals of the cesium salt of anion **3** used in this investigation lost solvent quickly, so they were mounted on glass fibers over dry ice. The data were collected at −100 °C on a Siemens P4/RA diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystals of the cesium salt of anion **6** were stable at room temperature, and the data were collected at 25 °C on the same diffractometer. Both structures were solved using SHELXL-PLUS (Siemens) direct methods for W, Sn, Cs, and Si, and were refined with SHELXL-93 (Sheldrick, G. M.) by full-matrix least-squares, the minimized function being $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was $w = 1/[\sigma^2(F^2) + (0.0922P)^2 + 12.05P]$, where $P = (\mathrm{Max}(F^2, 0) + 2F_c^2)/3$.

Crystal data and structure refinement parameters of **3** and **6** are listed in Table 1. Four cesium atoms were well refined for **3**. Final atomic coordinates and thermal parameters of **3** are given in Table 2, and selected bond lengths, in Table 3. In the structure of **6**, the butyl groups are disordered, and only the α-carbons were well refined. Nine restraints were introduced to fix the positions of the remaining carbons, although only the β-carbons of the butyl groups could be located. Nine cesium atoms and half a potassium atom (located at the 4-fold inversion center) are well refined.[8] The finding of nine cesium atoms is consistent with the elemental analysis. Three of the cesium atoms, Cs(1), Cs(2), and Cs(3), are located at special positions, on the crystallographic mirror plane containing three tin atoms. Each Cs is located between two Sn atoms and is bonded to four Sn−O−W bridging-oxygens. Final atomic coordinates and thermal parameters of **6** are given in Table 4, and selected bond lengths, in Table 5.

Results and Discussion

The structure of the sodium salt of β-$[SiW_9O_{34}]^{10-}$ (β-SiW_9) has been previously determined,[9] and the anion was confirmed as a lacunary derivative of β-$SiW_{12}O_{40}^{4-}$; see Figure 1a.

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(8) A potassium analysis of **6** has not been performed. During the process to precipitate out **6**, KCl was first added to the solution containing **6**. When no precipitation occurred, CsCl was then added. The presence of potassium in the crystals is therefore understandable. If the electron density at the inversion center is not assigned to any atom, or is assigned to H_2O, Na, or Cs instead of K, the temperature factor U_{eq} of the atom is too large for Na and H_2O and too small for Cs, and the final R increases by more than 0.5%.

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Table 2. Significant Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[(PhSn)_3(SiW_9O_{37})]^{7-}$

	x	*y*	*z*	*U*(eq)[a]
W(8)	1603(1)	9722(2)	1794(1)	28(1)
W(7)	1742(1)	11838(2)	536(1)	39(1)
W(3)	2014(1)	11491(2)	3115(1)	43(1)
W(9)	1298(1)	10521(2)	3066(1)	51(1)
W(6)	1572(1)	14531(2)	681(1)	57(1)
W(2)	2137(1)	13388(2)	1999(1)	62(1)
W(1)	1837(1)	14164(2)	3277(1)	81(1)
W(4)	1102(1)	13522(2)	3260(1)	79(1)
W(5)	1233(1)	15402(2)	2121(1)	89(1)
Sn(3)	921(1)	10455(3)	1480(2)	39(1)
Sn(2)	1063(1)	12661(3)	183(2)	36(1)
Sn(1)	712(1)	13553(3)	1674(2)	70(2)
Si	1419(4)	12603(11)	1908(7)	47(4)
O(99)[b]	1273(9)	9749(31)	3771(18)	61(11)
O(33)	2252(7)	10700(24)	3678(15)	36(8)
O(38)	1906(6)	10582(20)	2358(12)	19(6)
O(39)	1662(7)	11192(23)	3365(14)	32(8)
O(14)	1507(9)	13505(30)	3550(18)	58(11)
O(27)	1401(7)	11833(25)	−44(15)	38(8)
O(23)	2269(8)	12223(27)	2638(16)	48(9)
O(78)	1669(6)	10586(22)	1044(13)	26(7)
O(88)	1776(7)	8482(25)	1679(15)	37(8)
O(77)	1951(8)	11312(28)	45(17)	52(10)
O(89)	1496(8)	9428(27)	2614(16)	47(9)
O(26)	1250(9)	14174(31)	67(18)	61(11)
O(4)	1320(7)	11329(24)	1979(14)	34(8)
O(56)	1370(8)	15195(30)	1321(18)	61(11)
O(66)	1701(8)	15689(30)	331(18)	57(11)
O(1)	1742(7)	12835(25)	2385(15)	40(9)
O(27)	2026(8)	12289(28)	1340(17)	53(10)
O(3)	1430(7)	12810(23)	1112(14)	31(8)
O(55)	1267(10)	16796(39)	2160(23)	92(15)
O(26)	1879(10)	14358(35)	1462(21)	77(13)
O(67)	1774(8)	13370(28)	311(16)	49(9)
O(15)	1626(9)	15105(32)	2624(19)	65(11)
O(12)	2147(9)	14275(31)	2738(18)	61(11)
O(22)	2460(9)	13816(31)	1824(18)	62(11)
O(2)	1176(7)	13385(26)	2130(16)	43(9)
O(45)	1158(10)	15037(35)	2998(21)	77(13)
O(13)	2043(8)	12849(27)	3630(16)	46(9)
O(11)	1973(10)	15086(37)	3933(21)	82(14)
O(49)	1151(9)	11942(32)	3251(19)	65(12)
O(44)	1030(9)	13660(34)	4051(20)	74(13)
O(15)	855(8)	15159(30)	1687(18)	58(11)
O(39S)	963(8)	10139(29)	2480(18)	57(10)
O(14S)	755(10)	13409(38)	2698(23)	91(15)
O(13S)	704(8)	11841(26)	1653(16)	45(9)
O(12S)	817(7)	13539(22)	739(14)	29(7)
O(38S)	1249(7)	9392(25)	1342(15)	37(8)
O(23S)	954(7)	11224(23)	565(14)	30(8)
C(21)	767(13)	12653(45)	−776(27)	52(15)
C(11)	165	13918	763	130
C(31)	632(13)	9294(47)	1173(28)	56(16)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Labeling of oxygen atoms. Terminal: O(11), O(22) etc. attached to W(1), W(2) etc. respectively. Bridging: O(12) between W(1) and W(2), etc. All oxygens attached to tin have labels terminating with S.

