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Polyoxometalate Derivatives with Multiple Organic Groups. 1. Synthesis and Structures of Tris(organotin) β-Keggin and α-Dawson Tungstophosphates

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Tris(organotin)-substituted Keggin and Dawson tungstophosphates, $[(PhSnOH)_3(PW_9O_{34})_2]^{12-}$ (**1**), $[(BuSnOH)_3(PW_9O_{34})_2]^{12-}$ (**2**), $[(PhSn)_3P_2W_{15}O_{59}]^{9-}$ (**3**), and $[(BuSn)_3P_2W_{15}O_{59}]^{9-}$ (**4**), have been prepared by reaction of the organotin trichlorides with $Na_8H[A\text{-}PW_9O_{34}]\cdot xH_2O$ and $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$, respectively. The products were characterized by elemental analysis, infrared spectroscopy, multinuclear NMR, and X-ray crystallography. Crystals of $K_{11}H[(PhSnOH)_3(PW_9O_{34})_2]\cdot 16H_2O$ are tetragonal, space group *I4/amd*, with lattice constants $a = b = 35.522(5)$ Å, $c = 33.243(7)$ Å, $V = 41946(12)$ Å^3. $R = 0.0863$ for 350 variable parameters and 5664 reflections with $I > 2\sigma(I)$. The anion has nominal D_{3h} symmetry and contains three PhSnOH groups sandwiched between $A,\beta\text{-}PW_9O_{34}{}^{9-}$ anions. It is an isomer of the complex reported by Knoth (*Organometallics* **1985**, *4*, 62−68), which is presumed to contain $A,\alpha\text{-}PW_9O_{34}{}^{9-}$. Crystals of $K_5H_4[PhSn)_3P_2W_{15}O_{59}]\cdot 6H_2O$ are also tetragonal, space group *I4/m*, with lattice constants $a = b = 30.096(4)$ Å, $c = 22.196(5)$ Å, $V = 20105(6)$ Å^3. $R = 0.0936$ for 290 variable parameters and 5761 reflections with $I > 2\sigma(I)$. The anion has the anticipated C_{3v} Dawson structure with three cap $\{WO\}^{4+}$ replaced by $\{SnPh\}^{3+}$. Each of the Sn−O−Sn oxygens is protonated.

Introduction

The remarkable properties and structures of polyoxoanions of molybdenum, tungsten, and vanadium continue to stimulate investigation with respect to their widespread applications.[1] Areas of particular current interest are the biological activity exhibited by polyoxometalates and potential chemotherapy involving such species[2] and their versatility as catalysts.[3] In each of these fields it is desirable to be able to modify polyoxoanion surfaces in order to develop specific anion−substrate recognition, and, in the area of possible chemotherapy, to achieve membrane permeability. On the basis of the hydrolytic robustness of the tin−carbon bond, and the similar sizes of Sn(IV) and W(VI), we are seeking to produce water-stable polyoxotungstate structures in which domains of terminal WO^{4+} groups have been replaced by $\{SnR\}^{3+}$. Earlier work has demonstrated that isolated $\{SnR\}^{3+}$ groups can be incorporated into Keggin structures.[4] We report here the structural characterization of complexes derived from the lacunary anions $PW_9O_{34}{}^{9-}$ and $P_2W_{15}O_{56}{}^{12-}$.

Experimental Section

Synthesis. Sodium A-9-tungstophosphate ($Na_8H[A\text{-}PW_9O_{34}]\cdot xH_2O$) and sodium α-15-tungstodiphosphate ($Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$) were prepared following the published methods[5,6] and were identified by infrared spectroscopy. Phenyltin trichloride and butyltin trichloride were obtained from Aldrich and used without further purification.

$K_{11}H[(PhSnOH)_3(PW_9O_{34})_2]\cdot 16H_2O$. (**1**) To a solution of 0.6 mL of $PhSnCl_3$ (3 mmol) in 60 mL of water at room temperature was added sodium acetate to adjust the pH to 1.5. At this stage the solution is slightly turbid. Powdered $Na_8H[A\text{-}PW_9O_{34}]\cdot xH_2O$ (5.7 g, 1 mmol) was added quickly to this solution with stirring. Within a few seconds most of the tungstophosphate had dissolved and the solution had clarified. The final pH was 5.0. Traces of unreacted tungstophosphate were filtered out after 10 min. Potassium chloride was added to the filtrate in small portions until no more precipitation was observed. The precipitate was collected on a medium porosity sintered glass frit, dried under suction for 1 h, washed with saturated KCl solution, and dried overnight under suction, giving a yield of 5.1 g. Long needlelike crystals of this solid were obtained by the method of vapor diffusion with ethanol. Anal. Calcd for $K_{11}H[(PhSnOH)_3(PW_9O_{34})_2]\cdot 16H_2O$: K, 7.64; C, 3.84; Sn, 6.36; P, 1.10; W, 58.69; H_2O, 5.13. Found: K, 7.72; C, 3.82; Sn 6.23; P, 1.15; W, 58.98; H_2O, 5.10. NMR: ^1H, δ 8.15 (d, 2H, $^3J_{H-Sn} = 135$ Hz), 7.55 (m, 3H, $^4J_{H-Sn} = 65$ Hz); $^{13}C\{^1H\}$, δ 133.3, 133.2, 128.2, 127.6; ^{31}P, δ −9.9 (s, 2P); $^{119}Sn\{H\}$, δ −609.6 (s, 3Sn); ^{183}W, δ −123.4 (s, 6W, $^2J_{W-W} = 14$ Hz), −202.2 (s, 12W, $^2J_{W-Sn} = 33$Hz, $^2J_{W-W} = 14$ Hz).

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[1] A series of recent reviews can be found in *"Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity."* Pope, M. T.; Müller, A. eds., Kluwer Acadamic Publishers, Dordrecht, The Netherlands, 1994.

