Polyoxometalate Derivatives with Multiple Organic Groups. 3. Synthesis and Structure of Bis(phenyltin) Bis(decatungstosilicate), $[(PhSnOH_2)_2(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$

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A new phenyltin tungstosilicate derivative, $[(PhSnOH_2)_2(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ (**1**), has been prepared by reaction of phenyltin trichloride with $K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot xH_2O$. The new heteropolyanion was characterized by elemental analysis, infrared spectroscopy, multinuclear NMR, and X-ray crystallography. The crystals of $Cs_9H[(PhSnOH_2)_2(\gamma\text{-}SiW_{10}O_{36})_2]\cdot 16H_2O$ (Cs salt of **1**) are triclinic, space group $P\bar{1}$, with lattice constants $a = 12.401(3)$ Å, $b = 13.832(3)$ Å, $c = 16.313(3)$ Å, $\alpha = 96.17(2)°$, $\beta = 109.73(2)°$, $\gamma = 97.13(2)°$, $V = 2579.9(10)$ Å, and $Z = 1$. Anion **1** has a structure of virtual C_{2h} symmetry with two phenyltin groups sandwiched between two γ-SiW$_{10}$ groups. Such a structure is different from all previously reported polytungstates derived from $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ lacunary anions.

Introduction

The synthesis and characterization of new structural types of polyoxometalate complexes remains of great current interest in view of the potential and developed applications of these substances in many areas, including environmentally-benign catalytic processes and antiviral chemotherapies.[1] In the course of our investigations of polyoxometalates derivatized with multiple organic groups we have examined the reaction of organotin trihalides with a variety of lacunary polytungstate structures.[2,3] We report here a novel structure derived from the γ-decatungstosilicate anion.

Experimental Section

Potassium γ-decatungstosilicate ($K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot xH_2O$) was prepared by following the published method[4] and was identified by infrared spectroscopy.

$Cs_9H[(PhSnOH_2)_2(\gamma\text{-}SiW_{10}O_{36})_2]\cdot 16H_2O$ (Cs Salt of 1). Powdered $K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot xH_2O$ (3.0 g, 1 mmol) was added quickly into a slightly turbid suspension generated by the addition of 0.1 mL of $PhSnCl_3$ (1 mmol) to 60 mL of water at room temperature with stirring. Within a few seconds the tungstosilicate dissolved and the solution clarified. Traces of undissolved reactants were removed by filtration. Cesium 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 and dried under suction overnight. Single crystals, which were used for crystallography studies, were obtained by ethanol vapor diffusion into a solution of the product. Yield: 2.1 g (62%) Anal. Calc for $Cs_9H[(PhSnOH_2)_2(\gamma\text{-}SiW_{10}O_{36})_2]\cdot 25H_2O$: Cs, 17.18; C, 2.07; Sn, 3.41; W, 52.83. Found: Cs, 16.75; C, 1.77; Sn, 3.14; W, 52.75. IR: 1000, 955, 915, 870, 805, 735, 540 cm^{-1}. NMR: ^{119}Sn{H}; −617 ppm (s, 2Sn, $J_{Sn-W} = 20$ Hz); ^{183}W, −124.8 ppm (s, 2W, $\nu_{1/2} = 7.8$ Hz), −126.7 ppm (s, 2W, $\nu_{1/2} = 7.8$ Hz), −142.4 ppm (s, 2W, $\nu_{1/2} = 3.9$ Hz), −169.9 ppm (s, 2W, $\nu_{1/2} = 7.8$ Hz), −172.1 ppm (s, 2W, $\nu_{1/2} = 7.8$ Hz).

Physical Measurements. Elemental analysis was performed by E&R Microanalytical Laboratory Inc., Corona, NY. Infrared spectra were recorded on a MIDAC FTIR instrument. All NMR spectra were obtained on a Bruker AM-300WB spectrometer. Resonance frequencies were 111.925 MHz for ^{119}Sn and 12.505 MHz for ^{183}W in 10 mm tubes. Pulse widths (90°) were 11 μs for ^{119}Sn and 15 μs for ^{183}W. Chemical shifts are reported with respect to 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 tetramethyl tin)[5] 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. All the NMR experiments were carried out in aqueous unbuffered solutions at ambient temperature, *ca.* 21 °C. To achieve sufficiently concentrated solutions for ^{183}W NMR (*ca.* 1 g/2 mL), the cesium salt of **1** was treated with a solution of $NaClO_4$ and insoluble $CsClO_4$ removed by filtration.