Although no X-ray structure of α-$[SiW_9O_{34}]^{10-}$ (α-SiW_9) has been reported, all structurally characterized compounds made from α-SiW_9 retain the fragment illustrated in Figure 1b.[10] Two of the eight compounds reported here are shown to contain the same α or *β*-structures as the starting lacunary anions (Figures 2 and 3). It is presumed, based on spectroscopic evidence, that no isomerization has occurred in the other six complexes.

Table 3. Selected Bond Lengths (Å) for $[(PhSn)_3(SiW_9O_{37})]^{7-}$

	bond length	average
W−O(W)	1.84(4)−2.06(4)	1.93
W−O(Sn)	1.82(3)−1.89(3)	1.85
W−O(Si)	2.33(3)−2.46(3)	2.42
W═O	1.70(4)−1.77(4)	1.74
Sn−O(W)	2.04(4)−2.12(3)	2.07
Sn−O(Sn)	2.02(3)−2.12(3)	2.08
Sn−O(Si)	2.26(3)−2.32(2)	2.28
Sn−C	2.00(6)−2.17(6)	2.06
Si−O	1.63(3)−1.69(4)	1.66

Table 4. Significant Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[(BuSnOH)_3(SiW_9O_{34})_2]^{14-}$

	x	*y*	*z*	*U*(eq)[a]
W(8)	8710(1)	2127(1)	4835(2)	17(1)
W(7)	7923(1)	1337(1)	5190(2)	17(1)
W(6)	7353(1)	771(1)	3047(2)	22(1)
W(4)	8530(1)	1957(1)	348(2)	23(1)
W(5)	7645(1)	1059(1)	777(2)	23(1)
W(3)	9384(1)	1312(1)	3272(2)	20(1)
W(9)	9036(1)	2451(1)	2257(2)	21(1)
W(2)	8579(1)	506(1)	3622(2)	22(1)
W(1)	8882(1)	808(1)	1307(2)	25(1)
Sn(1)	8101(1)	3101(1)	1071(4)	24(2)
Sn(2)	6589(1)	1589(1)	1766(4)	29(2)
Sn(3)	7541(1)	2541(1)	5389(4)	22(1)
Si	8244(5)	1585(5)	2755(11)	16(3)
O(89)[b]	8875(10)	2412(11)	3595(24)	19(8)
O(4)	7780(12)	1322(12)	2276(28)	36(10)
O(45)	8000(15)	1594(15)	351(35)	63(14)
O(14)	8873(11)	1402(11)	699(25)	25(9)
O(88)	9065(10)	2322(10)	5656(23)	21(8)
O(3)	8418(9)	2010(9)	2040(21)	0(7)
O(2)	8642(12)	1183(12)	2727(29)	36(10)
O(1)	8183(9)	1755(9)	3854(22)	6(7)
O(13)	9420(13)	937(13)	2073(29)	43(11)
O(22)	8680(13)	2(14)	4209(29)	50(11)
O(12)	8812(14)	352(14)	2343(31)	51(12)
O(39)	9347(11)	1844(11)	2562(24)	20(9)
O(56)	7402(11)	614(10)	1722(24)	19(8)
O(15)	8255(9)	745(9)	1058(20)	3(7)
O(77)	7793(10)	1014(10)	6269(24)	18(8)
O(99)	9541(13)	2759(13)	2316(30)	44(11)
O(49)	9040(12)	2301(12)	990(27)	38(10)
O(38)	9130(9)	1599(9)	4295(21)	0(7)
O(78)	8465(9)	1676(9)	5697(22)	8(7)
O(66)	7070(13)	322(13)	3546(30)	49(12)
O(23)	9203(11)	748(11)	3965(24)	22(9)
O(67)	7506(10)	1073(10)	4236(22)	12(8)
O(44)	8672(12)	1946(12)	−840(27)	36(10)
O(55)	7566(10)	785(10)	−363(23)	15(8)
O(33)	9967(13)	1321(12)	3521(26)	33(9)
O(26)	7930(13)	502(12)	3200(28)	40(11)
O(11)	9158(11)	470(11)	438(24)	26(9)
O(38S)	8199(11)	2526(11)	5132(27)	32(9)
O(25S)	7131(9)	1400(9)	771(21)	3(7)
O(37S)	7540(9)	1840(9)	5367(21)	2(7)
O(14S)	8122(11)	2457(11)	258(26)	26(9)
O(26S)	6858(13)	1118(12)	2778(29)	40(11)
O(19S)	8615(10)	2910(10)	2065(22)	14(8)
O(27)	8390(9)	911(9)	4727(21)	2(7)
O(2S)	7070(14)	2070(14)	2219(45)	53(18)
O(1S)	7730(10)	2730(10)	1981(34)	20(12)
O(3S)	7467(10)	2467(10)	3908(32)	13(11)
C(11)	8477(14)	3477(14)	−150(54)	27(20)
C(21)	6083(18)	1083(18)	947(43)	34(21)
C(31)	7672(15)	2672(15)	7026(81)	69(32)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Labeling of oxygen atoms. Terminal: O(11), O(22) etc. attached to W(1), W(2) etc. respectively. Bridging: O(12) between W(1) and W(2), etc. All oxygens attached to tin have labels terminating with S.