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Table 1. Crystallographic Data

	1	2
formula	$K_{11}H[(PhSnOH)_3(W_9PO_{34})32]\cdot16H_2O$	$K_5H_4[(PhSn)_3W_{15}P_2O_{59})]\cdot6H_2O$
crystal size, mm	0.2 × 0.2 × 0.4	0.2 × 0.4 × 0.4
crystal system	tetragonal	tetragonal
space group	*I*4/*amd*	*I*4/*m*
a, Å	35.522(5)	30.096(4)
c, Å	33.243(7)	22.196(5)
V, Å^3	41946(12)	20105(6)
Z	16	8
T, °C	−70	−70
ϱ_{calc}, g/cm^3	3.588	3.028
μ, cm^{-1}	20.804	18.086
F(000)	39616	15927
θ, deg	1.62−25.01	1.77−28.85
index ranges	$-1 \leq h \leq 42$	$-1 \leq h \leq 35$
	$-1 \leq k \leq 42$	$-1 \leq k \leq 40$
	$-1 \leq l \leq 39$	$-1 \leq l \leq 30$
refl collected	20890	11334
independent refl	9578	9612
refinement method	full-matrix least-squares on F^2	
data/restrain/para	9571/9/350	9603/9/290
goodness-of-fit on F^2	1.132	1.274
$R(1)$, $[I > 2\sigma(I)]$	0.0863	0.0936
wR^2, $[(I > 2\sigma(I)]$	0.2051	0.2235
$R(1)$, (all data)	0.1509	0.1589
wR^2, (all data)	0.2416	0.2628
Lgst diff. peak & hole	6.990 & −2.742 e Å^{-3}	3.903 & −3.896 e Å^{-3}

$Cs_9[(BuSnOH)_3(PW_9O_{34})_2]\cdot12.5H_2O$ (2) was prepared analogously using the same quantities as above (0.6 mL of $BuSnCl_3$). Since this compound was more soluble than the phenyl analog, it was precipitated by adding CsCl instead of KCl. Recrystallization from hot water gave white needles. Anal. Calcd for $Cs_9[(BuSnOH)_3(PW_9O_{34})_2]\cdot12.5H_2O$: Cs, 20.16; C, 2.18; Sn, 5.40; P, 0.93; W, 50.20. Found: Cs, 19.92; C, 2.24; Sn, 6.53; P, 0.90; W, 49.85. NMR: ^{1}H, δ 1.95 (t, 2H, $^3J_{H-Sn} = 364$ Hz), 1.58 (m, 2H, $^4J_{H-Sn} = 265$ Hz), 1.51 (m, 2H), 0.95 (t, 3H); ^{13}C{^{1}H}, δ 28.0, 25.4, 23.5, 11.3; ^{31}P, δ −10.2 (s, 2P); ^{119}Sn{H}, δ −578.8 (s, 3Sn); ^{183}W, δ −125.1 (s, 6W), −200.6 (s, 12W).

$K_5H_4[(PhSn)_3P_2W_{15}O_{59}]\cdot6H_2O$ (3) and $K_{6.5}H_{2.5}[(BuSn)_3P_2W_{15}O_{59}]\cdot15H_2O$ (4) were prepared analogously. After adjustment of the pH of the solution of 0.6 mL of $RSnCl_3$, 4.5 g of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot24H_2O$ (1 mmol) was added. The final pH of the solution was 4.5. Addition of KCl yielded white precipitates which were filtered off and recrystallized from hot water.

Compound 3. Yield: 4.1 g. Anal. Calcd for $K_5H_4[(PhSn)_3P_2W_{15}O_{59}]\cdot6H_2O$: K, 4.21; C, 4.65; Sn, 7.67; P, 1.33; W, 59.44. Found: K, 4.01; C, 4.29; Sn, 7.54; P, 0.96; W, 59.5. NMR: ^{1}H, δ 7.84 (m, 2H, $^3J_{H-Sn} = 209$ Hz), 7.55 (m, 3H, $^4J_{H-Sn} = 95$ Hz); ^{13}C{^{1}H}, δ 133.5, 133.4, 128.9, 127.4; ^{31}P, δ −7.5 (s, 1P, $^2J_{P-Sn}$ = 14 Hz), −13.6 (s, 1P); ^{119}Sn{H}, δ −567.4 (s, 3Sn, $^2H_{Sn-P}$ = 14 Hz)); ^{183}W, δ −150.2 (s, 3W, $^2J_{W-W}$ = 19 Hz), −222.3 (s, 6W, $^2J_{W-W}$ = 19 Hz), −259.9 (s, 6W, $^2J_{W-Sn}$ = 78 Hz, $^2J_{W-W}$ = 26 Hz).

Compound 4. Yield: 4.0 g. Anal. Calcd for $K_{6.5}H_{2.5}[(BuSn)_3P_2W_{15}O_{59}]\cdot15H_2O$: K, 5.27; C, 2.99; Sn, 7.43; W, 57.12; P, 1.29. Found: K, 5.28; C, 2.95; Sn, 6.84; W, 59.47; P, 1.26. NMR: ^{1}H δ 1.80 (t, 2H, $^3J_{H-Sn} = 384$ Hz), 1.50 (m, 2H, $^4J_{H-Sn}$ = 213 Hz), 1.41 (m, 2H), 0.91 (t, 3H); ^{13}C{^{1}H}, δ 24.6, 23.4, 22.3, 11.3; ^{31}P, δ −6.6 (s, 1P, $^2J_{P-Sn}$ = 13 Hz), −13.8 (s, 1P); ^{119}Sn{H}, δ −517.2 (s, 3Sn, $^2J_{Sn-P}$ = 13Hz); ^{183}W, δ −152.7 (s, 3W, $^2J_{W-W}$ = 16Hz), −226.1 (s, 6W, $^2J_{W-W}$ = 16 Hz), −261.2 (s, 6W, $^2J_{W-Sn}$ = 49Hz, $^2J_{W-W}$ = 23 Hz).

