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Lone-Pair-Induced Chirality in Polyoxotungstate Structures: Tin(II) Derivatives of A-Type $XW_9O_{34}{}^{n-}$ (X = P, Si). Interaction with Amino Acids

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Abstract: Tin(II) tungstophosphate and tungstosilicate derivatives $[Sn^{II}{}_3(\alpha\text{-}PW_9O_{34})_2]^{12-}$ (**1**), $[Sn^{II}{}_3(\alpha\text{-}SiW_9O_{34})_2]^{14-}$ (**2**), and $[Sn^{II}{}_3(\beta\text{-}SiW_9O_{34})_2]^{14-}$ (**3**) have been prepared by reaction of tin(II) sulfate with $Na_8H[A,\beta\text{-}PW_9O_{34}]\cdot 24H_2O$, $Na_{10}[\alpha\text{-}SiW_9O_{34}]\cdot xH_2O$, and $Na_{10}[\beta\text{-}SiW_9O_{34}]\cdot 26H_2O$, respectively. Oxidation of **1** with Br_2 yields $[(HOSn^{IV}OH)_3(PW_9O_{34})_2]^{12-}$ (**1′**). The new heteropolyanions were characterized by elemental analysis, infrared spectroscopy, multinuclear NMR, and X-ray crystallography. Crystals of $Cs_{11}H[Sn^{II}{}_3(PW_9O_{34})_2]\cdot 14H_2O$ (anion **1**) are triclinic, space group $P\bar{1}$, with lattice constants a = 12.904(3) Å, b = 18.059(3) Å, c = 21.618(3) Å, α = 111.68(2)°, β = 94.04(2)°, γ = 101.41(1)°, V = 4531.5(14) Å^3, Z = 2. Crystals of $Cs_{12.5}H_{1.5}[Sn^{II}{}_3(\alpha\text{-}SiW_9O_{34})_2]\cdot 24.5H_2O$ (anion **2**) are triclinic, space group $P\bar{1}$, with lattice constants a = 13.101(5) Å, b = 18.140(7) Å, c = 21.367(8) Å, α = 111.54(4)°, β = 92.22(4)°, γ = 102.98(2)°, V = 4561(3) Å^3, Z = 2. Both **1** and **2** have structures in which three Sn^{II} cations are sandwiched between XW_9 units. In **1** the coordination of each Sn is trigonal bipyramidal with the "equatorial" unshared electron pair directed toward the center of the anion. The inequality of the equatorial (2.11 Å) and axial (2.33 Å) Sn−O bond lengths results in one PW_9 group being rotated by 7° with respect to the other PW_9. The overall anion symmetry is D_3. Anion **2** has a more pronounced (10°) rotation of the SiW_9 groups, which results in "tetrahedral" Sn coordination, again with the unshared electron pairs directed internally (overall anion symmetry C_3). The greater rotation in the structure of **2** may be a consequence of electrostatic repulsions between the more highly charged $SiW_9O_{34}{}^{10-}$ anions. All three anions display one-line ^{119}Sn-NMR and two-line ^{183}W-NMR (intensity 1:2) spectra, although the lines are broad (60−100 Hz) for **2** and **3** suggesting a slow fluxional process, probably racemization via an internal twist. In contrast, the two W-NMR lines of **1** are narrow and the more intense line shows two-bond coupling to P (1.7 Hz). This line is split into two by the addition of the chiral amino acids lysine, isoleucine, and histidine, but is unaffected by achiral glycine. Crystals of a lysine complex have been isolated, but have in all cases so far proved to be disordered.

Introduction

Current interest and activity in the chemistry of polyoxometalates is largely driven by potential applications in medicine and catalysis, which lead to searches for new structures with unusual combinations of properties.[1] In each of these application areas it would be desirable to have chiral polyoxometalates, since much biological activity is expected to depend on the chiral configuration, and chiral-selectivity in catalysis is also a major goal. Based on the fact that tin(II) demands a different coordination environment compared with W(VI) and other heteroatoms, we are seeking to produce new polyoxotungstate structures containing Sn^{II}. Earlier work had demonstrated that one Sn^{II} can be incorporated into lacunary Keggin structures.[2] We report here the syntheses and structural characterization of three complexes derived from the lacunary anions $[PW_9O_{34}]^{9-}$ and α- and β-$[SiW_9O_{34}]^{10-}$. The new complexes[3] prove to be chiral in contrast to other trimetallo derivatives.[4]

Experimental Section

Synthesis. Sodium 9-tungstophosphate[5] ($Na_8H[A,\beta\text{-}PW_9O_{34}]\cdot 24H_2O$) and sodium 9-tungstosilicates[6] ($Na_{10}[\alpha\text{-}SiW_9O_{34}]\cdot xH_2O$ and $Na_{10}[\beta\text{-}SiW_9O_{34}]\cdot 26H_2O$) were prepared following the published methods and were identified by infrared spectroscopy. Tin(II) sulfate was purchased from Aldrich and used without further purification.