Unlike the reaction of organotin trichloride with $[PW_9O_{34}]^{9-}$, which yields only $[(RSnOH)_3(PW_9O_{34})_2]^{12-}$,[4d] with SiW_9, two

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(10) Cadot, E.; Thouvenot, R.; Tézé, A.; Hervé, G. *Inorg. Chem.* **1992**, *31*, 4128.

(11) Chorghade, G. S. Ph.D. Thesis, Georgetown University 1985.

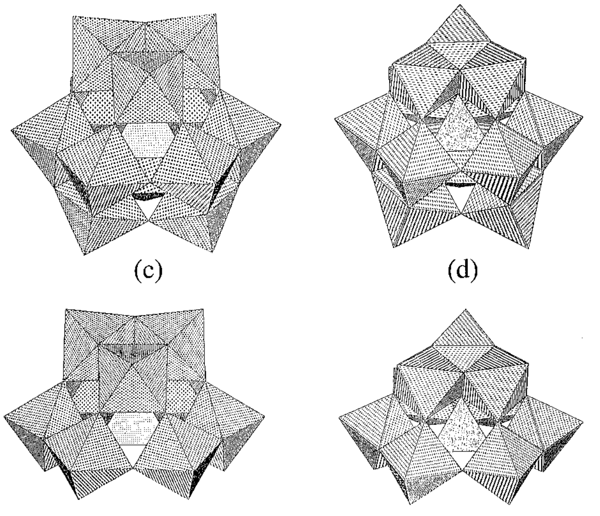

Figure 1. Polyhedral representations of the structures of A,α-$XW_9O_{34}^{m-}$ (a), A,β-$XW_9O_{34}^{m-}$ (b), α-$XW_{12}O_{40}^{n-}$ (c), and β-$XW_{12}O_{40}^{n-}$ (d).

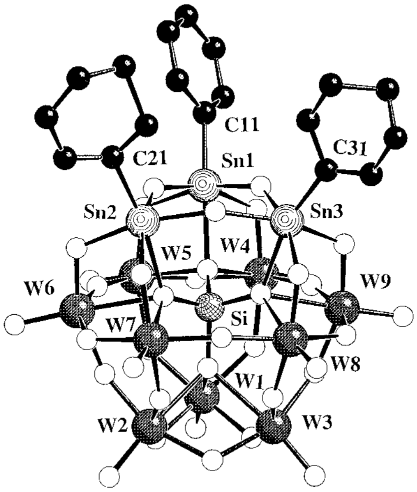

Figure 2. SCHAKAL representation of the structure of $[(PhSn)_3(\beta\text{-}SiW_9O_{37})]^{7-}$ (**3**) showing atom labels.

Table 5. Selected Bond Lengths (Å) for $[(BuSnOH)_3(SiW_9O_{34})_2]^{14-}$

	bond length	average
W−O(W)	1.74(3)−2.09(3)	1.91
W−O(Sn)	1.79(3)−1.90(3)	1.85
W−O(Si)	2.21(4)−2.33(3)	2.27
W=O	1.67(3)−1.76(3)	1.71
Sn−O(W)	1.95(3)−2.13(3)	2.05
Sn−OH	1.93(5)−2.06(5)	1.99
Sn−C	2.34(6)−2.51(8)	2.42
Si−O	1.59(3)−1.68(4)	1.64

kinds of products were formed, $[(RSn)_3(SiW_9O_{37})]^{7-}$ ($(RSn)_3(SiW_9)$) and $[(RSnOH)_3(SiW_9O_{34})_2]^{14-}$ ($(RSnOH)_3(SiW_9)_2$), depending upon the ratio of $RSnCl_3$ and SiW_9 used.