Physical Measurements. Infrared spectra were recorded on a MIDAC FTIR instrument. Elemental analyses were performed by E&R Microanalytical Laboratory Inc., Corona, NY. All NMR data were obtained on a Bruker AM-300WB spectrometer. Resonance frequencies were 300.113 MHz for ^{1}H and 75.469 MHz for ^{13}C in 5 mm tubes, 121.495 MHz for ^{31}P and 111.924 MHz for ^{119}Sn in 10mm tubes, and 12.505 MHz for ^{183}W in 20 mm tubes. Pulse widths (90°) were 2.1 μs for ^{13}C, 11 μs for both ^{31}P and ^{119}Sn, and 40 μs for ^{183}W. Chemical shifts are given with respect to external 85% H_3PO_4 for ^{31}P and saturated Na_2WO_4 for ^{183}W. For ^{119}Sn NMR, a solution of $SnCl_2$ in 12 M HCl (chemical shift −388.1 vs tetramethyl tin)[7] was used as external standard, 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 done with aqueous unbuffered solutions. To achieve sufficiently concentrated solutions for ^{183}W NMR (ca. 4 g/15 mL), the potassium and cesium salts were treated with $LiClO_4$. In the experiments to determine the pK_a's of **1** and **3**, ^{31}P NMR spectra were obtained at different pH, and 1 M LiCl solution was used to keep the ionic strength relatively constant.

Crystallography. Crystals of compounds **1** and **3** used in this investigation lost solvent quickly, so they were mounted on glass fibers over dry ice. The data were collected at −70 °C on a Siemens P4/RA diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved using SHELXL-PLUS (Siemens) direct methods for W, Sn, and P. Both compounds were refined with SHELXL-93 (Sheldrick, G. M.) by full-matrix least-squares, the minimized function being $\sum\omega(|F_o| - |F_c|)^2$. The weighting scheme was $\omega = 1/[\sigma^2(F^2) + (0.0922P)^2 + 12.05P]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$. Crystal data and structure refinement parameters are listed in Table 1. Since the three phenyl rings of $K_{11}H(PhSnOH)_3(PW_9)_2$ underwent thermovibration, nine restraints were introduced to fix the six-membered rings. Because of possible disorder of the cation positions, only eight potassiums of $K_{11}H(PhSnOH)_3(PW_9)_2$ and four potassium of $K_5H_4[(PhSn)_3(P_2W_{15}O_{59})]$ were located. Final atomic coordinates and thermal parameters of **1** are given in Tables 2 and 4, and selected bond lengths in Tables 3 and 5.

Results and Discussion

The two lacunary tungstophosphate anions $[(PO_4)_2W_{15}O_{48}]^{12-}$ ("P_2W_{15}") and $[(PO_4)W_9O_{30}]^{9-}$ ("A-PW_9") are reproducibly isolable as sodium salts, but are metastable in solution and yield a variety of hydrolysis products depending upon pH. Thus the current syntheses were carried out by rapidly adding the solid salts to freshly prepared solutions of the organotin trichloride. Such

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $[(PhSnOH)_3(PW_9O_{34})_2]^{12-}$ [a]

	x	*y*	*z*	*U*(eq)[b]
W(8)	899(1)	3417(1)	1232(1)	20(1)
W(7)	1010(1)	3414(1)	114(1)	19(1)
W(6)	1875(1)	3412(1)	−293(1)	22(1)
W(5)	2724(1)	3416(1)	372(1)	24(1)
W(4)	2618(1)	3419(1)	1374(1)	24(1)
W(9)	1655(1)	3426(1)	1830(1)	20(1)
W(3)	1465(1)	4278(1)	1243(1)	29(1)
W(2)	1566(1)	4276(1)	225(1)	30(1)
W(1)	2340(1)	4280(1)	829(1)	31(1)
Sn(3)	1388(1)	2500	−210(1)	23(1)
Sn(2)	1219(1)	2500	1635(1)	28(1)
Sn(1)	2790(1)	2500	892(1)	30(1)
P(1)	1798(2)	3458(3)	774(2)	18(2)
O(12)	2081(9)	4428(9)	364(8)	51(8)
O(13)	2018(7)	4360(7)	1233(7)	28(6)
O(23)	1326(7)	4409(7)	690(7)	29(6)
O(49)	2173(6)	3398(7)	1679(6)	21(5)
O(36S)	1802(7)	2905(7)	−308(7)	34(6)
O(3)	1564(6)	3329(6)	1120(6)	18(5)
O(2)	2205(6)	3311(6)	806(6)	22(5)
O(26)	1837(7)	3929(7)	−82(7)	33(6)
O(88)	442(7)	3524(7)	1340(7)	34(6)
O(78)	883(6)	3374(6)	660(6)	20(5)
O(1)	1802(7)	3912(7)	771(7)	28(6)
O(77)	599(7)	3518(6)	−107(6)	24(5)
O(37S)	1044(7)	2098(7)	43(7)	33(6)
O(89)	1132(7)	3500(6)	1741(6)	24(5)
O(29S)	1587(7)	2084(7)	1837(7)	32(6)
O(38)	1086(6)	3945(6)	1154(6)	16(5)
O(15S)	2758(7)	2910(7)	444(7)	33(6)
O(27)	1170(6)	3934(6)	234(6)	20(5)
O(56)	2348(6)	3358(6)	−28(6)	17(5)
O(4)	1642(6)	3311(7)	380(6)	23(5)
O(67)	1338(7)	3484(7)	−333(6)	27(6)
O(55)	3118(7)	3511(7)	88(6)	27(6)
O(14S)	2671(7)	2916(7)	1334(7)	34(6)
O(33)	1258(7)	4636(7)	1521(7)	35(6)
O(39)	1668(7)	3959(7)	1617(7)	29(6)
O(66)	2001(7)	3517(7)	−779(7)	30(6)
O(45)	2924(7)	3487(7)	908(6)	28(6)
O(44)	2941(8)	3518(8)	1745(7)	38(7)
O(99)	1683(6)	3531(6)	2335(6)	22(5)
O(28S)	911(8)	2911(8)	1325(7)	45(7)
O(14)	2466(7)	3944(7)	1247(7)	32(6)
O(15)	2546(7)	3947(7)	469(6)	27(6)
O(22)	1432(7)	4597(7)	−128(7)	36(7)
O(11)	2687(8)	4619(8)	858(7)	40(7)
C(11)	3399(15)	2500	946(14)	29(13)
C(12)	3560(19)	2866(18)	968(17)	134(29)
C(13)	3964(18)	2837(17)	1015(15)	121(25)
C(14)	4176(18)	2500	1032(16)	48(16)
C(21)	916(16)	2500	2161(15)	35(13)
C(22)	732(14)	2786(17)	2355(15)	118(23)
C(24)	528(25)	2500	2939(24)	88(28)
C(23)	547(15)	2826(16)	2715(14)	93(19)
C(31)	1210(15)	2500	−809(14)	30(12)
C(32)	1021(16)	2826(13)	−962(19)	107(23)
C(33)	829(15)	2826(13)	−1379(17)	92(19)
C(34)	917(17)	2500	−1563(17)	44(15)
O(1S)	2225(14)	2500	803(13)	66(14)
O(2S)	1557(16)	2500	1183(15)	80(16)
O(3S)	1622(12)	2500	354(12)	51(11)