$K_{11}H[Sn^{II}{}_3(PW_9O_{34})_2]\cdot 32H_2O$. (1) Powdered $Sn^{II}SO_4$ (0.67 g, 3 mmol) was added to 60 mL of water with stirring. Nitrogen gas was bubbled through this slightly turbid solution to remove oxygen. Solid $Na_8H[PW_9O_{34}]\cdot 24H_2O$ (5.7 g, 2 mmol) was quickly added to the above solution. Within a few seconds, most of the tungstophosphate dissolved and the solution clarified and turned orange-red. Sodium bicarbonate was added to this solution in small portions, until no further evolution of CO_2 was observed. The solution was stirred for an additional 10 min under nitrogen. At this stage the color of the solution was orange,

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[3] We have recently learned that the tungstophosphate derivative has been independently synthesized by Botar *et al.* starting from tungstate, phosphate, and tin(II) ions. The structure of the potassium salt was determined [A. Botar, J. Meyer, and A. Müller, personal communication].

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and the final pH was 8.0. Traces of unreacted tungstophosphate were filtered out. Potassium chloride was added in small portions until no more precipitation was observed. The precipitate was collected on a medium porosity sintered glass frit and dried under suction for 10 min, then washed with saturated KCl solution and dried overnight under suction, giving a yield of 4.5 g. Anal. Calcd for $K_{11}Sn_3P_2W_{18}O_{100}H_{65}$: K, 7.39; Sn, 6.12; P, 1.06; W, 56.83. Found: K, 7.34; Sn, 6.15; P, 1.68; W, 56.77. NMR: ^{31}P, δ −12.0 ppm (s, 2P); ^{119}Sn, δ −676.1 ppm (s, 3Sn); ^{183}W, δ −104.0 ppm (d, 12W, $J_{W-P} = 1.7$ Hz), −143.9 ppm (s, 6W).

$Cs_{11}H[Sn^{II}_3(PW_9O_{34})_2]\cdot 14H_2O$. Solid $K_{11}H[Sn^{II}_3(PW_9O_{34})_2]\cdot 32H_2O$ (3 g) was redissolved in 40 mL of water. Cesium chloride was added in small portions until no more precipitation was observed. The orange precipitate was collected on a sintered glass frit and dried under suction overnight. Recrystallization from hot water gave thin orange plates, which were used for the single-crystal X-ray diffraction investigation.

$K_{11}H[(HOSn^{IV}OH)_3(PW_9O_{34})_2]\cdot 20H_2O$ (1′). **1′** was synthesized by addition of 1.0 mL of bromine to 40 mL of a water solution containing 3 g of $K_{11}H[Sn^{II}_3(PW_9O_{34})_2]$. This solution was stirred for 5 min, then CCl_4 was introduced to extract excess Br_2. Addition of potassium chloride yielded a white precipitate which was filtered out and dried under suction. Yield: 2.0 g. Anal. Calcd for $K_{11}Sn_3P_2W_{18}O_{94}H_{47}$: K, 7.54; Sn, 6.24; P, 1.09; W, 57.98. Found: K, 7.55; Sn, 6.80; P, 0.93; W, 57.27. NMR: ^{31}P, δ −11.5 ppm (s, 2P); ^{119}Sn, δ −659.4 ppm (s, 3Sn, $J_{Sn-W} = 138$ Hz); ^{183}W, δ −129.4 ppm (s, 6W), −201.4 ppm (s, 12W, $J_{W-Sn} = 137$ Hz).

$Cs_{12.5}H_{1.5}[Sn^{II}_3(\alpha\text{-}SiW_9O_{34})_2]\cdot 24.5H_2O$ (2). **2** was prepared analogously to anion **1**. After $Sn^{II}SO_4$ (0.67 g, 3 mmol) was mixed with $Na_{10}[\alpha\text{-}SiW_9O_{34}]\cdot xH_2O$ (5.7 g, 2 mmol) in aqueous solution, sodium bicarbonate was added to adjust the pH to 8. Cesium chloride was used to precipitate out the orange product. Recrystallization from hot water gave thin orange plates, which were used in single-crystal X-ray diffraction studies. Yield: 4.7 g. Anal. Calcd for $Cs_{12.5}Sn_3Si_2W_{18}O_{92.5}H_{50.5}$: W, 48.31; Sn, 5.20; Cs, 23.29; Si, 0.82. Found: W, 48.32; Sn, 5.52; Cs, 23.05; Si, 0.71. NMR: ^{29}Si, δ −85.2 ppm (s, 2Si); ^{119}Sn, δ −617.1 ppm (s, 3Sn, $\nu_{1/2} = 71$ Hz); ^{183}W, δ −113.8 ppm (s, 12W, $\nu_{1/2} = 94$ Hz), −153.4 ppm (s, 6W, $\nu_{1/2} = 94$ Hz).

$Cs_9H_5[Sn^{II}_3(\beta\text{-}SiW_9O_{34})_2]\cdot 30H_2O$ (3). **3** was prepared analogously to anion **1**. After $Na_{10}[\beta\text{-}SiW_9O_{34}]$ had been added to the solution of $Sn^{II}SO_4$ under N_2, CsCl was added to precipitate out **3** without adjusting the pH with $NaHCO_3$. Recrystallization from hot water gave thin red plates. Yield: 4.1 g. Anal. Calcd for $Cs_9Sn_3Si_2W_{18}O_{98}H_{65}$: W, 50.51; Sn, 5.43; Cs, 18.26; Si, 0.86. Found: W, 50.50; Sn, 5.73; Cs, 18.40; Si, 0.96. NMR: ^{29}Si, δ −85.0 ppm; ^{119}Sn, δ −621.0 ppm (s, 3Sn, $\nu_{1/2} = 85$ Hz); ^{183}W, δ −137.7 ppm (s, 6W, $\nu_{1/2} = 72$ Hz), −141.2 ppm (s, 12W, $\nu_{1/2} = 59$ 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 121.495 MHz for ^{31}P, 59.623 MHz for ^{29}Si, 111.924 MHz for ^{119}Sn, and 12.505 MHz for ^{183}W in 10-mm tubes. Pulse widths (90°) were 11 μs for both ^{31}P and ^{119}Sn, 13.8 μs for ^{29}Si, and 40 μs for ^{183}W. Chemical shifts are given with respect to external 85% H_3PO_4 for ^{31}P, 30% 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 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 done with aqueous unbuffered solutions. To achieve sufficiently concentrated solutions for ^{183}W NMR (ca. 1.5 g/2mL), the potassium and cesium salts were treated with $LiClO_4$ and the resultant insoluble perchlorates were removed by filtration or decantation.