Reaction of $RSnCl_3$ with SiW_9 (α or β isomer) in a 3:1 mole ratio cleanly gives $[(RSn)_3(SiW_9O_{37})]^{7-}$ (**1**, **2**, **3**, and **4**) in good yields (48%−75%). The structure of **3**, shown in Figure 2, confirms that no isomerization of the precursor lacunary anions (β in this case) has occurred. Anion **3** has a β-Keggin structure with three corner-sharing WO_6 octahedra replaced by three $PhSnO_5$ groups. The phenyl groups are oriented in such a way that virtual C_{3v} symmetry is maintained. Elemental analyses and multinuclear NMR spectroscopy (Table 6) of compounds **1**, **2**, **3**, and **4** are fully consistent with this structure.

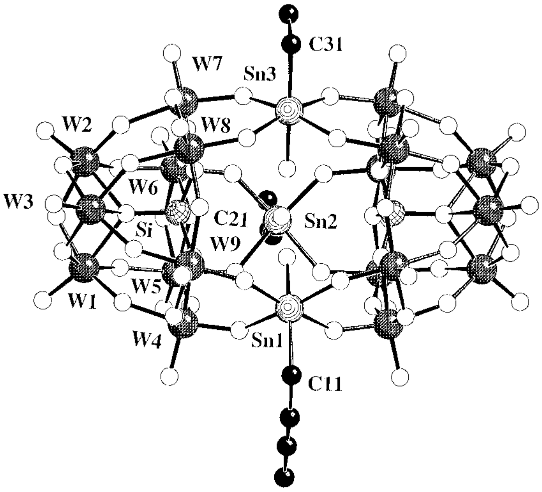

Figure 3. SCHAKAL Representation of the structure of $[(BuSnOH)_3(\alpha\text{-}SiW_9O_{34})_2]^{14-}$ (**6**) showing atom labels.

Table 6. ^{119}Sn and ^{183}W NMR Data

anion	$\delta(^{119}Sn)$, ppm	$\delta(^{183}W)$, ppm (intensity)	J_{Sn-W}, Hz
1	−578	−85 (2), −166 (1)	12
2	−518	−95 (2), −172 (1)	26
3	−581	−99 (2), −137 (1)	14
4	−524	−100 (2), −138 (1)	
5	−622	−150 (1), −189 (2)	35
6	−576	−151 (1), −190 (2)	15
7	−621	−126 (1), −208 (2)	27
8	−575	−128 (1), −211 (2)	

When 3 mol of $RSnCl_3$ react with 2 mol of SiW_9, a mixture containing two kinds of compounds is obtained. One product is identified by NMR as $(RSn)_3(SiW_9)$ (**1**, **2**, **3**, or **4**). The other compound has a similar NMR pattern, with one line ^{29}Si and ^{119}Sn resonance, and two ^{183}W lines with intensity ratio of 2:1. The chemical shifts are different from those of the other product (Table 6).

When an additional mole of SiW_9 was used in the reaction ($[RSn]:[SiW_9] = 1:1$), the second compound (**5**, **6**, **7**, or **8**) is the only product. Infrared spectra (Figure 4) also confirm that **2** and **6**, and **4** and **8**, are different compounds. The structure of **6**, shown in Figure 3, consists of two A-type α-SiW_9 anions linked by three butyltin groups into an assembly of virtual D_{3h} symmetry, analogous to that observed for $[(PhSnOH)_3(PW_9O_{34})_2]^{12-}$.[4b] The elemental analyses and multinuclear NMR spectra of **5**, **6**, **7**, and **8** are fully consistent with this structure.

Reactivity. Both $(RSn)_3(SiW_9)$ and $(RSnOH)_3(SiW_9)_2$ structures are stable in aqueous solution at pH 2−6, either separately or as mixtures. On the basis of the manner in which $(RSn)_3(SiW_9)$ and $(RSnOH)_3(SiW_9)_2$ are prepared, there might be an equilibrium linking the two anions. Three preliminary experiments have been carried out in order to explore this possibility: (1) α-SiW_9 reacted with α-$(BuSn)_3(SiW_9)$; (2) β-SiW_9 reacted with α-$(PhSn)_3(SiW_9)$; (3) $RSnCl_3$ reacted with $(RSnOH)_3(SiW_9)_2$.

