Polyoxoanions Derived from A-β-$SiW_9O_{34}^{10-}$: Synthesis, Single-Crystal Structural Determination, and Solution Structural Characterization by ^{183}W NMR and IR of A-β-$Si_2W_{18}Ti_6O_{77}^{14-}$

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The previously unknown polyoxometalate A-β-$Si_2W_{18}Ti_6O_{77}^{14-}$ has been prepared by the reaction of A-β-$HSiW_9O_{34}^{9-}$ with $Ti(O)(C_2O_4)_2^{2-}$ or $Ti(O)SO_4$ under controlled pH conditions; yield optimization experiments are also reported. Isolation of this new Ti^{IV}-substituted polyoxometalate was accomplished both as its water-soluble K^+ salt and as its organic-solvent-soluble Bu_4N^+ salt. The unambiguous characterization of A-β-$Si_2W_{18}Ti_6O_{77}^{14-}$ was accomplished by means of elemental analysis, IR and ^{183}W NMR spectroscopy, and a single-crystal X-ray structural analysis of the Bu_4N^+/H^+ salt, $(Bu_4N)_7H_7Si_2W_{18}Ti_6O_{77}$ (*Pbcm*; a = 19.958(11), b = 36.880(8), c = 28.936(5) Å; Z = 4; R = 0.072 for 4614 observed independent reflections). The X-ray diffraction structural analysis reveals that the correct structural formulation is A-β-$(SiW_9O_{37})_2(Ti\text{-}O\text{-}Ti)_3^{14-}$, a condensed aggregate of two hypothetical "A-β-$SiW_9(TiOH)_3O_{37}^{7-}$" Keggin units that have lost three H_2O by forming three Ti–O–Ti bridges. The present synthesis and characterization, plus recent results from the literature, reveal that a new subclass of polyoxoanions of general formula $X_2M_{18}M'_6O_{77}^{n-}$ can be prepared for M′ in at least three different oxidation states, M′(III), M′(IV), and M′(V).

Polyoxoanions are a broad class of compounds that are of considerable current interest, from both fundamental and practical points of view.[1-3] Especially important presently are the synthesis and characterization of new polyoxoanion compositions and structural types, as only a small percentage of the possible polyoxometalates have been prepared to date.[1]

Several years ago, we initiated a program aimed at the synthesis and characterization of a series of Keggin-type, $PM_{12}O_{40}^{n-}$, and Wells–Dawson-type, $P_2W_{18}O_{62}^{6-}$, polyoxoanions that were trisubstituted[4-6] with lower-valent metals such as M = Nb^V, Zr^{IV}, Ti^{IV} and thus of general formulas $SiW_9M_3O_{40}^{n-}$ and $P_2W_{15}M_3O_{62}^{m-}$. We reasoned that such new polyoxometalates would be important in their own right and might also serve as novel soluble-oxide catalyst-support systems. Over the intervening decade, this latter goal has been realized,[4,7] with polyoxoanions such as $SiW_9Nb_3O_{40}^{7-}$ and $P_2W_{15}Nb_3O_{62}^{9-}$ having been synthesized and successfully utilized as oxide-support materials.[2,8] The first example of polyoxoanion-supported catalysis, based on these high-symmetry, high-basicity, and custom-designed trisubstituted polyoxoanions, is also now available as reported elsewhere.[9]

Attempts to replace W^{VI} in the Keggin or Wells–Dawson structures with increasingly lower-valent metals such as Zr^{IV} or Ti^{IV} can be problematic, yielding surprises in the resultant product's composition or structure.[10] A case in point here is the Zr^{IV}-containing, crystallographically characterized [(A-β-$SiW_9O_{34})_2(ZrOH)_3]^{11-}$ in which only 1.5 Zr^{IV}, and not the anticipated 3.0 Zr^{IV}, can be added per each $SiW_9O_{34}^{10-}$ lacunary anion.[11] A second case in point is provided by the attempts to prepare the still unknown tri-Zn^{2+}-substituted Keggin "$SiW_9[Zn(OH_2)]_3O_{37}^{10-}$" or Wells–Dawson "$P_2W_{15}[Zn(OH_2)]_3O_{59}^{12-}$" polyoxoanions; efforts by both our and a separate research group have to date been unsuccessful.[11b,c] These attempted syntheses

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(10) For this reason, Pope and co-worker's recent report of A-α- and A-β-$SiW_9M_3(H_2O)_3O_{37}^{n-}$ [M = Al^{III}, Ga^{III}, Cr^{III}, Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, and Cu^{II} (but not Zn^{2+})[11c]] is noteworthy: Liu, J.; Ortéga, F.; Sethuraman, P.; Katsoulis, D. E.; Costello, C. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **1992**, 1901.

(11) (a) Finke, R. G.; Rapko, B.; Weakley, T. J. R. *Inorg. Chem.* **1989**, *28*, 1573. (b) Another case in point is our finding (see Pope's related work[11c]) that attempts to trisubstitute either $PW_9O_{34}^{9-}$ or $P_2W_{15}O_{56}^{12-}$ with Zn^{2+} leads to only di-Zn^{2+}-substituted dimers, $P_2W_{18}Zn_4O_{68}^{10-}$ and $P_4W_{30}Zn_4O_{112}^{16-}$: Finke, R. G; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886 and references therein. (c) Pope and co-workers find similarly that they cannot tri-Zn^{2+}-substitute $SiW_9O_{34}^{10-}$ (see ref 10).

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provide another example demonstrating that the synthesis of lower-valent-metal trisubstituted Keggin or Wells–Dawson polyoxoanions can be problematic.