Table 1. Crystal Data and Structure Refinement for $Cs_9H[(PhSnOH_2)_2(SiW_{10}O_{36})_2]\cdot 16H_2O$ (Cs Salt of **1**)

chem formula	$Cs_9H[(PhSnOH_2)_2(SiW_{10}O_{36})_2]\cdot 16H_2O$
fw	6744
T	293(2) K
λ	0.710 73 Å
space group	$P\bar{1}$ (No. 2)
unit cell dimens	$a = 12.401(3)$ Å, $\alpha = 96.17(2)°$ $b = 13.832(3)$ Å, $\beta = 109.73(2)°$ $c = 16.313(3)$ Å, $\gamma = 97.13(2)°$
V	2579.9(10) Å^3
Z	1
ρ_{calcd}	4.341 Mg/m^3
μ	25.903 mm^{-1}
final R [$I > 2\sigma(I)$]^a	$R1 = 0.0906$, w$R2 = 0.1786$

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

Crystallography. Crystals of the cesium salt of anion **1** used in this investigation lost solvent quickly, so the data were collected at −100 °C on a Siemens P4/RA diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 73 Å). The structure was solved using SHELXL-PLUS (Siemens) direct methods for W, Sn, Cs, and Si and was refined with SHELXL-93 (G. M. Sheldrick) by full-matrix least squares. Crystal data and structure refinement parameters are listed in Table 1. Final atomic coordinates and thermal parameters of **1** are given in Table 2, and selected bond lengths are in Table 3.

Results and Discussion

The decatungstosilicate[6] and -phosphate[7] anions, $[SiW_{10}O_{36}]^{8-}$ and $[PW_{10}O_{36}]^{7-}$, can be regarded as divacant lacunary deriva-

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($A^2 \times 10^3$) for $Cs_9H[(PhSnOH_2)_2(SiW_{10}O_{36})_2]\cdot 16H_2O$

	x	*y*	*z*	*U*(eq)[a]
W(5)	3886(2)	6954(2)	1645(1)	23(1)
W(2)	8964(2)	5478(2)	2281(1)	22(1)
W(6)	5754(2)	8091(2)	905(1)	23(1)
W(1)	7060(2)	4339(2)	3006(1)	25(1)
W(7)	8885(2)	8034(2)	1878(1)	22(1)
W(4)	4816(2)	5553(2)	3465(1)	27(1)
W(8)	9631(2)	7710(2)	3960(1)	32(1)
W(9)	5647(2)	7965(2)	3982(1)	36(1)
W(3)	7497(2)	6421(2)	4785(1)	39(1)
W(10)	7766(2)	9260(2)	3152(1)	35(1)
Sn	6596(3)	3685(2)	664(2)	21(1)
Si	6782(10)	6714(10)	2572(7)	17(3)
O(2S)[b]	8123(22)	4674(20)	1249(15)	14(6)
O(11)	7195(25)	3405(23)	3618(18)	26(7)
O(55)	2528(25)	7168(23)	1701(18)	26(7)
O(14)	7785(24)	5412(22)	4102(17)	23(7)
O(5S)	3434(24)	6123(22)	590(17)	20(7)
O(66)	5739(25)	9150(23)	442(18)	25(7)
O(38)	8663(28)	7269(26)	4628(19)	36(8)
O(22)	10344(24)	5339(22)	2373(16)	21(7)
O(27)	8821(22)	6627(21)	1706(16)	16(6)
O(59)	4761(25)	7854(23)	2826(17)	24(7)
O(45)	4105(22)	5927(20)	2320(15)	14(6)
O(3)	7241(23)	5690(22)	2344(16)	19(7)
O(99)	5137(29)	8845(26)	4531(20)	40(9)
O(67)	7305(22)	7867(20)	1088(15)	13(6)
O(28)	9534(24)	6464(22)	3443(17)	23(7)
O	5785(27)	4915(25)	585(19)	32(8)
O(77)	9636(23)	8347(21)	1224(16)	18(6)
O(81S)	6404(24)	3654(22)	1890(17)	22(7)
O(14)	5595(22)	4647(21)	2978(16)	16(6)
O(2)	5735(20)	6900(19)	1718(14)	8(5)
O(910)	6917(27)	8809(25)	3816(19)	33(8)
O(12)	8532(25)	4494(23)	2924(18)	26(7)
O(6S)	5094(23)	7134(21)	−32(16)	18(6)
O(710)	8649(25)	9217(24)	2391(18)	27(7)
O(44)	3730(25)	4768(23)	3549(18)	27(7)
O(56)	4332(23)	8042(22)	1150(16)	19(6)
O(49)	4582(29)	6777(26)	3963(20)	39(9)
O(610)	6470(29)	8948(27)	2187(21)	41(9)
O(101)	7962(27)	10472(26)	3401(19)	36(8)
O(4)	6349(23)	6672(22)	3425(16)	19(6)
O(34)	6030(28)	5571(26)	4576(20)	35(8)
O(39)	6766(23)	7564(22)	4963(17)	21(7)
O(1)	7866(26)	7637(24)	2835(18)	29(7)
O(33)	8227(32)	6229(29)	5882(23)	52(10)
O(88)	10971(28)	7928(26)	4746(20)	36(8)
O(78)	10096(25)	8110(23)	2978(17)	24(7)
O(810)	9190(28)	9033(25)	4051(20)	36(8)
C(1)	7545(31)	2475(30)	788(22)	10(8)
C(4)	8806(75)	936(67)	997(51)	97(26)
C(5)	7832(61)	831(55)	1213(42)	70(20)
C(6)	7175(45)	1695(42)	1124(32)	41(13)
C(2)	8781(110)	2642(99)	550(76)	183(48)
C(3)	9263(80)	1709(75)	648(56)	113(30)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Labeling of oxygen atoms is as follows. 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.