(1) Powdered α-SiW_9 (0.1 g, 4.1×10^{-2} mmol) was added to an unbuffered solution of 0.5 g (1.4×10^{-1} mmol) of $[(BuSn)_3(\alpha\text{-}SiW_9O_{37})]^{7-}$ in a 10-mm NMR tube. The ^{119}Sn-{H} NMR spectrum of the freshly-made solution contained three lines, δ −518 ppm ($\Delta\nu_{1/2}$ 52 Hz, assigned to **2**), δ −576 ppm ($\Delta\nu_{1/2}$ 30 Hz, assigned to **6**), and an unidentified line at δ −524 ppm ($\Delta\nu_{1/2}$ 143 Hz). After a day, the same solution showed only the lines of **2** and **6** with an intensity ratio of about 3:1. The ^{183}W NMR of this solution contained four lines assigned to **2** and **6** also in a ratio of about 3:1.

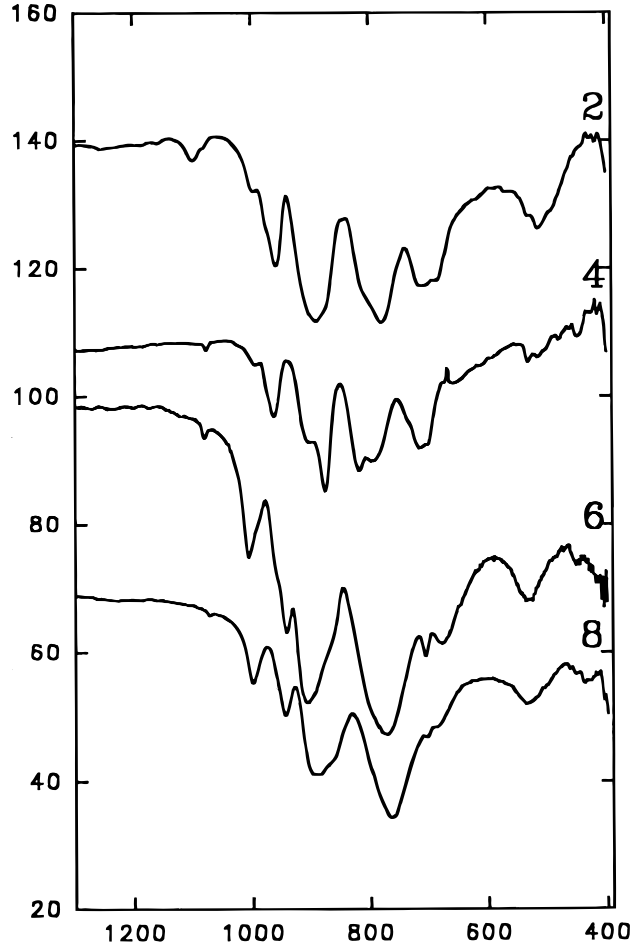

Figure 4. Infrared spectra of cesium salts of **2, 4, 6,** and **8**, recorded on KBr pellets.

(2) When powdered β-SiW$_9$ (0.2 g, 9 × 10^{-2} mmol) was added to a solution of 0.4 g (0.12 mmol) (PhSn)$_3$(α-SiW$_9$), the ^{119}Sn and ^{183}W NMR spectra of this solution showed the lines of unreacted (PhSn)$_3$(α-SiW$_9$), as well as α- and β-(PhSnOH)$_3$(SiW$_9$)$_2$ (**5** and **7**). There is one extra ^{119}Sn line at -574 ppm and two new ^{183}W lines at -192, and -206 ppm with equal intensity. These are assigned to the α,β mixed sandwich structure, $[(\alpha\text{-SiW}_9O_{34})(RSnOH)_3(\beta\text{-SiW}_9O_{34})]^{14-}$. The two new ^{183}W lines at -192 and -206 ppm are assigned to the belt-tungsten atoms of α- and β-SiW$_9$ of this mixed sandwich compound respectively, while the chemical shifts of the cap-W of this compound overlap with those of **5** and **7**. From the intensity ratios, the molar ratio of **5**, **7**, and the α,β mixed compound was determined to be *ca.* 6:2:5. Further investigation is underway.

(3) Butyltin trichloride (0.15 mL) was added to a solution of α-(BuSnOH)$_3$(SiW$_9$)$_2$ (0.5 g) in a 10-mm NMR tube. The ^{183}W NMR of this solution shows only two peaks from (RSnOH)$_3$(α-SiW$_9$)$_2$.

On the basis of these experiments, it is concluded that (RSn)$_3$(SiW$_9$) is kinetically stable, but (RSnOH)$_3$(SiW$_9$)$_2$ is the thermodynamically stable product. A 3 mol sample of RSnCl$_3$ first reacts with 1 mol of SiW$_9$ to give (RSn)$_3$(SiW$_9$). When extra SiW$_9$ is present, (RSn)$_3$(SiW$_9$) reacts further to give the final thermodynamically stable compound (RSnOH)$_3$(SiW$_9$)$_2$:

$$3RSnCl_3 + SiW_9 \rightarrow (RSn)_3(SiW_9) \qquad (1)$$

$$(RSn)_3(SiW_9) + SiW_9 \rightarrow (RSnOH)_3(SiW_9)_2 \qquad (2)$$

Table 7. Tin Mössbauer Effect Hyperfine Parameters for Tungstostannate(IV) Compounds[a]