[a] Symmetry transformations used to generate equivalent atoms: (1) $x, -y + 1/2, z$; (2) $-y + 3/4, x - 1/4, -z + 1/4$; (3) $y + 3/4, -x + 3/4, -z + 1/4$; (4) $y + 1/4, -x + 3/4, -z + 1/4$; (5) $-x + 1, -y + 1, -z$; (6) $-y + 3/4, x + 1, z - 1/4$; (7) $x, -y + 1, -z$; (8) $-y + 1/4, -x + 3/4, z + 1/4$; (9) $y - 1/4, -x + 3/4, z + 1/4$; (10) $-x, y, z$. [b] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[(PhSnOH)_3(PW_9O_{34})_2]^{12-}$ Anion

W(8)−O(88)	1.70(3)	W(2)−O(22)	1.70(3)
W(8)−O(28S)	1.83(3)	W(2)−O(23)	1.83(2)
W(8)−O(78)	1.91(2)	W(2)−O(27)	1.86(2)
W(8)−O(89)	1.91(2)	W(2)−O(26)	1.87(2)
W(8)−O(38)	2.01(2)	W(2)−O(12)	1.96(3)
W(8)−O(3)	2.41(2)	W(2)−O(1)	2.38(2)
W(7)−O(77)	1.68(2)	W(1)−O(11)	1.72(3)
W(7)−O(37S)	1.83(3)	W(1)−O(13)	1.79(2)
W(7)−O(78)	1.88(2)	W(1)−O(15)	1.84(2)
W(7)−O(67)	1.90(2)	W(1)−O(12)	1.88(3)
W(7)−O(27)	1.98(2)	W(1)−O(14)	1.89(2)
W(7)−O(4)	2.44(2)	W(1)−O(1)	2.33(2)
W(6)−O(66)	1.71(2)	W(5)−O(55)	1.72(2)
W(6)−O(36S)	1.82(3)	W(5)−O(15S)	1.82(3)
W(6)−O(56)	1.91(2)	W(5)−O(56)	1.89(2)
W(6)−O(67)	1.93(2)	W(5)−O(45)	1.93(2)
W(6)−O(26)	1.97(3)	W(5)−O(15)	2.01(2)
W(6)−O(4)	2.41(2)	W(5)−O(2)	2.37(2)
W(4)−O(44)	1.72(3)	W(9)−O(99)	1.72(2)
W(4)−O(14S)	1.80(3)	W(9)−O(29S)	1.83(3)
W(4)−O(49)	1.88(2)	W(9)−O(89)	1.90(2)
W(4)−O(45)	1.91(2)	W(9)−O(49)	1.91(2)
W(4)−O(14)	1.99(3)	W(9)−O(39)	2.02(2)
W(4)−O(2)	2.42(2)	W(9)−O(3)	2.41(2)
W(3)−O(33)	1.73(3)	W(3)−O(23)	1.96(2)
W(3)−O(38)	1.82(2)	W(3)−O(13)	1.98(2)
W(3)−O(39)	1.83(2)	W(3)−O(1)	2.36(2)
Sn(3)−O(3S)	2.05(4)	Sn(2)−O(2S)	1.92(5)
Sn(3)−O(37s)	2.06(2)	Sn(2)−C(21)	2.05(5)
Sn(3)−C(31)	2.09(5)	Sn(2)−O(29S)	2.08(2)
Sn(3)−O(36S)	2.08(3)	Sn(2)−O(28S)	2.09(3)
Sn(1)−O(1S)	2.03(5)	Sn(1)−O(15S)	2.08(2)
Sn(1)−O(14S)	2.13(2)	Sn(1)−C(11)	2.17(6)
P(1)−O(3)	1.49(2)	P(1)−O(4)	1.52(2)
P(1)−O(2)	1.54(2)	P(1)−O(1)	1.61(3)
C(11)−C(12)	1.42(4)	C(12)−C(13)	1.45(4)
C(13)−C(14)	1.42(4)	C(21)−C(22)	1.37(4)
C(22)−C(23)	1.37(4)	C(24)−C(23)	1.38(4)
C(31)−C(32)	1.43(6)	C(32)−C(33)	1.54(8)
C(33)−C(34)	1.35(5)		

solutions are slightly turbid at pH 1.5 as a result of partial hydrolysis, but react cleanly and rapidly with the added tungstophosphates to give the desired products in nearly quantitative yield. The reaction stoichiometries were established from preliminary studies monitored by ^{31}P NMR. Elemental analyses of the recrystallized materials and multinuclear NMR spectroscopy are fully consistent with the structures revealed by X-ray crystallography for **1** and **3**. The characteristic IR spectra, shown in Figure 1, convincingly demonstrate the structural analogies of **1** with **2** and **3** with **4**.