tives of the γ-isomers[8] of the Keggin structure. Reaction of SiW_{10} with vanadate,[9] molybdate, and tungstate[10] leads to complete γ-$SiW_{10}M_2O_{40}$ structures which, under hydrolytic conditions, isomerize to species with α- or β-Keggin frameworks.[9,10] Recently, hydrolytically-stable derivatives of SiW_{10} with lower-valent metals have been structurally characterized. The manganese(III) complex[11] has the anticipated γ-Keggin framework incorporating $\{(H_2O)Mn(\mu\text{-}OH)_2Mn(OH_2)\}^{4+}$, whereas the chromium(III) derivative[12] contains $\{(H_2O)Cr(\mu\text{-}OH)(\mu\text{-}OOCCH_3)_2Cr(OH_2)\}^{3+}$. Since the organotin group RSn^{3+} is known to "replace" OW^{4+} in species such as $[SiW_{11}O_{39}SnPh]^{5-}$,[13] $[\alpha\text{-}SiW_9O_{37}(SnPh)_3]^{7-}$,[3] $[P_2W_{15}O_{59}H_3(SnBu)_3]^{6-}$,[2] and $[\alpha\text{-}PW_{10}O_{38}(SnPh)_2]^{5-}$ (mixture of isomers),[14] it was anticipated that SiW_{10} would react with RSn^{3+} to yield γ-$SiW_{10}(SnR)_2$ species. Initial experiments with the stoichiometric ratio of reactants ($Sn{:}SiW_{10} = 2{:}1$) yielded only the 1:1 complex **1** and excess organotin hydroxide. High yields of **1** were produced from reactions with $Sn{:}SiW_{10} = 1{:}1$ as described in the Experimental Section.

Table 3. Selected Bond Lengths and Averages (Å) of $[(PhSnOH_2)_2(SiW_{10}O_{36})_2]^{10-}$

	bond length (Å)	av
W═O	1.65(3)−1.78(3)	1.71
W−O(W)	1.79(3)−2.06(3)	1.93
W−O(Sn)	1.79(3)−1.83(3)	1.81
W−O(Si)	2.23(3)−2.38(3)	2.29
Sn−O(W)	2.05(3)−2.11(3)	2.08
Sn−O	2.07(3)	2.07
Sn−C	2.15(4)	2.15
Si−O	1.62(3)−1.66(3)	1.64
C−C	1.36(6)−1.70(13)	1.47

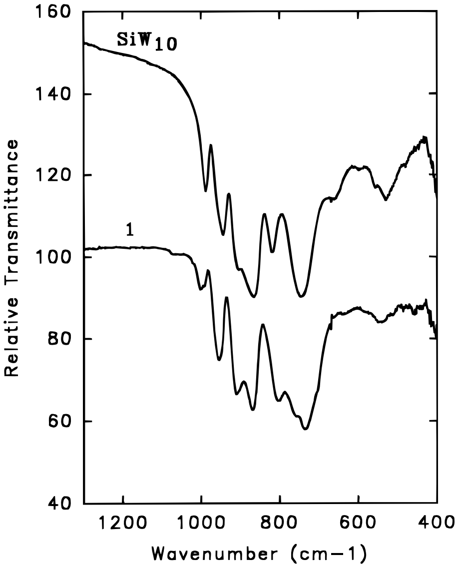

Figure 1. Infrared spectra of $K_8[\gamma\text{-}SiW_{10}O_{36}]$ and the cesium salt of **1**, recorded in KBr pellets.