Metal ionic-size considerations are always crucial, but in the case of Ti^{IV} they suggest the ready replacement of W^{VI} (the ionic radius of Ti^{IV} of 0.745 Å is very close to that of W^{VI}, 0.74 Å[12]). Consistent with this, several *mono*- and *di*-titanium-substituted Keggin polyoxoanions[13] have been reported in the literature, notably $PW_{11}(TiCp)O_{39}^{4-}$,[14] $PW_{11}TiO_{40}^{5-}$,[15] and $PW_{10}Ti_2O_{40}^{7-}$.[16] However, neither tri- or higher Ti^{IV}-substituted polyoxoanions nor an X-ray crystallographic structural investigation of the A-β-$X_2M_{18}M'_6O_{77}^{n-}$ structural type had been reported until our disclosure of the present work.[17] The very recent report by Yamase and co-workers of a different composition, but structurally closely related, complex A-α-$Ge_2W_{18}Ti_6O_{77}^{14-}$ is, however, noteworthy in this context.[18]

Besides their fundamental significance as new types of polyoxometalates, titanium (and titanium–peroxo[19]) substituted polyoxoanions are also of interest as potential catalysts in photooxidations[20] and alkene epoxidations,[21] especially in light of recent findings employing Ti-containing zeolites[22] plus H_2O_2 as organic oxidation catalysts. Titanium-substituted polyoxometalates have also been explored as antiviral agents by Yamase and co-workers.[23]

Herein, we report the synthesis and unequivocal characterization of A-β-$Si_2W_{18}Ti_6O_{77}^{14-}$. A single-crystal X-ray crystallographic structural analysis reveals that two A-β-$SiW_9Ti_3O_{40}^{10-}$ Keggin units have been fused via three Ti–O–Ti bridging oxygens to yield $[SiW_9O_{37})_2(Ti–O–Ti)_3]^{14-}$ (the other three O^{2-} are lost as H_2O following the addition of 6 H^+). As such, $Si_2W_{18}Ti_6O_{77}^{14-}$ is only the second structurally characterized example (and only the third member) of the little studied subclass[7a,17,18] of A-$X_2M_{18}M'_6O_{77}^{n-}$ type polyoxometalates.

Experimental Section

Materials. All compounds were of reagent grade and were used as received unless indicated otherwise: $K_2Ti(O)(C_2O_4)_2 \cdot 2H_2O$ (Alfa; it was recrystallized before use from a 1% aqueous solution of $K_2C_2O_4$); $Ti(O)(SO_4) \cdot 0.6H_2SO_4 \cdot 1.2H_2O$ (Aldrich; Lot No. 10521KX), Na_2WO_4 (Spectrum); Bu_4NBr (Fluka); KCl, $LiClO_4$, Me_2SO, CH_3CN (all from Baker); and Me_2SO-d_6 (Cambridge Isotope Laboratories). A-β-$Na_9HSiW_9O_{34} \cdot 23H_2O$ was synthesized according to our procedure,[4] a slightly modified version of the original work of Hervé and Tézé,[24] and its purity was checked by IR spectroscopy in comparison to the literature.[4,24]

Instrumentation and Analytical Procedures. IR spectra were recorded as KBr disks using a Nicolet 5DX spectrometer. ^{183}W NMR spectra were obtained using 10-mm-o.d. sample tubes on a Nicolet NT 360 NMR at 21 °C unless otherwise noted. Chemical shifts are reported in parts per million with negative values upfield of the standard (saturated Na_2WO_4/D_2O). Spectral parameters include the following: pulse width = 70 μs; acquisition time = 819.4 ms; delay time = 1 s; sweep width = ±2500 Hz; and a 1-Hz exponential apodization of the FID. (This added line-broadening has been removed from any line widths reported.) Solution molecular weights were measured by the ultracentrifuge sedimentation–equilibrium method.[4,25] Thermal gravimetric analysis (TGA) was performed using a Du Pont Instruments 951 thermogravimetric analyzer interfaced to a computer. Elemental analyses were obtained from Mikroanalytisches Labor Pascher, Remagen, Germany.

Preparation of $K_{12}H_2Si_2W_{18}Ti_6O_{77} \cdot 25H_2O$. Nine grams (25.0 mmol) of $K_2Ti(O)(C_2O_4)_2 \cdot 2H_2O$ was dissolved in 400 mL of water in a beaker to give a clear, pH 4.0 solution. Next, 14 mL of 6 M HCl was added, yielding a pH of 0.7. To the rapidly stirred solution 24.0 g (8.4 mmol) of A-β-$Na_9HSiW_9O_{34} \cdot 23H_2O$, was added slowly in small portions and the reaction mixture was stirred for an additional 15 min (the resultant pH was 1.4). The crude product was precipitated by the addition of excess (40 g, 53.6 mmol) KCl and collected on a glass frit. Recrystallization from hot H_2O followed by drying in the air overnight gave 2 g (8.1%) of pure crystalline material. (The low yield is partially due to the high solubility of the K^+ salt, which cannot be fully recovered by KCl precipitation since, along with the desired $K_{12}H_2Si_2W_{18}Ti_6O_{77}$ crystals, large amounts of $K_2Ti(O)(C_2O_4)_2$ crystals form from the K^+-saturated reaction solution after several hours.)