Crystallography. Crystals of cesium salts of **1** and **2** were not stable under the X-ray beam at room temperature. The data were collected at −100 °C on a Siemens P4/RA diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved using SHELXL-PLUS (Siemens) direct methods for W, Sn, Cs, P, and Si. The structures 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 $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$. Crystal data and structure refinement parameters are listed in Table 1. Final atomic coordinates and thermal parameters of **1** and **2** are given in the supporting information, and selected bond lengths are given in Tables 2 and 3.

Table 1. Crystal Data and Structure Refinement for **1** and **2**

	1	**2**
chemical formula	$Cs_{11}H_{29}O_{82}P_2Sn_3W_{18}$	$Cs_{12.5}H_{50.5}O_{92.5}Si_2Sn_3W_{18}$
formula wt	6531	6914
T	−100 °C	−100 °C
λ	0.71073 Å	0.71073 Å
space group	$P\bar{1}(2)$	$P\bar{1}(2)$
unit cell dimensions		
a	12.904(3) Å	13.101(5) Å
b	18.059(3) Å	18.140(7) Å
c	21.618(3) Å	21.367(8) Å
α	111.68(2)°	111.54(4)°
β	94.04(2)°	92.22(4)°
γ	101.41(1)°	102.98(2)°
V	4531.5(14) Å^3	4561(3) Å^3
Z	2	2
ϱ_{calcd}	4.786 Mg/m^3	5.034 Mg/m^3
μ	27.868 mm^{-1}	28.442 mm^{-1}
final R [$I > 2\sigma(I)$][a]	$R(F_o) = 0.0944$	
final R [$I > 3\sigma(I)$][a]		$R(F_o) = 0.0881$

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.

Table 2. Selected Bond Lengths [Å] for $[Sn^{II}_3(PW_9O_{34})_2]^{12-}$

	bond lengths (Å)	av (Å)
$W{=}O$	1.65−1.77	1.71
$W-O(W)$	1.82−2.07	1.93
$W-O(P)$	2.29−2.42	2.36
$W-O(Sn)_{\text{short Sn−O}}$	1.84−1.89	1.87
$W-O(Sn)_{\text{long Sn−O}}$	1.79−1.84	1.82
$Sn-O(W)_{\text{short}}$	2.08−2.15	2.11
$Sn-O(W)_{\text{long}}$	2.27−2.45	2.35
$P-O(W)$	1.51−1.58	1.55

Table 3. Selected Bond Lengths [Å] for $[Sn^{II}_3(SiW_9O_{34})_2]^{14-}$

	bond length (Å)	av (Å)
$W{=}O$	1.69−1.79	1.75
$W-O(W)$	1.78−2.17	1.96
$W-O(Si)$	2.21−2.35	2.29
$W-O(Sn)$	1.78−1.85	1.80
$W-O$	1.75−1.81	1.78
$Sn-O(W)$	2.12−2.29	2.22
$Si-O(W)$	1.62−1.74	1.66

The crystals of **1** and **2** underwent slow decomposition under the X-ray beam even at −100 °C. The standard check reflections dropped to 60% for **1** and 80% for **2**, after a 3-day data collection. The color of both crystals changed from orange to green. If the X-ray beam was stopped for several minutes, the check reflections would recover to almost 100%. This suggests that there might be reversible intramolecular electron transfer between Sn^{II} and PW_9 or SiW_9 groups. The high R values (0.0944 for **1**, and 0.0881 for **2**) could also be caused by the decomposition, although the structures were well solved.

Results and Discussion

Tin(II) monosubstituted polyoxotungstates are easily oxidized by air in aqueous solution.[2] The current syntheses were therefore carried out under a constant stream of N_2, and the reaction stoichiometries and pH conditions for the synthesis of **1** were established from preliminary studies monitored by ^{31}P NMR. Since $[PW_9O_{34}]^{9-}$ is not stable in aqueous solution, the reaction of Sn^{II} and PW_9 was carried out by addition of the solid sodium salt of PW_9 to a solution of $Sn^{II}SO_4$ under N_2. As soon as the two reactants were mixed, PW_9 dissolved and the solution turned orange-red. Addition of CsCl precipitated an