$(RSn)_3(PW_9)_2$ Anions (1 and 2). The structure of **1** shown in Figure 2 consists of two A-type PW$_9$ anions linked by three phenyltin groups into an assembly of virtual D_{3h} symmetry. The PW$_9$ groups are formed by removal of three adjacent corner-shared WO$_6$ octahedra (thus, "A-type")[8] from the currently unknown β-isomer of $[(PO_4)W_{12}O_{36}]^{3-}$. In 1985, Knoth *et al.*[9] prepared a phenyltin complex of identical composition to **1** by adding PhSnCl$_3$ dropwise to an aqueous solution of Na$_8$HPW$_9$O$_{34}$. Knoth's compound, which we have successfully reproduced, has different ^{31}P (−10.9 vs −9.9) and ^{183}W (−138.6(3W), −190.0(6W) vs −123.4(3W), −202.2(6W)) chemical shifts from **1**. Knoth proposed that his compound contained two A,α-PW$_9$ groups, and this would now appear to be correct. The complexes K$_9$H$_2$(OCe)$_3$(PW$_9$O$_{34}$)$_2$26H$_2$O and K$_{11}$H$_3$[Cu$_3$(NO$_3$)](PW$_9$O$_{34}$)$_2$·28H$_2$O prepared in a similar manner by Knoth were shown by X-ray structural investigation also to contain

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[8] Hervé, G.; Tézé, A. *Inorg. Chem.* **1977**, *16*, 2115.

[9] Knoth, W. H.; Domaille, P. J.; Farlee, R. D. *Organometallics* **1985**, *4*, 62.

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $[(PhSn)_3P_2W_{15}O_{59}]^{9-}$ [a]

	x	*y*	*z*	*U*(eq)[b]
W(1)	7788(1)	1049(1)	5823(1)	17(1)
W(2)	7898(1)	2302(1)	5830(1)	22(1)
W(3)	6819(1)	1137(1)	6582(1)	21(1)
W(4)	5770(1)	1235(1)	5761(1)	24(1)
W(5)	6937(1)	2384(1)	6580(1)	28(1)
W(6)	5879(1)	2486(1)	5751(1)	34(1)
W(8)	7654(1)	3346(1)	5000	32(1)
W(7)	6677(1)	3430(1)	5766(1)	39(1)
Sn(1)	6365(1)	155(1)	5799(1)	18(1)
Sn(2)	7385(1)	58(1)	5000	17(1)
P(2)	6783(4)	1079(4)	5000	16(2)
P(1)	6906(4)	2448(4)	5000	24(3)
O(94)	5913(7)	656(7)	5718(9)	24(5)
O(1S)	6125(10)	−113(10)	5000	30(8)
O(91)	7609(6)	485(6)	5631(9)	18(4)
O(22P)	6328(9)	1269(9)	5000	19(6)
O(91)	6950(6)	−175(6)	5656(9)	18(4)
O(2P)	6738(8)	540(8)	5000	6(5)
O(67)	6193(8)	3101(8)	5684(11)	40(6)
O(11)	7896(8)	1192(8)	5000	12(6)
O(13)	7443(6)	1047(6)	6558(9)	18(5)
O(57)	6920(7)	2986(7)	6317(9)	27(5)
O(44)	5320(7)	1215(7)	6226(10)	32(6)
O(11P)	6425(11)	2341(10)	5000	34(8)
O(12P)	7152(6)	2277(6)	5576(9)	19(5)
O(93)	6712(6)	574(6)	6348(8)	15(4)
O(56)	6338(7)	2368(7)	6279(9)	25(5)
O(22′)	7979(9)	2208(9)	5000	17(6)
O(23P)	7043(6)	1188(6)	5565(9)	22(5)
O(78)	7288(7)	3618(7)	5618(10)	33(6)
O(46)	5760(7)	1903(7)	5661(10)	31(5)
O(66)	5603(10)	2638(10)	5000	30(8)
O(34)	6251(6)	1324(7)	6300(9)	23(5)
O(19)	8306(6)	953(6)	6092(9)	21(5)
O(25)	7562(6)	2439(7)	6540(9)	21(5)
O(13P)	6968(10)	2954(10)	5000	29(8)
O(44′)	5465(10)	1217(10)	5000	24(7)
O(22)	8430(6)	2368(6)	6093(9)	17(4)
O(12)	7810(7)	1699(7)	5970(10)	31(5)
O(33)	6730(8)	1081(8)	7334(11)	42(7)
O(55)	6857(8)	2494(8)	7328(11)	38(6)
O(35)	6976(7)	1771(7)	6610(10)	32(6)
O(77)	6533(12)	3683(12)	5000	52(10)
O(88)	8127(11)	3719(11)	5000	43(9)
O(28)	7833(7)	2903(7)	5572(10)	26(5)
O(77′)	6527(9)	3850(9)	6243(12)	54(7)
O(66′)	5441(10)	2620(10)	6179(14)	68(9)
C(11)	6053(9)	−268(9)	6449(12)	11(6)
C(12)	5574(13)	−277(13)	6428(18)	44(10)
C(13)	5372(14)	−554(13)	6917(19)	51(11)
C(14)	5658(16)	−712(16)	7334(22)	71(14)
C(15)	6090(14)	−686(14)	7360(19)	54(11)
C(16)	6304(11)	−424(11)	6891(16)	34(9)
C(21)	7884	−405	5000	34
C(22)	8211	−348	5424	251
C(23)	8567	−642	5455	326
C(24)	8596	−992	5000	71
C(25)	8269	−1050	4614	300
C(26)	7913	−757	4584	262