Anal. Calcd for $K_{12}H_2Si_2W_{18}Ti_6O_{77} \cdot 25H_2O$: Si, 0.97; W, 56.99; Ti, 4.95; K, 8.08; H, 0.90; O, 28.11; total, 100.0 . Found: Si, 0.94; W, 57.0; Ti, 4.83; K, 7.79; H, 0.95; O, 27.4; total, 98.9. TGA (up to 250 °C): calcd for 25 H_2O, 7.75%; found, 7.18%. IR (cm^{-1}, KBr disk, polyoxoanion region): 997 (m), 955(m), 899 (s), 800–720(s, br). ^{183}W NMR (0.1 M in D_2O, pH 3.2, as the Li^+ salt following metathesis with excess $LiClO_4$ and removal of the insoluble $KClO_4$): -131.3 (6W, $\Delta\nu_{1/2} = 1.0 \pm 0.1$ Hz), -145.8 ppm (12W, $\Delta\nu_{1/2} = 1.2 \pm 0.1$ Hz); $^2J_{W-O-W} = 15.5$ Hz. Ultracentrifugation solution molecular weight determination (1×10^{-5} M in 0.1 M $LiCl/H_2O$; pH 3.1; partial molar volume 0.2 $cm^3 \cdot g^{-1}$): calcd for $Si_2W_{18}Ti_6O_{77}^{14-}$, 4885; found, 4500 ± 500.

Preparation of $(Bu_4N)_{7.5}H_{6.5}Si_2W_{18}Ti_6O_{77}$. Nine grams (25.0 mmol) of $K_2Ti(O)(C_2O_4)_2 \cdot 2H_2O$ was dissolved in 400 mL of water to give a clear, pH 4.0 solution. To the rapidly stirred solution was added slowly in small portions 24.0 g (8.4 mmol) of A-β-$Na_9HSiW_9O_{34} \cdot 23H_2O$. The reaction mixture was stirred for an additional 15 min (the resultant pH was 4.6), and the crude product was precipitated by addition of excess (56 g, 173.6 mmol) Bu_4NBr. The precipitate was collected on a medium frit, washed with H_2O (ca. 1000 mL), and dried at 50 °C to yield 3 g of white solid. Recrystallization was achieved by vapor diffusion of acetone into a near-saturated CH_3CN solution of the crude product. Several days later, colorless crystals were collected on a glass frit and dried at 50 °C under vacuum overnight, to give 5–6 g (17–21%) of pure material.

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Anal. Calcd for $(Bu_4N)_{7.5}H_{6.5}Si_2W_{18}Ti_6O_{77}$: C, 21.48; H, 4.06; N, 1.57; Si, 0.84; W, 49.32; Ti, 4.28; O, 18.36; total, 100.0. Found: C, 21.72; H, 4.24; N, 1.74; Si, 0.88; W, 49.5; Ti, 4.05; O, 18.0; total, 100.1.TGA showed the absence of lattice solvent in the vacuum-dried product. IR (cm^{-1}, KBr disk, polyoxoanion region): 997 (m), 963(m), 899 (s), 815(s), 702 (s, br). ^{183}W NMR (0.1 M in 1:1 Me_2SO-d_6/Me_2SO-d_0, 21 °C): −127.7 (6W, $\Delta\nu_{1/2} = 33.8 \pm 0.6$ Hz), −155.8 ppm (12W, $\Delta\nu_{1/2} = 40.0 \pm 0.5$ Hz). Such broad ^{183}W NMR peaks for basic polyoxoanions in "dry" solvents are well-understood and are due to slow proton-exchange (slow tautomerization) processes on the surface oxygens of the polyoxoanion.[4,26] Confirming this, the ^{183}W NMR peaks sharpened either following the diagnostic[4] addition of small amounts of water or in spectra collected at higher temperature as detailed below. ^{183}W NMR (0.1 M in 1:1 Me_2SO-d_6/Me_2SO-d_0, with the addition of three drops of H_2O, 21 °C): −123.1 ($\Delta\nu_{1/2} = 22.0 \pm 0.4$ Hz), −151.0 ppm ($\Delta\nu_{1/2} = 21.5 \pm 0.5$ Hz). ^{183}W NMR (the same "dry" sample run above at 21 °C except now at 50 °C): −120.3 ppm ($\Delta\nu_{1/2} = 22.9 \pm 0.5$ Hz), −148.1 ppm ($\Delta\nu_{1/2} = 23.7 \pm 0.4$ Hz). Ultracentrifugation solution molecular weight determination (1×10^{-5} M in 0.1 M Bu_4NPF_6/CH_3CN; partial molar volume 0.35 cm^3·g^{-1}): calcd for $(Bu_4N)_2Si_2W_{18}Ti_6O_{77}^{12-}$, 5369; found, 5300 ± 500.

Yield Optimization Experiments. In a series of five experiments designed to improve the modest ≤21% yield of the above syntheses of $Si_2W_{18}Ti_6O_{77}^{14-}$, the yield was determined as a function of the following three variables: the pH, the amount of TiO^{2+} (i.e. relative to $SiW_9O_{34}^{10-}$), and the Ti^{IV} source [$K_2Ti(O)(C_2O_4)_2$ or $Ti(O)(SO_4)$]. The details of these five experiments are reported in the supplementary materials, along with a table and additional discussion of the results. Only experiment V, the most successful of the five experiments which resulted in a doubling of the yield to ca. 41%, is detailed below.