compound	δ	ΔE_Q	Γ	A_1/A_2	ref
$Cs_{4.5}H_{2.5}[(BuSn)_3(\alpha\text{-SiW}_9O_{37})]$ (**2**)	0.73	1.37	0.96	1.15	this work
$Cs_xH_{7-x}[(BuSn)_3(\beta\text{-SiW}_9O_{37})]$ (**4**)	0.82	1.37	0.96	1.13	this work
$Cs_9H_5[(BuSnOH)_3(\alpha\text{-SiW}_9O_{34})_2]$ (**6**)	0.80	1.57	1.05	1.07	this work
$Cs_xH_{14-x}[(BuSnOH)_3(\beta\text{-SiW}_9O_{34})_2$ (**8**)	0.82	1.92	1.09	0.98	this work
$K_{11}H[(PhSn)_3(\beta\text{-PW}_9O_{34})_2]$	0.55	1.70	0.96	1.18	27
$K_5H_4[(BuSn)_3(P_2W_{15}O_{59})]$	0.75	1.12	0.86	1.00	27
$K_5[(BuSn)(SiW_{11}O_{39})]$	0.84	1.26	1.02	1.01	27
$K_5[(MeSn)(SiW_{11}O_{39})]^b$	0.59	1.26	0.99	1.00	11
$(Me_4N)_4[(HOSn)(PW_{11}O_{39})]^b$	0.08	0.36	0.81	1.00	11
$(Me_4N)_5[(HOSn)(SiW_{11}O_{39})]^b$	0.06	0.28	0.84	1.00	11
$(Me_4N)_5[(HOSn)(GeW_{11}O_{39})]^b$	0.06	0.39	0.82	1.00	11
$(Me_4N)_6[(HOSn)(BW_{11}O_{39})]^b$	0.05	0.31	0.79	1.00	11
$(Me_4N)_4[(HOSn)(GaW_{11}O_{39})]^b$	0.06	0.55	0.84	1.00	11
$K_7[(HOSn)(\alpha_2\text{-P}_2W_{17}O_{61})]^b$	0.06	0.30	0.84	1.00	11

[a] All data measured at 78 K and given in mm/s with the isomer shifts given relative to room temperature BaSnO$_3$. [b] Mössbauer data collected at A.E.R.E., Harwell, England.

Since reaction 2 is slow, and SiW$_9$ is unstable in aqueous solution, excess SiW$_9$ is needed in order to form (RSnOH)$_3$(SiW$_9$)$_2$.

In experiment 2, when β-SiW$_9$ reacted with α-(PhSn)$_3$(SiW$_9$), three products were formed: $[(\alpha\text{-SiW}_9O_{34})(RSnOH)_3(\beta\text{-SiW}_9O_{34})]^{14-}$, $[(RSnOH)_3(\alpha\text{-SiW}_9O_{34})_2]^{14-}$, and $[(RSnOH)_3(\beta\text{-SiW}_9O_{34})_2]^{14-}$. This suggests that in reaction 2, (RSn)$_3$(SiW$_9$) dissociates first, then reacts with SiW$_9$ to give the three kinds of stable sandwich compounds.

Mössbauer Spectral Results. The tin-119 Mössbauer parameters of **2**, **4**, **6**, and **8** are compared with those of several related tin(IV) and organotin polyoxotungstates in Table 7. The isomer shifts, δ, of anions with the Keggin structure in which one WO$_6$ octahedron has been replaced by Sn^{IV}O$_6$, are characteristic of tin(IV) and are close to zero. The small quadrupole splittings, ΔE_Q, of 0.3 to 0.6 mm/s are indicative of a fairly regular O$_6$ octahedral coordination environment for the tin(IV) ions.

The isomer shifts of 0.55 to 0.84 mm/s for the organotin species are larger than those of hydroxytin(IV) species as expected. Because the isomer shifts of tin are dependent on the s-electron density at the ^{119}Sn nucleus,[12,13] the loss of valence-shell electrons, particularly from the 5s-orbital, results in a decrease in the isomer shift. Similarly, the quadrupole splittings of 1.12−1.92 mm/s for the organotin species are larger than those of the hydroxytin species as a consequence of the lower symmetry of the PhSnO$_5$ coordination environment.

The quadrupole splitting parameters may be divided into two groups, those which fall in the 1.6−2.4 mm/s range typical[13] of RSnX$_5$ compounds and those which are smaller. The first group contains the three compounds with the sandwich structure, $[(BuSnOH)_3(\alpha\text{-SiW}_9O_{34})_2]^{14-}$, $[(BuSnOH)_3(\beta\text{-SiW}_9O_{34})_2]^{14-}$, and $[(PhSnOH)_3(\beta\text{-PW}_9O_{34})_2]^{12-}$, with $\Delta E_Q = 1.57-1.92$ mm/s. The second group includes the three organotin trisubstituted Keggin and Dawson complexes, $[(BuSn)_3(\alpha\text{-SiW}_9O_{37})]^{7-}$, $[(BuSn)_3(\beta\text{-SiW}_9O_{37})]^{7-}$, and $[(BuSn)_3(P_2W_{15}O_{59})]^{9-}$, and the two organotin monosubsitituted compounds, $[(BuSn)(SiW_{11}O_{39})]^{5-}$ and $[(MeSn)(SiW_{11}O_{39})]^{5-}$, with $\Delta E_Q = 1.12-1.37$ mm/s. We provisionally attribute these differences to differences in the axial components of the electric field gradient tensors. Although all the complexes contain "octahedral" O$_5$R coordination spheres for tin, the ligand trans to the organic group is hydroxy (Sn−O = 2 Å) in the sandwich structures, but is a weakly bound silicate