[a] Symmetry transformations used to generate equivalent atoms: (1) $y + 1, -x + 1, z$; (2) $-x + {}^3/_2, -y + {}^1/_2, -z + {}^3/_2$; (3) $x, y, -z + 1$; (4) $y + 1, -x + 1, -z + 1$; (5) $y, -x + 1, -z + 1$; (6) $-y + 1, x, z$; (7) $-y + 1, x - 1, z$. [b] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[(PhSn)_3P_2W_{15}O_{59}]^{9-}$

W(1)−O(19)	1.69(2)	W(8)−O(88)	1.81(3)
W(1)−O(91)	1.83(2)	W(8)−O(28)	1.92(2)
W(1)−O(11)	1.904(7)	W(8)−O(78)	1.94(2)
W(1)−O(13)	1.93(2)	W(8)−O(13P)	2.38(3)
W(1)−O(12)	1.98(2)	W(7)−O(67)	1.77(2)
W(1)−O(23P)	2.35(2)	W(7)−O(77′)	1.71(3)
W(2)−O(22)	1.72(2)	W(7)−O(77)	1.91(2)
W(2)−O(12)	1.86(2)	W(7)−O(78)	1.95(2)
W(2)−O(22′)	1.880(5)	W(7)−O(57)	1.95(2)
W(2)−O(28)	1.91(2)	W(7)−O(13P)	2.39(2)
W(2)−O(25)	1.92(2)	W(3)−O(33)	1.70(2)
W(2)−O(12P)	2.31(2)	W(3)−O(93)	1.80(2)
W(3)−O(13)	1.90(2)	W(3)−O(23P)	2.36(2)
W(3)−O(34)	1.90(2)	W(3)−O(35)	1.97(2)
W(4)−O(44)	1.70(2)	W(5)−O(55)	1.71(2)
W(4)−O(94)	1.80(2)	W(5)−O(35)	1.85(2)
W(4)−O(34)	1.90(2)	W(5)−O(25)	1.89(2)
W(4)−O(44′)	1.922(14)	W(5)−O(57)	1.90(2)
W(4)−O(46)	2.02(2)	W(5)−O(56)	1.92(2)
W(4)−O(22P)	2.38(2)	W(5)−O(12P)	2.34(2)
W(6)−O(66′)	1.67(3)	W(6)−O(66)	1.92(2)
W(6)−O(46)	1.80(2)	W(6)−O(67)	2.08(2)
W(6)−O(56)	1.85(2)	W(6)−O(11P)	2.38(2)
Sn(1)−O(94)	2.04(2)	Sn(1)−O(93)	2.04(2)
Sn(1)−O(91)	2.05(2)	Sn(1)−O(1S)	2.08(2)
Sn(1)−C(11)	2.14(3)	Sn(1)−O(2P)	2.40(2)
Sn(2)−O(91)	2.02(2)	Sn(4)−C(21)	2.050(3)
Sn(2)−O(91)	2.08(2)	Sn(2)−O(2P)	2.43(2)
P(2)−O(22P)	1.49(3)	P(2)−O(23P)	1.52(2)
P(2)−O(2P)	1.63(3)	P(1)−O(11P)	1.48(3)
P(1)−O(13P)	1.53(3)	P(1)−O(12P)	1.57(2)
C(11)−C(16)	1.32(4)	C(11)−C(12)	1.44(4)
C(12)−C(13)	1.50(5)	C(13)−C(14)	1.35(6)
C(14)−C(15)	1.30(6)	C(15)−C(16)	1.46(5)
C(21)−C(22)	1.37	C(22)−C(23)	1.39
C(23)−C(24)	1.46		

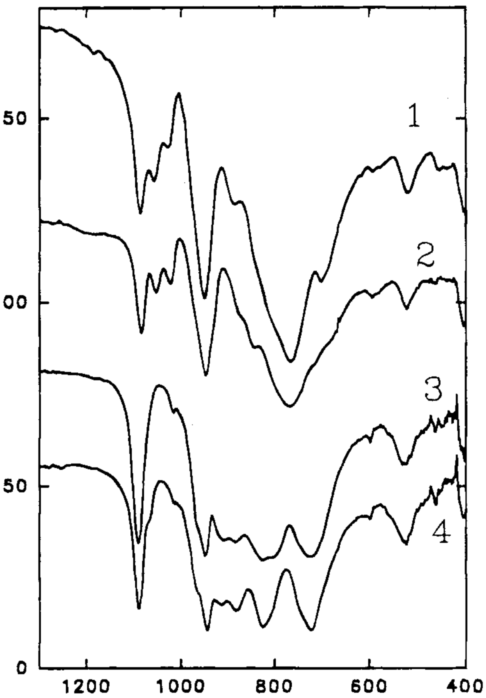

Figure 1. Infrared spectra of **1**−**4**, recorded in KBr pellets.

A,α-PW$_9$ groups.[10] On the other hand, Kawafune and Matsubayashi[11] have recently shown that $[N(CH_3)_4]_3[PMo_3W_9O_{40}]$, prepared by adding $Na_8HPW_9O_{34}$ to a solution of Na_2MoO_4, has an A,β-structure. Taken together, all of the above observations strongly suggest that the lacunary precursor anion in *unthermolyzed* $Na_8HPW_9O_{34} \cdot xH_2O$ *has an A,β structure in the solid state*, as had originally been proposed.[12] Upon dissolution, isomerization to the A,α-isomer presumably takes place at a rate which is slow relative to that of reaction with Sn or Mo(VI).

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[10] Knoth, W. H.; Domaille, P. J.; Harlow, R. L. *Inorg. Chem.* **1986**, *25*, 1577.

[11] Kawafune, I.; Matsubayashi, G. *Chem. Lett.* **1992**, 1869.