In experiment V, $Ti(O)(SO_4)\cdot0.6H_2SO_4\cdot1.2H_2O$ was used instead of $K_2Ti(O)(C_2O_4)_2$. Thus, 3.5 g of $Ti(O)(SO_4)\cdot0.6H_2SO_4\cdot1.2H_2O$ (14.5 mmol; 6.9 equiv vs $SiW_9O_{34}^{10-}$) was dissolved in 100 mL of water by stirring for 0.5 h at room temperature to give a slightly turbid, pH 1.0 solution. (Heating should be avoided as, otherwise, a precipitate forms.) To this solution was added slowly in small portions 6.0 g (2.1 mmol) of A-β-$Na_9HSiW_9O_{34}\cdot23H_2O$, and the reaction mixture was stirred for an additional 20 min. Next, 10 g (134 mmol) of KCl was added, the precipitate was collected on a frit, and the clear filtrate was placed in a refrigerator overnight, from which needlelike crystals were formed and collected the next morning (1.8 g, after air drying). The precipitate was recrystallized to give 0.7 g of crystalline material, for a total yield of 2.5 g (41%). The purity of the both crops was checked by both IR and ^{183}W NMR spectroscopy. It is worth noting that the mixed K^+/H^+ salt is quite soluble in water and, therefore, it is probable that the yield can be improved further if desired (e.g. by the use of less solvent or different or mixed countercations).

X-ray Structural Analysis (Tetrabutylammonium Salt). Colorless tablet-shaped crystals up to 0.5 mm in length were grown from an acetonitrile/acetone mixture, manipulated under Apiezon grease (to prevent loss of solvent of crystallization), and sealed in glass capillaries. The diffraction profiles of the majority of crystals examined on the Rigaku AFC6R diffractometer were broad and weak and exhibited high backgrounds. Eventually, an adequate crystal with approximate dimensions 0.20 × 0.25 × 0.30 mm^3 was obtained which exhibited sharp, although still weak, diffraction peaks. The orientation matrix and cell dimensions were obtained from the setting angles of 25 centered reflections in the 2θ range 10.7–13.3°. Measurement of the intensities of reflections equivalent to these 25 confirmed that the Laue symmetry was *mmm*. A summary of crystal data including the final residuals is given in Table I. A complete table provided in the supplementary material contains details of the data collection and structure refinement. The incidence of observed reflections [$I \geq 3\sigma(I)$] fell from *ca.* 85% at low θ to *ca.* 15% near $\theta = 40°$, at which point data collection was halted. Altogether, 4614 (43%) out of 10 846 independent reflections were observed.

The systematic absences and centric distribution of intensities gave the space group unambiguously as *Pbcm*. An *E* map (SHELXS[27]) showed the 10 independent W atoms as the 10 strongest peaks, with weaker indications of the Ti and Si atoms. The oxygen atoms were located from difference syntheses. An empirical absorption correction (DIFABS[28]) based on the isotropically-refined structure was applied. Subsequently the W and Ti atoms were refined anisotropically. A difference synthesis at $R = 0.085$ then clearly showed fragments of five independent cations, a total of seven per anion. Attempts to refine the carbon and nitrogen atoms, with various combinations of site occupancy factors, lowered the residual ($R = 0.072$, $N/V = 4614/409$) but also led to several very large thermal parameters and to many improbably long or short C–C and C–N bonds. Accordingly, the C and N atoms were constrained at their original positions with *B* values arbitrarily set at 6 Å^2 for N and 8, 10, 12, and 14 Å^2 for α, β, γ, and δ C atoms, respectively. The same residual, $R = 0.072$ ($N/V = 4614/290$), was attained as when no constraints were applied. The final difference synthesis showed peaks of up to 1.6 e Å^{-3} in the interanion voids; these may have represented atoms of other, disordered cations or of solvent molecules, but the inclusion of these in the model seemed unlikely to improve the resolution of the structure of the anion, the matter of greatest interest. The TEXSAN-program suite,[29] incorporating standard atomic scattering factors,[30] was used in all calculations.

Table I. Crystallographic Data

compn	$C_{112}H_{259}N_7O_{77}Si_2Ti_6W_{18}$	d_{calc}	2.093 g cm^{-3}
fw	6589.2	*T*	25 °C
space group	*Pbcm*	λ	0.710 69 Å
a	19.958(11) Å	μ	101.9 cm^{-1}
b	36.880(8) Å	rel transm coefft	0.32–1.00 (ψ)
c	28.936(5) Å	No. of obsd rflns	4614 [$I \geq 3\sigma(I)$]
V	21298(20) Å^3	$R(F)^a$	0.072
Z	4	$R_w(F)^b$	0.095

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Results and Discussions

Synthesis. The reaction of A-β-$HSiW_9O_{34}^{9-}$ with the $Ti(O)^{2+}$ sources $Ti(O)(C_2O_4)_2^{2-}$ or $Ti(O)SO_4$ at pH *ca.* 1–4 provides the new Ti^{IV}-substituted polyoxometalate $Si_2W_{18}Ti_6O_{77}^{14-}$, which can be readily isolated in pure form as either its water-soluble K^+ salt or its organic-solvent-soluble Bu_4N^+ salt. In the case of the Bu_4N^+ salt, the analysis best fits a $(Bu_4N)_{7.5}H_{6.5}Si_2W_{18}Ti_6O_{77}$ fractional-cation formulation (these are common in our experience[3a,4,31] and reflect, presumably, a 1:1 mixture of the $(Bu_4N)_8H_6^{14+}$ and $(Bu_4N)_7H_7^{14+}$ salts).

Although the initial synthesis provides adequate amounts of material for most studies, optimization experiments were undertaken to improve the initial ≤21% yield. Since virtually nothing is known in detail about the mechanisms of formation of such polyoxoanions (other than they can be viewed as a series of 2 M–OH to M–O–M + H_2O condensation reactions; see the further mechanistic discussion presented later in eqs 1–3), one is left to "intuitive prospecting" to try to improve such polyoxoanion syntheses. In the present case, the most obvious variables were changed in a series of five experiments designed to improve the yield; specifically, the reaction pH, the quantity of TiO^{2+} relative to $SiW_9O_{34}^{10-}$, and the TiO^{2+} source of each were varied. The most successful of these five experiments, the use of a 2-fold excess (i.e. over the stoichiometrically required 3.0 equiv) of $Ti(O)SO_4$ as the TiO^{2+} source, followed by isolation of the mixed $K_{12}H_2^{14+}$ salt of $Si_2W_{18}Ti_6O_{77}^{14-}$, resulted in a 41% yield, a more than 2-fold increase in the yield. (Details of these experiments,

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(26) Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 2991.