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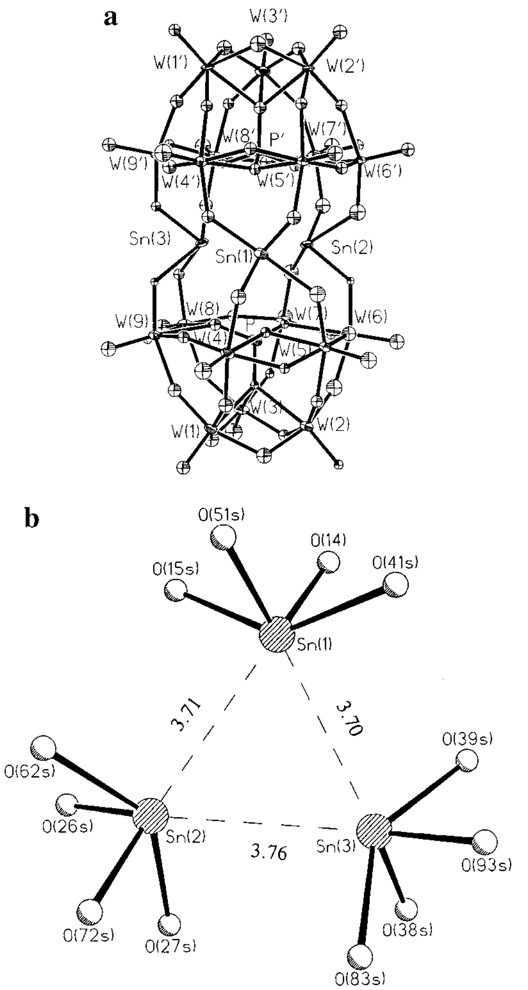

Figure 1. (a) Structure of $[Sn^{II}_3(PW_9O_{34})_2]^{12-}$ (**1**) showing 50% probability thermal ellipsoids. (b) SHELXP representation of the coordination spheres of the tin atoms in **1**.

orange-red product. The ^{31}P NMR spectrum of an unbuffered aqueous solution of this precipitate showed peaks at −11.3, −12.0, and −13.0 ppm, with an intensity ratio of 1:1:3. Solutions which were made by dissolving the precipitate in acetate buffer (pH 2.5 to 6.0) gave the same three ^{31}P lines but with different intensities. Upon addition of $NaHCO_3$ to the unbuffered solution, the ^{31}P NMR spectrum showed only one line at −12.0 ppm. Subsequently, addition of sodium bicarbonate during the synthesis (see Experimental Section) resulted in good yields of **1**. Elemental analysis and multinuclear NMR spectroscopy of **1** are fully consistent with the structure revealed by X-ray crystallography (Figure 1). Anion **1** is stable in the solid state, but it is slowly oxidized by air to **1′** in aqueous solution. Potassium salts of anions **1** and **1′** give similar infrared spectra in the P−O stretching region, but slightly different W−O peaks (Figure 2).

It has been demonstrated that the starting material A,β-PW_9 can be transformed to B,α-PW_9 simply by heating the solid.[8] A reaction of 2 mmol of B-$[PW_9O_{34}]^{9-}$ prepared in this way with an aqueous solution of 3 mmol of $Sn^{II}SO_4$ generated anion **1** directly with no need for pH adjustment. The crystal structure (see below) reveals that anion **1** contains two A,α-PW_9 units, which indicates that the synthesis involves a structural rearrangement of both of the possible starting materials, A,β-PW_9[4l] or B,α-PW_9.

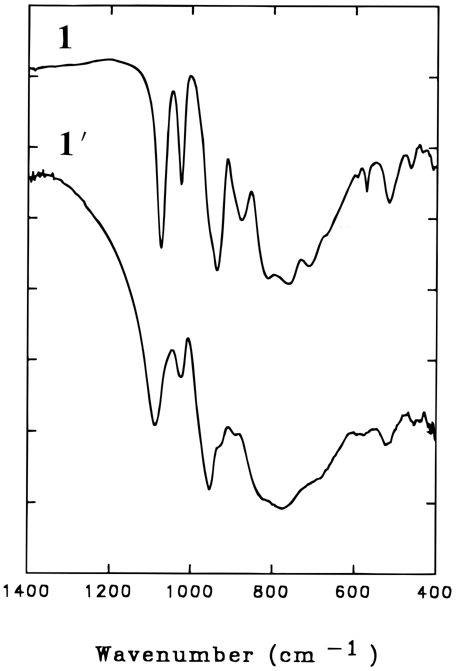

Figure 2. Infrared spectra of potassium salts of anions **1** and **1′**.

The reaction stoichiometries and pH conditions for the reactions of α- and β-SiW_9 with $Sn^{II}SO_4$ were established from preliminary studies monitored via ^{119}Sn NMR. It was found that addition of $NaHCO_3$ was necessary in order to synthesize **2** efficiently. Elemental analysis and multinuclear NMR spectroscopy of **2** are fully consistent with the structure revealed by X-ray crystallography (Figure 3). The characteristic IR spectra, shown in Figure 4, demonstrate the structural similarity of **2** with **3**.