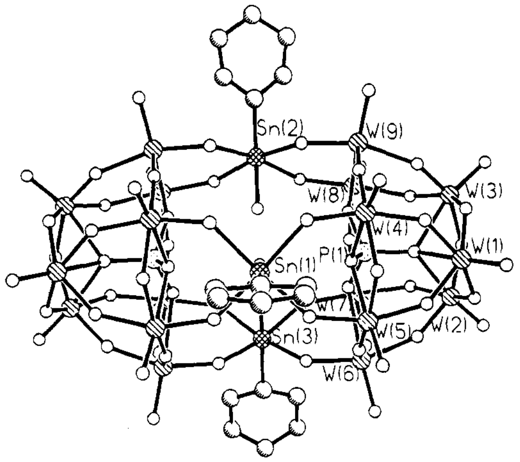

Figure 2. SHELXP representation of the structure of **1**.

Table 6. Bond Valence Sums of Selected Oxygen Atoms of 1 and 3

$K_{11}H[(PhSnOH)_3(PW_9O_{34})_2]$ (**1**)			$K_5H_4[(PhSn)_3(P_2W_{15}O_{59})]$ (**3**)		
	BVS	ave BVS		BVS	ave BVS
internal Sn–O			Sn–O–Sn		
O(1S)	0.71		O(91)	1.29	1.27
O(2S)	0.96	0.78	O(1S)	1.25	
O(3S)	0.67		Sn–O–W		
Sn–O–W			O(93)	2.07	
O(14)	1.90		O(94)	2.07	2.04
O(15)	1.92		O(91)	1.99	
O(28)	1.87	1.91	W–O–W		
O(29)	1.89		O(12)	2.01	
O(36)	1.92		O(25)	2.07	
O(37)	1.92		O(34)	2.09	
W–O–W			O(46)	2.12	2.05
O(12)	2.00		O(56)	2.19	
O(14)	1.90		O(67)	2.13	
O(23)	2.15	2.05	O(78)	1.85	
O(38)	2.07				
O(49)	2.12				
O(67)	2.01				

In the structure of **1**, the Sn atoms which act as the filling in a two-PW$_9$ sandwich, have slightly distorted octahedral coordination. Each Sn atom is displaced 0.25 Å out of the plane of the four bridging oxygens toward the phenyl group, with an average equatorial O–Sn bond length of 2.09 Å (2.06–2.13 Å), axial O–Sn bond length of 2.00 Å (1.92–2.05 Å) and C–Sn bond length of 2.11 Å (2.06–2.17 Å). The W–O(Sn) bond lengths (1.82–1.83 Å) are somewhat shorter than those for W–O(W) (1.84–2.01; average 1.91 Å). Nevertheless, bond valence sum (BVS) calculations[13] for all bridging oxygens yield values of 1.9–2.3 (Table 6). That the internal Sn–O groups are protonated is revealed by BVS values of 0.7, 1.0, and 0.7 for O(1S), O(2S), and O(3S) respectively.

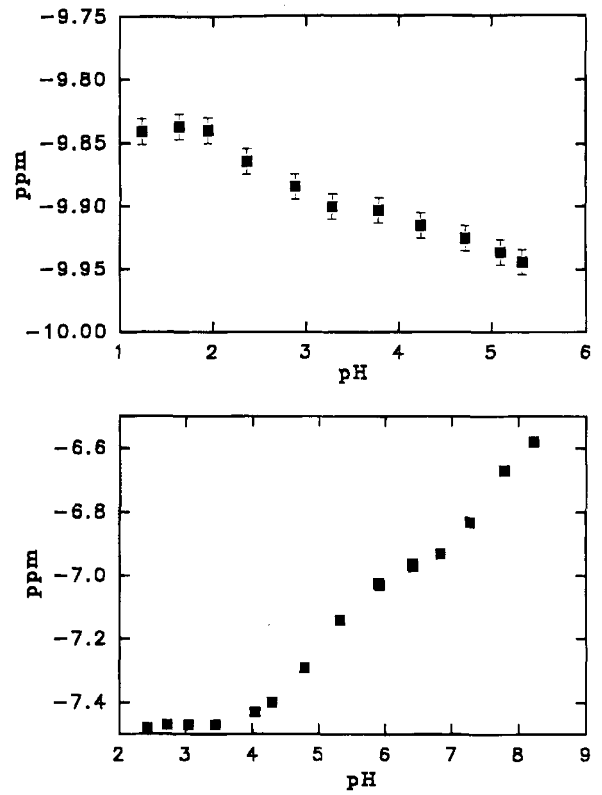

Figure 3. Phosphorus-31 chemical shifts as a function of pH, recorded in 1 M LiCl solution at *ca.* 298 K: upper, anion **1**; lower, anion **3**.

The $K_{11}H$[anion] stoichiometry of the crystals suggests that an additional proton is also present. In their investigations of the presumed α-isomer, Knoth *et al.*[9] isolated $Cs_8K[(PhSnOH_2)_3(PW_9O_{34})_2]$ at pH 1 and $[(CH_3)_4N]_9K_2[(PhSnOH_2)(PhSnOH)_2(PW_9O_{34})_2]$ at pH 7. Given the oxygen BVS values noted above, our anion (isolated at pH 5.0) could be formulated as $[(PhSnOH)_2(PhSnOH_2)(PW_9O_{34})_2]^{11-}$. The pH dependence of the ^{31}P-NMR spectrum of **1** in 1 M LiCl is illustrated in Figure 3. The data between pH 1.2 and 5.3 were fitted to pK_a's of 2.58 ± 0.19 and 4.74 ± 0.30 by means of the computer program LAKE.[14] We conclude that these correspond to deprotonations of $PhSnOH_2$ to PhSnOH. Since the *monoprotonated* crystals of **1** were isolated at pH 5.0, it is plausible to assume that the most acidic species (δ 9.933) is triprotonated, i.e. is $[(PhSNOH_2)_3(PW_9O_{34})_2]^{9-}$. This would correspond with Knoth's observation for the α-isomer. However, one could equally well postulate that the equilibria involve $(PhSnOH_2)_2(PhSnOH)$, $(PhSnOH)_2(PhSnOH)_2$, and $(PhSnOH)_3$. The second scenario is supported by our observation that further attempted deprotonation of the anion above pH 5.5 results in processes that cause the NMR line to broaden and shift significantly (e.g. 58 Hz and −10.3 ppm at pH 6.5). Ultimately, the resonance is replaced first by a new narrow signal at −8.8 ppm and then by multiple resonances. The nature of the exchange and decomposition processes responsible for these observations is unclear.