(27) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R. Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175–189.

(28) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(29) *TEXSAN: Texray Program for Structure Analysis*, version 5.0; Molecular Structure Corp.: 3200A Research Forest Dr., The Woodlands, TX 77381, 1989.

(30) Cromer, D. T.; Waber, J. T. In *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 71, 148.

(31) (a) Weakley, T. J. R.; Finke, R. G. *Inorg. Chem.* **1990**, *29*, 1235. (b) If desired, a single cation composition can probably be prepared by Droege's procedure[7a,46] for preparing $(Bu_4N)_6H_2$[A-β-$Si_2W_{18}Nb_6O_{77}$] (i.e. by adding an aqueous acid solution such as aqueous HCl to an acetonitrile solution of the mixed salt $(Bu_4N)_{7.5}H_{6.5}Si_2W_{18}Ti_6O_{77}$ to reprecipitate it, followed by recrystallization to yield the $(Bu_4N)_{7-x}H_{7+x}^{14+}$ salt, where *x* would depend upon the pK_a of the acid used).

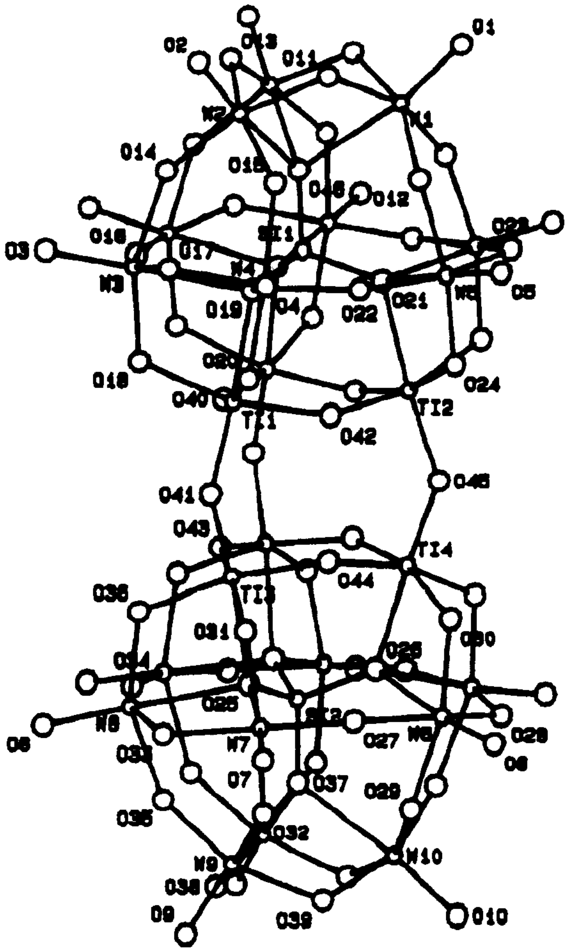

Figure 1. Structure of A-β-$Si_2W_{18}Ti_6O_{77}^{14-}$.

a table of conditions and yields, and additional discussion of the results are available as supplementary material.)

X-ray Single-Crystal Structure Analysis of the Bu_4N^+ Salt. The structure and a stereoview of $Si_2W_{18}Ti_6O_{77}^{14-}$ are shown in Figures 1 and 2, respectively. The anion contains two "$SiW_9Ti_3O_{40}$" Keggin anion halves linked via three Ti–O–Ti bonds, with each half having the same A-β structure as the precursor, A-β-$SiW_9O_{34}^{10-}$. As expected, the three TiO_6 octahedra in each "SiW_9Ti_3" Keggin unit replace the three corner-sharing WO_6 octahedra missing from the trivacant lacunary precursor ion, A-β-$SiW_9O_{34}^{10-}$ (i.e. missing in relation to A-β-$SiW_{12}O_{40}^{4-}$). Atomic coordinates are given in Table II, and derived bond lengths for the anion are given in Table III. Although the resolution obtained for the structure of the salt has been limited by the poor quality of the available crystals (even after more than a dozen trials to obtain better crystals) and by the considerable disorder of the cations and the solvent of crystallization (features all too common in polyoxoanion crystallography[32]), the main features of the structure of the anion are fortunately still quite clear. Bond lengths around Ti (esd 0.03–0.05 Å): Ti–O–Ti (between monomer units) 1.79–1.83, average 1.81 Å; other Ti–O–Ti 1.90–1.98, average 1.94 Å; Ti–O (W), 1.82–2.02, average 1.93 Å; Ti–O (Si, W) 2.12–2.24, average 2.21 Å; see also Table III. The corresponding bond valences[33] at the Ti atoms, based on averaged bond lengths: 1.00(8), 0.71(6) (twice), 0.73 (6) (twice), and 0.34(3), summing to 4.2(2) (note that the calculated bond valences for the shorter bonds are particularly sensitive to errors in bond length). The Ti–O–Ti angles between β-Keggin units are all 141(3)° (supplementary material, Table D). Overall, the general structure of A-β-$Si_2W_{18}Ti_6O_{77}^{14-}$ is quite similar (but not identical[34]) to that which Yamase recently reported for A-α-$Ge_2W_{18}Ti_6O_{77}^{14-}$.[18]