Structures. The structure of **1** (Figure 2) consists of two A-type α-PW_9 anions linked by three tin(II) cations into an assembly of virtual D_3 symmetry. All previously reported $M_3(PW_9)_2$ and $M_3(SiW_9)_2$ compounds have D_{3h} symmetry with two PW_9 or SiW_9 units related by a mirror plane, i.e. they are “eclipsed”.[4a,4g,4j,4l,9] In **1**, one PW_9 group is rotated by 7° around the C_3 axis from the eclipsed position. Each Sn^{II} is coordinated by two oxygen atoms from two edge-sharing belt-tungstens of each PW_9 unit. Because of the relative rotation of the PW_9 groups each Sn^{II} has pseudo-trigonal-bipyramidal coordination with two long axial Sn−O bonds (2.33 Å), two short equatorial Sn−O bonds (2.11 Å), and, presumably, the lone-pair of electrons occupying the third equatorial position pointing toward the anion’s C_3 axis. The axial O−Sn−O bond angle is about 141.4° (139.7−142.3°), and the equatorial O−Sn−O angle is about 97.2° (96.5−97.7°). These bond lengths and bond angles are consistent with reported values for other trigonal-bipyramidal tin(II) structures.[10]

The structure of **2** (Figure 2) is similar to the structure of **1**, and consists of two A-type α-SiW_9 anions linked by three tin(II) groups into an assembly of virtual C_3 symmetry. Here the rotation angle between two SiW_9 units is larger than that of **1**. This causes the two potentially axial oxygens to be separated too far to bind tin(II) at same time. The structure can be described as one in which one of the SiW_9 units (Si(1)W_9) of an eclipsed structure is twisted 10° around the C_3 axis. This rotation moves three oxygens of the Si(1)W_9 unit (O(37S), O(25S), O(19S)) into positions equidistant from the center of

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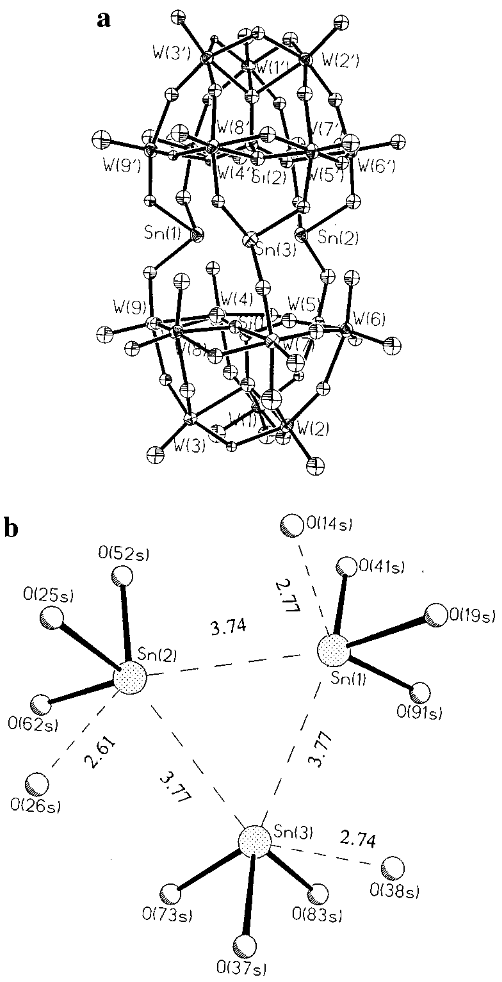

Figure 3. Structure of $[Sn^{II}_3(SiW_9O_{34})_2]^{14-}$ (**2**) showing 50% probability thermal ellipsoids. (b) SHELXP representation of the coordination spheres of the tin atoms in **2**.

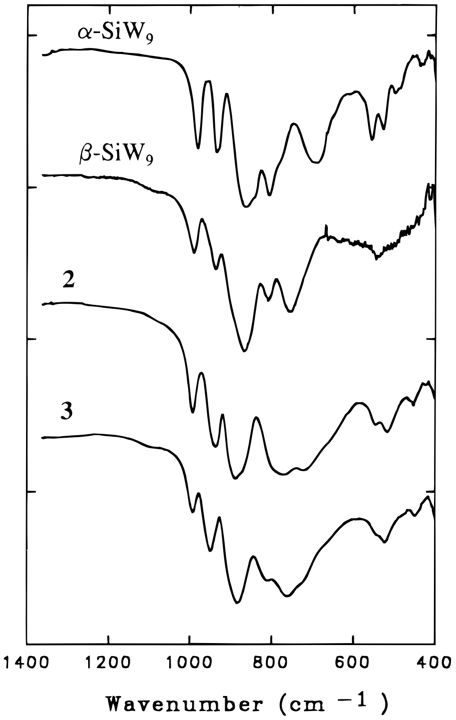

Figure 4. Infrared spectra of sodium salts of α-SiW_9 and β-SiW_9 and cesium salts of anions **2** and **3**.

three pairs of oxygens of the edge-sharing WO_6 octahedra of the $Si(2)W_9$ unit (O(73S) and O(83S), O(52S) and O(62S), O(41S) and O(91S)). Each Sn^{II} is coordinated by three oxygens, with its lone-pair of electrons occupying the fourth position of a tetrahedron and, as in **1**, pointing toward the interior of the structure. The average Sn−O bond lengths are 2.21 Å (2.12−2.29 Å), and average O−Sn−O bond angles are 85.7 Å (78.9−94.1°). These bond lengths and bond angles are consistent with reported values for other trigonal-pyramidal tin(II) structures.[10] The shortest "nonbonded" Sn••O contact is 2.71 Å. The W−O(Sn) bond lengths (1.78−1.85 Å, average 1.80 Å) are somewhat shorter than those of W−O(W) (1.78−2.11 Å, average 1.91 Å). The three W−O bonds of $Si(1)W_9$ (1.75−1.81 Å, average 1.78 Å) for the oxygen atoms (O(38S), O(26S), O(14S)), which do not form bonds with Sn, are slightly shorter than those of W−O(Sn). Bond valence sum (BVS) calculation[11] shows that these oxygen atoms have average BVS values of 1.45, which suggests that each oxygen is partially protonated on average by 0.5 H. This would be consistent with the elemental analysis and the crystallographic results which found 12.5 cesium cations for each 14− anion. An alternative explanation is that the W−O bond lengthening indicates weak interaction with Sn.