$(RSn)_3(P_2W_{15})$ Anions (3 and 4). The structure of anion **3** (Figure 4) is based on the well-known Dawson anion α-$[(PO_4)_2W_{18}O_{54}]^{6-}$ with three of the "cap" $\{WO^{4+}\}$ groups replaced by $\{SnPh^{3+}\}$. All NMR data (two-line ^{31}P, one-line ^{119}Sn, and three-line ^{183}W) are consistent with overall C_{3v} symmetry for the anion. Unlike the

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[12] Both α- and β-PW$_9$ (and AsW$_9$) were reported in 1974 [Contant, R.; Fruchart, J. M.; Hervé, G.; Tézé, A. *C. R. Hebd. Seances Acad. Sci. Ser. C* **1974**, *278*, 199.]. The isomers were distinguished by electrochemical identification of the products of reaction with Mo(VI), α-PW$_9$Mo$_2$, and β-PW$_9$Mo$_2$, respectively. The β-isomer is easier to isolate and the preparation of the sodium salt was reported in 1977.[5] The first X-ray structures of complexes derived from PW$_9$ contained α-PW$_9$ groups,[10] from which Knoth *et al.* concluded that it was "quite likely that unthermolized $Na_8HPW_9O_{34}$, also has an A,α-PW$_9$ group, not an A,β-PW$_9$ group."

[13] Bond valence sums are computed as the sum of "bond strengths" at each atom. Bond strength: $s = \exp[(r_0 - r)/B]$, where r is the observed bond distance (Å) and r_0 and B are empirical parameters. Values of r_0 for $W^{VI}-O^{2-}$ and $Sn^{IV}-O^{2-}$ are 1.917 and 1.905 Å, respectively; $B = 0.37$. [Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.]

case of **1** and **2**, tin is bonded to the center phosphorus through a bridging oxygen in **3** and **4**, and Sn-P two-bond coupling is observed (14Hz for **3**, 13Hz for **4**). Two-bond Sn-W coupling is observed for all four compounds, but the $(RSn)_3(P_2W_{15})$ anions have larger coupling constants than $(RSn)_3(PW_9)_2$ (78Hz for **3**, 33Hz for **1**). This is consistent with the greater Sn−O−W bond angles for **3** than for **1** (147−158° and 139−142°, respectively).

The crystals of **3** contain a tetraprotonated anion. Three of the protons can be located with some degree of confidence on the oxygens bridging the tin atoms (Sn−O−Sn); BVS values for these oxygens are 1.3 (Table 6).[13] The fourth proton is probably randomly located on one of several other surface bridging oxygens. The pH-dependence of the chemical shift of P(2) between pH 2.3 and 8.2, recorded in 1 M LiCl (Figure 3), was fitted to the following equilibria by means of the program LAKE.[14]

$$[H_4(PhSn)_3P_2W_{15}O_{59}]^{5-} \leftrightarrows [H_3(PhSn)_3P_2W_{15}O_{59}]^{6-} + H^+$$

$$pK_a \pm 3\sigma = 4.99 \pm 0.07$$

$$[H_3(PhSn)_3P_2W_{15}O_{59}]^{6-} \leftrightarrows [H_2(PhSn)_3P_2W_{15}O_{59}]^{7-} + H^+$$

$$pK_a \pm 3\sigma = 7.60 \pm 0.16$$

Chemical shifts for the tetra-, tri-, and diprotonated anions are −7.48, −6.99(2), and −6.48(4) ppm, respectively.

Conclusions

X-ray single-crystal analyses have confirmed the structures of $[(PhSnOH)_2(PhSnOH_2)(PW_9O_{34})_2]^{11-}$ and $[(PhSn)_3(P_2W_{15}O_{59}H_4)]^{5-}$ anions. The second of these anions, with three adjacent organometallic groups, represents a new type of polyoxoanion. Unlike all previously known $M_3(PW_9)_2$ anions, **1** is shown to contain β-PW_9 groups and is only the second confirmed example of the β-tungsto*phosphate* conformation. It is thus very likely that the precursor anion A−$[PW_9O_{34}]^{9-}$ has a β-structure as was originally proposed based on indirect evidence.

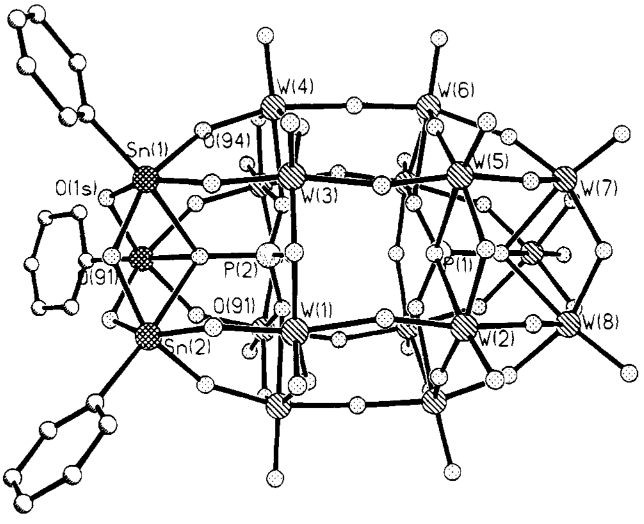

Figure 4. SHELXP representation of the structure of **3**.

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Supplementary Material Available: Complete tables of positional parameters, bond lengths and angles, and thermal parameters for **1** and **3** (27 pages). Ordering information is given on any current masthead page.

OM940536R

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[14] Calculations were performed by I. Andersson and L. Pettersson at the University of Umeå.