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(12) Omae, I. *Organotin Chemistry*; Elsevier Science Publishers B.V.: Amsterdam, The Netherlands, 1989; p 277.

(13) Parish, R. V. *Mössbauer Spectroscopy Applied to Inorganic Chemistry*; Long, G. J., Ed., Plenum: New York, 1984; Vol 1, p 530.

or phosphate oxygen (Sn−O = 2.3−2.4 Å) in the substituted Keggin and Dawson species.

NMR. The eight tris(organotin) polyoxotungstates can be well characterized by multinuclear NMR spectroscopy; see Table 6. The four structure types are: α-Keggin (**1** and **2**), β-Keggin (**3** and **4**), α-sandwich (**5** and **6**), and β-sandwich (**7** and **8**). Since the α and β-Keggin structures have C_{3v} symmetry and α and β-sandwich structures have D_{3h} symmetry, all eight compounds have similar NMR spectra: typical phenyl or butyl ^{1}H and ^{13}C NMR, one line ^{29}Si and ^{119}Sn NMR, and two-line ^{183}W NMR with relative intensity 1:2. The W−W coupling constants ($^{2}J_{\mathrm{w-o-w}}$) of all eight are *ca.* 15 Hz, are typical of coupling between corner-shared WO_6 octahedra, and are consistent with structures of A-type SiW_9 fragments.[14]

The ^{119}Sn chemical shifts are very sensitive to the chemical environment change around the tin.[15] The chemical shifts of the phenyl complexes are 50−60 ppm upfield of those of butyl complexes with the same structure, a trend that has been noted before.[16] This might be caused by back-donation of the p-electrons of the phenyl carbon into an empty 5d orbital on tin, increasing the shielding of the tin atom.[16] We also note that the chemical shifts of the sandwich compounds are 40−50 ppm upfield relative to those of Keggin compounds with the same organic ligand on tin. This could be caused by the different coordination around tin. As noted above, in the Keggin structure the tin could be considered as five-coordinate, since the axial Sn−O bond is very weak. In the sandwich structure tin is clearly six-coordinate. An increase in the coordination number of tin usually produces a large upfield shift of $\delta(^{119}\mathrm{Sn})$.[17] The tin chemical shift patterns have also been observed in the similar compounds: $[(PhSnOH)_3(PW_9O_{34})_2]^{12-}$ (δ −609 ppm), $[(BuSnOH)_3(PW_9O_{34})_2]^{12-}$ (δ −578 ppm), $[(PhSn)_3(P_2W_{15}O_{59})]^{9-}$ (δ −567 ppm), and $[(BuSn)_3(P_2W_{15}O_{59})]^{9-}$ (δ −518 ppm).[4d] For α and β isomers, the coordination environment around tin is almost the same, and the isomers (**1** and **3**, **2** and **4**, **5** and **7**, and **6** and **8**) give virtually identical ^{119}Sn NMR spectra.

Different organic ligands on tin do not have any significent effects on the ^{183}W chemical shifts. However the different structures show characteristic ^{183}W patterns, as illustrated in Figure 5. All spectra contain two lines with intensity ratio of 1:2 corresponding to the cap- and belt-tungsten atoms respectively. Two kinds of patterns are observed:

1. For Keggin-type anions $\delta_{\mathrm{belt}} > \delta_{\mathrm{cap}}$, whereas for sandwich-type anions $\delta_{\mathrm{belt}} < \delta_{\mathrm{cap}}$.
2. $\Delta = |\delta_{\mathrm{belt}} - \delta_{\mathrm{cap}}|$ is greater for α-isomers of the Keggin anions, but is greater for β-isomers of the sandwich structures.

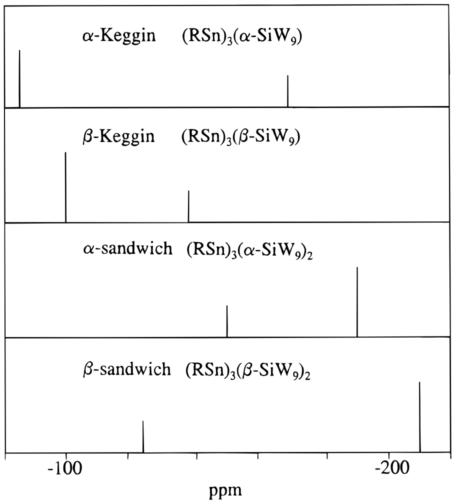

Figure 5. Stick diagrams representing characteristic ^{183}W NMR spectra of the four types of tungstosilicate.