A crystallographic data set was collected for a crystal of the cesium salt of **3**. The crystals are orthorhombic, space group *Pnma*, with lattice constants $a = 28.296(4)$ Å, $b = 16.906(3)$ Å, $c = 17.806(5)$ Å, and $V = 8517.9(10)$ Å^3. The crystals are disordered, and the structure could be only partially solved, with $R = 0.1474$ for 330 parameters and 2408 independent reflections with $I > 2\sigma$ out of 7764 reflections collected. The partial structure shows a crystallographic mirror plane through the structure coincident with a mirror plane of one of the SiW_9 groups. Since the other SiW_9 unit is rotated by 15°, that unit and the three Sn atoms are disordered. Because of the disorder, the reflections at high angle were weak and the structure could not be totally solved. However, the heavy atom positions and the SiW_9 unit that is not disordered are well defined. The partial structure clearly shows the two SiW_9 units to be β-type as anticipated and the rotation between the two SiW_9 units to appear to be about 15°. A table of atomic coordinates and equivalent isotropic parameters together with a figure showing the atom labeling are given in the supporting information. The structure is consistent with the elemental analysis and IR spectrum of **3**. There is a possible electrostatic reason for a large twist angle in the SiW_9 derivatives. A large rotation moves the negatively-charged O(Sn,W) atoms further apart in the 14− anion.

Since the rotation of the two PW_9 and SiW_9 units can occur either to the left or to the right, **1**, **2**, and **3** are chiral. The space groups of the X-ray structures of both **1** and **2** are $P\bar{1}$, therefore each unit cell contains one pair of enantiomers, related by the center of symmetry.

NMR. Each of the three complexes exhibits a two-line W-NMR spectrum that is inconsistent with the solid-state structures, D_3 for **1** (three lines expected) and C_3 for **2** and **3** (six lines expected). This indicates exchange processes leading to an average structure of D_{3h} symmetry. The most plausible process would be an oscillatory twist, depicted in Figure 5, leading to interconversion of the enantiomers. During this process each tin atom in **1** undergoes a pseudorotation with the "equatorial" lone pair of the trigonal bipyramidal coordination sphere acting as the pivot. Further, the configuration of **1** would appear to be an intermediate state in the racemization processes of **2** and **3**. Broad NMR lines for **2** and **3** indicate that these

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[11] 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 and B for $W^{VI}-O^{2-}$ are 1.917 Å and 0.37, respectively. [Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.]

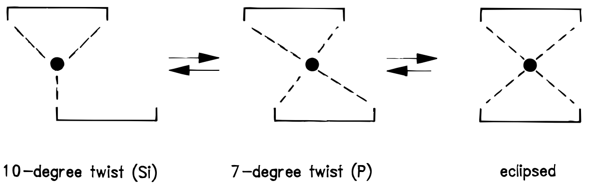

Figure 5. Representation of the first half to the proposed fluxional process leading to racemization of **1**, **2**, and **3**. The square brackets define the positions of oxygen atoms attached to pairs of edge-shared belt-WO_6 octahedra of XW_9 groups. The filled circle represents a tin atom.

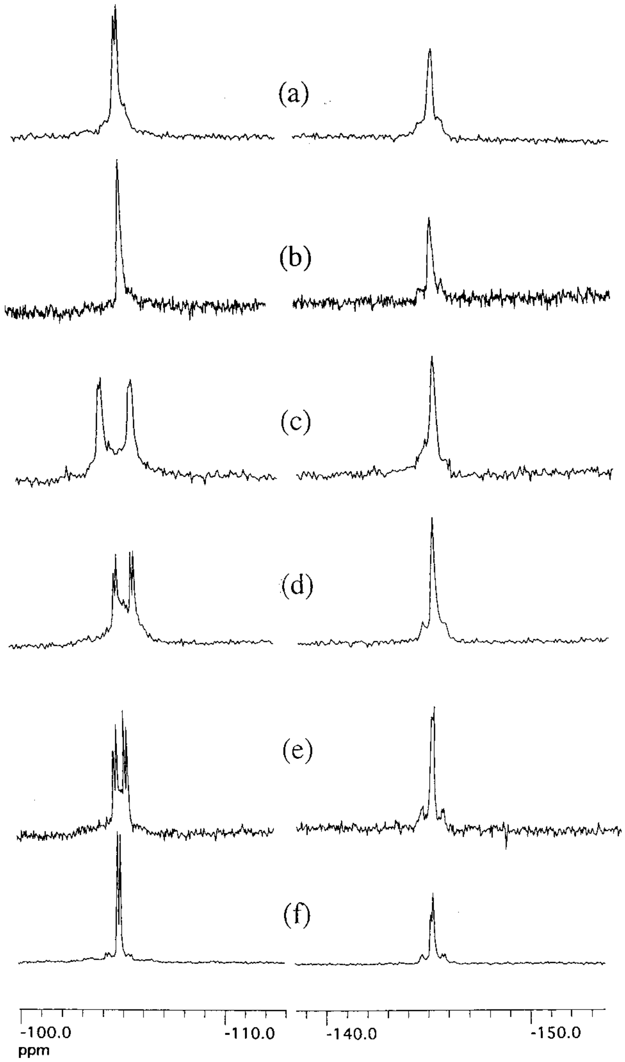

Figure 6. 12.50-MHz ^{183}W NMR spectra of 0.05 M solution of **1**: (a) in D_2O, (b) in D_2O ($^{183}W\{P\}$), (c) in 0.5 M lysine, (d) in 0.5 M histidine, (e) in 0.5 M isoleucine, and (f) in 0.5 M glycine.