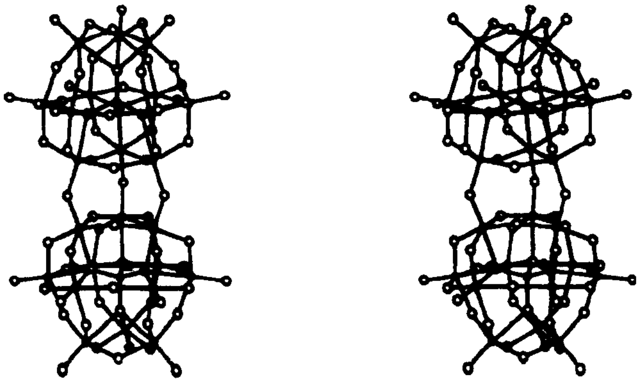

Figure 2. Stereoview of A-β-$Si_2W_{18}Ti_6O_{77}^{14-}$.

The structure of A-β-$Si_2W_{18}Ti_6O_{77}^{14-}$ provides an interesting contrast with that of A-β-$Si_2W_{18}Zr_3O_{71}^{14-}$, in which the larger Zr atoms, in capped trigonal-prismatic (6 + 2) coordination, are symmetrically shared between the two SiW_9 units.[11a] The W···W distances in $Si_2W_{18}Ti_6O_{77}^{14-}$ (Table IV) are similar to corresponding distances in $Si_2W_{18}Zr_3O_{71}^{14-}$. The crystallographically determined structure for $Si_2W_{18}Ti_6O_{77}^{14-}$ is the same as that deduced,[7a,35] on the basis of synthesis and ^{183}W NMR, IR, and FAB-MS spectra (and in the absence of suitably diffracting single crystals[36]), for $Si_2W_{18}Nb_6O_{77}^{8-}$, the first member of the $X_2M_{18}M'_6O_{77}^{n-}$ series of polyoxometalates.

Structural Characterization of $Si_2W_{18}Ti_6O_{77}^{8-}$ in Solution. Ultracentrifugation solution molecular weight measurements, of both the K^+ salt in aqueous solution and the Bu_4N^+ salt in CH_3CN solution, indicate that the $Si_2W_{18}Ti_6O_{77}^{14-}$ structure is retained in both aqueous and nonaqueous solutions. The ^{183}W NMR spectrum of $Si_2W_{18}Ti_6O_{77}^{14-}$ in aqueous solution (Figure 3), gives two clean peaks with relative intensity of 1:2 and $^2J_{W-O-W}$ of 15.5 Hz, indicating that the A-type[37] structure of the $SiW_9O_{34}^{7-}$ starting material is fully retained in solution. It is interesting to note that the peak pattern of the ^{183}W NMR spectrum (i.e. the fact that the six belt tungstens appear *upfield* of the three cap tungstens) is the same as that of $Si_2W_{18}Zr_3O_{71}^{14-}$ [11a] and $Si_2W_{18}Nb_6O_{77}^{8-}$ [7a] but the opposite of that of Yamases[18] $Ge_2W_{18}Ti_6O_{77}^{14-}$ or Pope's[10] $SiW_9[M(H_2O)]_3O_{37}^{n-}$ (i.e. where the six belt tungstens now appear *downfield* of the three cap tungstens). However, a careful examination of the available trisubstituted polyoxoanion (and relevant reference polyoxoanion) ^{183}W NMR chemical shift data

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(32) A more detailed discussion of the general problem of disordered cations and solvent molecules in crystals of heteropolyanion salts is available elsewhere for the interested reader.[31a]

(33) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.

(34) In particular, the six Ti atoms in A-α-$Ge_2W_{18}Ti_6O_{77}^{14-}$ play the same structural role (bridging Ti–O–Ti) and have the same distorted-octahedral coordination geometry[18] as in A-β-$Si_2W_{18}Ti_6O_{77}^{14-}$. One difference between the two structures is that the Ti–O–Ti angles between the two Keggin anion halves are slightly larger in A-β-$Si_2W_{18}Ti_6O_{77}^{14-}$ [all are 141(3)° compared with 132–136 (2)° in A-α-$Ge_2W_{18}Ti_6O_{77}^{14-}$]. Other small differences in corresponding dimensions are ascribable to the smaller size of Si compared with Ge and to the different orientation (α vs β) of the W_3 cap.

(35) Suslick, K. S.; Cook, J. C.; Rapko, B.; Droege, M. W.; Finke, R. G. *Inorg. Chem.* **1986**, *25*, 241.

(36) Crystals of $(Bu_4N)_6H_2[Si_2W_{18}Nb_6O_{77}]$, grown by vapor diffusion or slow cooling from various combinations of Me_2SO or MeCN and the less polar 1,2-dihydroxyethane or toluene, were sealed in capillaries and examined on the diffractometer but never proved suitable for data collection. In general, their diffraction peaks were broad and weak with high backgrounds and exhibited a marked decrease in average intensity at higher scattering angles. The crystal system and the unit cells proved sensitive to the conditions of crystallization: the largest unit cell was 42 000 Å^3, at least when one could be obtained from 25 reflections located by the diffractometer. One crystal from a MeCN/toluene mixture was orthorhombic, with a = 20.217(6) Å, b = 36.696(6) Å, c = 28.297(8) Å, and V = 20993 Å^3, and thus possibly isomorphous with the present compound.

(37) Lefebvre, J.; Chauveau, F.; Doppelt, P. *J. Am. Chem. Soc.* **1981**, *103*, 4589.