Table 8. ^{183}W NMR Chemical Shift Patterns for A-Type Keggin Polyoxoanions

compound	δ_{belt}	δ_{cap}	$\Delta(\delta_{\mathrm{belt}} - \delta_{\mathrm{cap}})$	ref
Keggin Structure				
α-$[(AlOH_2)_3GeW_9O_{37}]^{7-}$	−78.2	−142.9	64.7	18
β-$[(AlOH_2)_3GeW_9O_{37}]^{7-}$	−90.4	−140.8	50.4	18
α-$[(InOH_2)_3GeW_9O_{37}]^{7-}$	−68.3	−158.9	90.6	18
β-$[(InOH_2)_3GeW_9O_{37}]^{7-}$	−84.0	−126.3	42.3	18
β-$[(GaOH_2)_3GeW_9O_{37}]^{7-}$	−81.6	−112.4	30.8	18
α-$[(AlOH_2)_3SiW_9O_{37}]^{7-}$	−97.4	−162.1	64.7	19
β-$[(AlOH_2)_3SiW_9O_{37}]^{7-}$	−109.6	−122.8	23.2	19
α-$[(GaOH_2)_3SiW_9O_{37}]^{7-}$	−80.4	−159.7	79.3	19
β-$[(GaOH_2)_3SiW_9O_{37}]^{7-}$	−97.3	−124.3	27.0	19
β-$[Nb_3SiW_9O_{40}]^{7-}$	−97.9	−114.5	16.6	20
β-$[HV_3SiW_9O_{40}]^{6-}$	−100	−105	5	21
α-$[V_3PW_9O_{40}]^{6-}$	−86.6	−130.1	43.5	22
β-$[V_3SiW_9O_{40}]^{7-}$	−115.4	−120	−4.6	21
α-$[Mo_3PW_9O_{40}]^{3-}$	−91.4	−101.5	−10.1	23
Sandwich Structure				
α-$[(PhSnOH)_3(PW_9O_{34})_2]^{12-}$	−138.6	−190.0	−51.4	5(b)
β-$[(PhSnOH)_3(PW_9O_{34})_2]^{12-}$	−123.4	−202.2	−78.8	4(d)
β-$[(BuSnOH)_3(PW_9O_{34})_2]^{12-}$	−125.1	−200.6	−75.5	4(d)
α-$[(CpFe(CO)_2Sn)_3(PW_9O_{34})_2]^{12-}$	−109.2	−169.7	−60.5	5(b)
α-$[(OCe)_3(PW_9O_{34})_2]^{12-}$	−151.9	−161.1	−9.2	5(b)
β-$[(ZrO)_3(SiW_9O_{34})_2]^{14-}$	−125.1	−200.6	−75.5	24
Keggin Dimer Structure				
α-$[(GaOH_2Ga)_3(GeW_9O_{37})_2]^{14-}$	−127.0	−141.8	−14.8	18
β-$[(TiOTi)_3(SiW_9O_{37})_2]^{14-}$	−131.3	−145.8	−13.5	25
β-$[(NbONb)_3(SiW_9O_{37})_2]^{12-}$	−114	−189	−75	20
α-$[(TiOTi)_3(GeW_9O_{37})_2]^{14-}$	−107.4	−127.8	20.4	26

A careful examination of the available ^{183}W NMR chemical shift data of trisubstituted Keggin and sandwich polyoxoanions (Table 8) shows that all compounds follow these patterns, except β-$V_3SiW_9O_{40}^{7-}$ and β-$Mo_3PW_9O_{40}^{3-}$. A third structural type, the so called Keggin dimer (with a chemical formula of $[(M\text{-}O\text{-}M)_3(XW_9O_{34})_2]^{n-}$) is also a possible structure. Among the four known dimers (Table 8), three have δ_{cap} larger than δ_{belt}, and one has the δ_{cap} smaller than δ_{belt}. More ^{183}W NMR data are needed in order to draw conclusions for the dimer compounds.

Conclusion

The reaction of A-$[SiW_9O_{34}]^{10-}$ with organotin trihalides with appropriate stoichiometry control leads to both 1:3 (trisubstituted Keggin) and 2:3 (sandwich-type) complexes, as confirmed by the crystallographic structure determinations of $[(PhSn)_3(SiW_9$-

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$O_{37})]^{7-}$ and $[(BuSnOH)_3(SiW_9O_{34})_2]^{14-}$. The substituted Keggin anions appear to be kinetically stable and are transformed by excess $[SiW_9O_{34}]^{10-}$ to the sandwich species. A review of all known trisubstituted Keggin anions and related species demonstrates characteristic patterns of W-NMR chemical shifts.

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Supporting Information Available: Complete tables of crystal data, atomic coordinates, bond lengths and angles, and thermal parameters for **3** and **6** (33 pages). Ordering information is given on any current masthead page.

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