processes have not reached the fast exchange limit. Preliminary observations show that the rates are both temperature and pH dependent: the W-NMR line widths of **3** decrease from 72 and 59 Hz at 25 °C to 15 and 18 Hz at 42 °C; the Sn-NMR line width of **2** is 71 Hz at pH 8.0 and 170 Hz at pH 4.7. A complete analysis will require careful control of pH and temperature.

The W-NMR lines of **1** are narrow enough for two-bond W−P coupling of 1.7 Hz to be resolved on the more intense line. That this splitting did not represent nearly degenerate resonances of belt tungstens in a static structure was confirmed by a W{P} experiment (Figure 6, parts a and b). These observations imply that the racemization process for **1** is faster than for **2** or **3**, a result that is consistent with the smaller amplitude of the twisting motion required (Figure 5).

Interactions with Amino Acids. Chiral polyoxometalate structures may be divided into three classes: (a) those which undergo rapid racemization via water exchange, partial hydrolysis, or fluxional behavior (examples are $[X_2M_5O_{21}]^{n-}$ (X = OP, RP, S, Se; M = Mo, W),[12] $[(MeAsO_3)Mo_6O_{18}(H_2O)_6]^{2-}$,[13] $[X^{V}Mo_9O_{31}(H_2O)_3]^{3-}$ [14] and $[X^{V}{}_2Mo_{18}O_{62}]^{6-}$ (X = P, As),[15] and $[M^{IV}Mo_9O_{32}]^{6-}$ (M = Mn, Ni));[16] (b) those which are nonlabile but with enantiomers so similar that separation has not been achieved (e.g. $[\beta_2\text{-}SiW_{11}O_{39}]^{6-}$, $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ and their metal substituents,[17,18] and $[WM_3(H_2O)_2(XW_9O_{34})_2]^{12-}$ (M = X = Zn, Co));[19] and (c) those which are nonlabile, with separable enantiomers ($[Co_2Mo_{10}O_{38}H_4]^{6-}$ [20] and $[P_6W_{18}O_{79}]^{20-}$).[21] The dicobaltate anion has been resolved by classical diastereomer formation, and the chirality of the tungstophosphate anion in solution has been demonstrated by the doubling of all P-NMR lines when the spectrum was recorded in the presence of lysine.

Although anions **1**, **2**, and **3** would appear to belong to class a, some preliminary experiments with chiral amino acids have been carried out. Addition of lysine hydrochloride to solutions of **2** and **3** had no significant effect on the broad Sn- and W-NMR lines, but further splitting was observed in the W-NMR spectrum of **1**.

A solution containing 0.7 g (0.1 mmol) of $K_{11}H[Sn^{II}{}_3(PW_9O_{34})_2]$ in 2 mL of water was treated with $LiClO_4$ to convert anion **1** to its lithium salt to increase solubility. Then 0.18 g (1 mmol) of lysine•HCl was added to this solution. The ^{31}P- and ^{119}Sn-NMR spectra of this solution were unchanged, but the ^{183}W NMR spectrum showed three lines. The cap-tungsten line at −144 ppm remained, while the belt-tungsten line split into two lines at −103.0 and −104.9 ppm, a separation of 18.9 Hz. Each line was a doublet (J_{P-W} = 1.9 Hz), see Figure 6c.

In order to study the influence of lysine concentration on the belt-tungsten W-NMR line splitting, W-NMR spectra were collected on samples containing **1** and lysine•HCl with mole ratios ranging from 1:1 to 1:20 (see Figure 7). The data plotted in Figure 7 are consistent with the formation of a labile complex of **1** with lysine. Similar behavior was observed with other amino acids. At a 10:1 ratio of acid:**1**, the belt-tungsten line was split by 10.5 (histidine) and 6.7 Hz (isoleucine), but no splitting was observed with achiral glycine, see Figure 6, parts d−f.

Interactions of amino acids with polyoxometalates have been noted previously.[22] Crans' group has shown that the interaction

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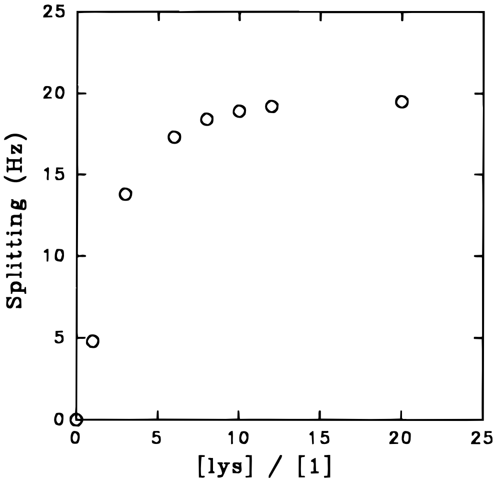

Figure 7. Apparent splitting of 104-ppm ^{183}W resonance of **1** as a function of lysine concentration.

can occur via hydrogen bonding[23] and that amino acids or peptides can serve as counterions. An attempt was made to isolate crystals of the lysine complex of **1** by the method of ethanol vapor diffusion into a solution containing lys:**1** = 10:1. The resulting crystals were shown via ^{1}H NMR (intensity ratios of lysine and Tiers salt resonances) to contain 8.0 ± 0.4 mol of lysine per polyoxometalate anion. A crystallographic data set was collected, but could not be solved owing to considerable disorder.