Table II. Atomic Coordinates and Isotropic (Si, O, C, N) or Equivalent Isotropic (W, Ti) Thermal Parameters (Å^2) (Parameters for Carbon and Nitrogen Atoms Not Refined)

atom	x	y	z	B_{eq}[a]
W(1)	0.58261(20)	0.31353(11)	0.25000	4.4(3)
W(2)	0.47688(15)	0.25988(7)	0.19211(12)	4.6(2)
W(3)	0.29736(14)	0.28195(7)	0.18464(11)	4.0(2)
W(4)	0.40230(14)	0.33577(7)	0.12744(10)	3.6(2)
W(5)	0.51996(12)	0.39705(7)	0.19265(10)	3.3(2)
W(6)	0.22014(13)	0.56628(6)	0.19268(10)	3.0(1)
W(7)	0.10228(14)	0.50536(7)	0.12762(10)	3.2(2)
W(8)	–0.00097(13)	0.45081(7)	0.18491(10)	3.3(2)
W(9)	–0.03466(14)	0.54910(8)	0.19204(12)	4.7(2)
W(10)	0.07013(22)	0.60388(11)	0.25000	4.3(3)
Ti(1)	0.2788(4)	0.3704(2)	0.1850(03)	1.1(5)
Ti(2)	0.3928(6)	0.4293(3)	0.2500	1.6(8)
Ti(3)	0.1606(4)	0.4374(2)	0.1851(03)	0.9(5)
Ti(4)	0.2743(6)	0.4966(3)	0.2500	1.1(7)
Si(1)	0.4093(13)	0.3363(7)	0.2500	3.3(6)
Si(2)	0.1048(13)	0.5082(7)	0.2500	3.5(7)
O(1)	0.6680(33)	0.3120(17)	0.2500	7.5(20)
O(2)	0.4952(22)	0.2245(11)	0.1560(16)	6.8(13)
O(3)	0.2501(17)	0.2440(10)	0.1669(13)	3.8(10)
O(4)	0.4247(20)	0.3361(10)	0.0684(15)	5.1(11)
O(5)	0.5770(19)	0.4154(10)	0.1532(14)	4.7(10)
O(6)	0.2554(20)	0.5953(10)	0.1522(15)	5.6(12)
O(7)	0.1031(17)	0.5188(9)	0.0711(13)	3.5(9)
O(8)	–0.0707(19)	0.4271(10)	0.1659(14)	4.4(10)
O(9)	–0.1013(21)	0.5593(11)	0.1537(16)	6.1(12)
O(10)	0.0758(26)	0.6498(14)	0.2500	4.2(14)
O(11)	0.5647(18)	0.2766(9)	0.2025(14)	4.3(10)
O(12)	0.5616(18)	0.3504(19)	0.2012(13)	4.2(10)
O(13)	0.4872(26)	0.2350(14)	0.2500	4.1(14)
O(14)	0.3821(17)	0.2562(9)	0.1970(13)	3.9(9)
O(15)	0.4707(19)	0.2996(10)	0.1507(14)	4.6(10)
O(16)	0.2834(25)	0.2787(13)	0.2500	3.3(13)
O(17)	0.3437(16)	0.2950(8)	0.1259(12)	2.7(8)
O(18)	0.2393(16)	0.3210(9)	0.1789(12)	2.9(9)
O(19)	0.3632(15)	0.3336(8)	0.2024(11)	1.6(7)
O(20)	0.3268(17)	0.3668(9)	0.1281(13)	3.8(9)
O(21)	0.4482(23)	0.3767(12)	0.2500	2.4(12)
O(22)	0.4621(18)	0.3715(9)	0.1502(13)	3.6(10)
O(23)	0.5639(25)	0.4101(13)	0.2500	3.1(13)
O(24)	0.4622(15)	0.4352(8)	0.1998(12)	2.2(8)
O(25)	0.0955(14)	0.4849(7)	0.2033(11)	1.4(7)
O(26)	0.1823(19)	0.5251(10)	0.2500	0.1(9)
O(27)	0.1677(19)	0.5365(10)	0.1502(15)	4.9(11)
O(28)	0.2441(25)	0.5875(13)	0.2500	3.2(13)
O(29)	0.1311(17)	0.5915(9)	0.2025(13)	3.5(9)
O(30)	0.2875(16)	0.5321(8)	0.2030(12)	2.6(8)
O(31)	0.1536(17)	0.4633(9)	0.1318(13)	3.2(9)
O(32)	0.0389(19)	0.5402(10)	0.1485(14)	4.7(11)
O(33)	0.0267(16)	0.4733(9)	0.1256(12)	2.9(9)
O(34)	–0.0090(26)	0.4441(14)	0.2500	4.3(14)
O(35)	–0.0430(17)	0.4992(9)	0.1967(13)	3.4(9)
O(36)	0.0723(15)	0.4179(8)	0.1757(11)	1.8(8)
O(37)	0.0491(23)	0.5410(12)	0.2500	2.3(12)
O(38)	–0.0830(27)	0.5525(14)	0.2500	4.4(15)
O(39)	0.0043(20)	0.5959(11)	0.2023(15)	6.0(12)
O(40)	0.2504(21)	0.3665(11)	0.2500	1.3(11)
O(41)	0.2066(16)	0.3980(9)	0.1678(12)	2.8(9)
O(42)	0.3359(16)	0.4106(9)	0.2030(13)	3.2(9)
O(43)	0.1480(21)	0.4222(11)	0.2500	1.3(111)
O(44)	0.2358(15)	0.4664(8)	0.2040(11)	1.7(8)
O(45)	0.3547(26)	0.4745(13)	0.2500	3.7(14)
O(46)	0.4612(27)	0.3034(14)	0.2500	4.0(14)
N(1)	0.4717	0.2500	0.5000	6.0
N(2)	0.3676	0.0122	0.5723	6.0
N(3)	0.7792	0.0991	0.7500	6.0
N(4)	0.6849	0.1874	0.2500	8.0
N(5)[b]	0.2394	0.1755	0.2500	8.0
N(6)[b]	1.0007	0.0705	0.5114	6.0
C(1)	0.4310	0.2402	0.4584	8.0
C(2)	0.4130	0.2093	0.4661	10.0
C(3)	0.3558	0.1926	0.4245	12.0
C(4)	0.5145	0.2327	0.5125	8.0
C(5)	0.5672	0.2198	0.5385	10.0
C(6)	0.6018	0.1865	0.5663	12.0
C(7)	0.3197	0.0446	0.5790	8.0
C(8)	0.2875	0.0623	0.5351	10.0
C(9)	0.2351	0.0871	0.5418	12.0
C(10)	0.2243	0.1146	0.5017	14.0
C(11)	0.3966	0.0067	0.6248	8.0
C(12)	0.4475	–0.0135	0.6360	10.0
C(13)	0.4569	–0.0323	0.6749	12.0
C(14)	0.5253	–0.0404	0.6850	14.0
C(15)	0.4274	0.0309	0.5559	8.0
C(16)	0.4704	0.0666	0.5703	10.0
C(17)	0.5179	0.0789	0.5254	12.0
C(18)	0.3444	–0.0150	0.5550	8.0
C(19)	0.2844	–0.0405	0.5651	10.0
C(20)	0.2708	–0.0664	0.5352	12.0
C(21)	0.2160	–0.0929	0.5385	14.0
C(22)	0.7344	0.1062	0.6997	8.0
C(23)	0.7620	0.1006	0.6549	10.0
C(24)	0.8456	0.1169	0.7500	8.0
C(25)	0.8440	0.1570	0.7500	10.0
C(26)	0.8005	0.0572	0.7500	8.0
C(27)	0.7529	0.0338	0.7500	10.0
C(28)	0.7891	–0.0086	0.7500	12.0
C(29)	0.7442	–0.0330	0.7500	14.0
C(30)[b]	0.2935	0.1585	0.2500	8.0
C(31)[b]	0.1651	0.1356	0.2096	10.0
C(32)[b]	0.1767	0.1587	0.2500	8.0
C(33)[b]	0.1608	0.1485	0.2250	10.0
C(34)	0.3624	0.1612	0.2500	10.0
C(35)	0.1672	0.1836	0.2500	8.0
C(36)[b]	0.7631	0.1786	0.2500	8.0
C(37)[b]	0.7011	0.2256	0.2168	8.0
C(38)	1.0601	0.0575	0.4909	8.0
C(39)	1.0000	0.0989	0.5480	8.0
C(40)	0.9718	0.0842	0.4614	8.0