The infrared spectrum of the cesium salt of **1** is very similar to that of $K_8[SiW_{10}O_{36}]$ (Figure 1) indicating probable retention of the γ-tungstosilicate framework. The structure of the anion revealed by X-ray analysis of the cesium salt is shown in Figure 2. Two tin atoms are sandwiched between two SiW_{10} groups, and each tin is bound equatorially by two oxygen atoms of two edge-shared WO_6 octahedra of each SiW_{10} group. The axial phenyl groups are directed externally, and the "internal" ligands are *tentatively* identified as water molecules (rather than hydroxides) for the following reasons. The salt is isolated as

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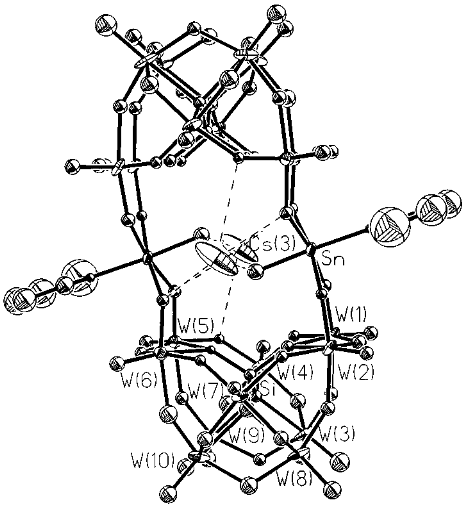

Figure 2. Structure of $[(PhSnOH_2)_2(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ (anion **1**), showing 50% probability thermal ellipsoids. The mean distance of the disordered[16] Cs(3) cation from the internal aqua ligands is 3.40(3) Å.

an acid salt (nine cesium cations), and the $Sn-O_{axial}$ bond length is 2.07 Å, which corresponds to a bond-valence sum[15] of 0.6 for the oxygen atom. Corresponding Sn--O distances in $[(PhSnOH)_2(PhSnOH_2)(PW_9O_{34})_2]^{11-}$ are marginally shorter at 1.92−2.05 Å.[2] However, we note that there are two closely-associated cesium cations[16] (Figure 2) which could also be responsible for the low bond-valence sums for the internal oxygens, so the identification of these as water molecules is not unambiguous. The other bond lengths fall within normal ranges, e.g. W−O(Sn) = 1.79−1.83 Å [2] and Sn−O(W) = 2.05−2.11 Å.[17]

Overall, the anion has virtual C_{2h} symmetry with the mirror plane defined by the Si and Sn atoms. The "slipped" configuration, as opposed to one with eclipsed SiW_{10} groups and coplanar phenyl groups, is presumably a result of crowding by the "internal" aqua ligands. The structure of **1** is different from all the known metal ion substituted $\gamma\text{-}SiW_{10}$ anions. It represents a new type of sandwich structure.

NMR studies of anion **1** in aqueous solution at room temperature show one ^{119}Sn line (δ −617 ppm) and five ^{183}W lines (δ −124.8, -126.7, −142.4, −169.9, 172.1; intensity ratio 1:1:1:1:1). These spectra are consistent with the static structure revealed by X-ray crystallography. Incipient fluxionality (presumably a reciprocating motion) is suggested by NMR line widths that are broader than those of other tungstostannate complexes[2,3] and by the elongated thermal ellipsoids of the tungsten atoms.

Conclusion

A bis(phenyltin) bis(decatungstosilicate), $[(PhSnOH_2)_2(\gamma\text{-}SiW_9O_{36})_2]^{10-}$, derived from the $\gamma\text{-}[SiW_{10}O_{36}]^{8-}$ lacunary anion was prepared. X-ray crystallographic investigation of this complex reveals that it has a sandwich structure, different from all other disubstituted γ-Keggin tungstates. This new structure suggests possibilities of designing and preparing linear arrays of polytungstates.

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Supporting Information Available: Complete tables of crystallographic data and structure refinement, positional parameters, bond lengths and angles, and thermal parameters for **1** (34 pages). Ordering information is given on any current masthead page.

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(15) Bond valence sums are computed as the sum of "bond strengths" at each atom. $r_0 = 1.905$ for $Sn^{IV}-O^{2-}$. See: Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

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