The results shown in Figures 6 and 7 are open to more than one interpretation. Although no firm conclusion can be reached in the absence of a structure of an amino acid complex, the following points can be made.

1. The most likely targets of ion-pair interaction of the zwitterionic amino acids with **1** are the "equatorial" oxygen atoms bound to the tin atoms, since these are expected to be the most electronegative (they are the sites of protonation in the molybdate analog of the $[PW_9O_{34}]^{9-}$ unit[24]).

2. The achiral glycine molecule has no effect on the W-NMR spectrum of **1**. This suggests that the observed effects are related to diastereomeric interactions. In order to seek further confirmation of this, some experiments were made with the non-carboxylate (and therefore non-chiral) analogue of lysine, 1,5-diaminopentane. Unfortunately, only insoluble salts of the polyoxometalate were formed.

3. No splitting is observed for the Sn-, P-, and the cap-W resonances of **1**, and only two lines were observed for the belt-tungstens (four lines would be expected: two for each diastereomer) in the presence of the chiral amino acids. Although this would seem to rule out the above explanation that the splitting demonstrates a mixture of polyanion−amino acid diastereomers, the possibility cannot be excluded that the splittings of the Sn-, P-, W(cap)-, and the two kinds of belt-W resonances are too small to be detected.

4. Another possible explanation is that the splitting of the belt-W resonance is caused by the two different kinds of belt-W in one enantiomer. Since the racemization of **1** is rapid on the NMR time scale, it is conceivable that the interaction with a chiral amino acid will displace the racemic equilibrium toward a single enantiomer. Such interactions in optically-labile systems are well-documented (Pfeiffer Effect[25]). According to this interpretation the "split" W-NMR spectrum is that of a single enantiomer of **1** stabilized by interaction with a chiral counterion. But this does not explain why achiral glycine, which would bind equally to both enantiomers, does not split the belt-tungsten line as other chiral amino acids do. The binding ability of glycine to the anion is expected to be similar to that of isoleucine which does induce splitting.

5. Anions **2** and **3** are less optically-labile than **1** (broad NMR lines). There would seem to be no reason to exclude the possibility of formation of amino acid complexes with these anions, but conditions for well-resolved NMR spectra have not been discovered.

Oxidation. All three tin(II)-substituted tungstates **1**, **2**, and **3** can be oxidized to their tin(IV) counterparts by bromine. The preparation of the oxidized form of **1** (**1′**) is given in the Experimental Section. In order to confirm the number of Sn(II) in anions **2** and **3**, 25 mL of an aqueous solution of bromine (0.03194 M, standardized by iodometric titration[26]) was added to solutions of 1.00 g of cesium salts of **2** or **3** in 20 mL of water. After the solutions had been stirred for 5 min to allow complete reaction, excess Br_2 was determined by iodometric titration. The amount of bromine solution consumed was determined to be 13.02 mL for **1** (4.158×10^{-4} mol of Br_2 for 1.460×10^{-4} mol of **1**, mole ratio, 2.86:1) and 13.56 mL for **2** (4.331×10^{-4} mol of Br_2 for 1.526×10^{-4} mol of **2**, mole ratio, 2.83:1). These results show that all three tin(II) atoms in **2** and **3** are oxidized to tin(IV). Tungsten-183 NMR spectra of all the oxidized compounds showed two lines (oxidized **1**: −129.4 ppm (1), −201.4 ppm (2); oxidized **2**: −135 ppm (1), −199 ppm (2); oxidized **3**: −104 ppm (1), −222 ppm (2)). According to their ^{183}W chemical shift patterns, the oxidized **1**, **2**, and **3** maintained their respective α or β structures.[4l,9] Their structures are presumed to be analogous to those of $[(RSnOH)_3(\alpha\text{- or }\beta\text{-}XW_9O_{34})_2]^{n-}$ with two eclipsed XW_9 units and the R^- group replaced by OH^-.[4l,9]

Conclusions

The structures of the new heteropolyanions $[Sn^{II}_3(XW_9O_{34})_2]^{n-}$ (X = P, Si) are shown to be chiral as a result of the stereochemical demand of Sn^{II}. Although relatively facile racemization can occur via the twisting process described above, interactions with the chiral amino acids lysine, histidine, and isoleucine lead to W-NMR line splitting. These results indicate diastereotopic recognition, which should prove to be important in both catalytic and biological activity of polyoxometalates. Further investigation is in progress.

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Supporting Information Available: Complete tables of crystal data, atomic coordinates, bond lengths and angles, and thermal parameters for **1** and **2** and heavy atom coordinates and figure for anion **3** (11 pages). See any current masthead page for ordering and Internet access instructions.

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