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$. [b] Site occupancy factor 0.5.

(supplementary material, Table B) fails to reveal an obvious structural or other reason for this (relatively small) peak-pattern difference.

The IR spectra of both the K$^+$ and Bu$_4$N$^+$ salts (Figure 4) show a new, strong band at 700 cm^{-1} (in addition to the expected bands typical of Keggin-type tungstosilicates[38] at ca. 1000, 950, 900, and 800 cm^{-1}). By comparison to $C_5H_5Cl_2Ti{-}O{-}TiCl_2C_5H_5$ (Ti–O–Ti, 720 cm^{-1})[39] and by analogy to the Nb analog $Si_2W_{18}Nb_6O_{77}^{8-}$ which has a Nb–O–Nb band at 690 cm^{-1},[7a] this new-700 cm^{-1} band is reasonably assigned to the Ti–O–Ti bonds linking the two "$SiW_9Ti_3O_{40}$" units.

Interestingly, an IR band at ca.700 cm^{-1} is also found by Pope and co-workers in A-β-$SiW_9M_3(H_2O)_3O_{37}^{n-}$(M = Mn^{III}, Ni^{III}, other metals[10]). These workers provided fast atom bombardment mass spectroscopy evidence suggestive of "small to modest" amounts of M–O–M linked "dimer" products.[10] (Polyoxoanion monomer vs dimer distinctions via FAB-MS can be misleading, however, due to dimer formation or cleavage during the FAB desorption process.[40]) Overall, both our and Pope's data suggest that a *strong* IR band[41] in the ~700-cm^{-1} range is one indicator that the $Si_2W_{18}M_6O_{77}^{n-}$ type structure may be present.

Plausible Mechanism of Formation of $Si_2W_{18}Ti_6O_{77}^{14-}$. The mechanisms of formation or degradation of polyoxometalates are a little studied subject, other than a few key papers by Kepert, Kyle, and co-workers.[42] Cation ion-pairing effects on the highly charged polyoxoanions are also generally important, a conclusion fully supported by Kepert's classic papers (all of which emphasize

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(38) (a) Thouvenot, R.; Fournier, M.; Franck, R.; Rocchiccioli-Deltcheff, C. *Inorg. Chem.* **1984**, *23*, 598. (b) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207.

(39) Giddings, S. A. *Inorg. Chem.* **1964**, *3*, 684.

(40) Trovarelli, A.; Finke, R. G. *Inorg. Chem.*, submitted for publication.

(41) In the case of the Co^{III} derivative $SiW_9Co_3O_{40}^{13-}$only a very weak 700-cm^{-1}band is detected and no dimer could be detected by FAB-MS.[10]

Table III. Bond Lengths in the Anion (Å)

W(1)–O(1)	1.71(7)	W(8)–O(25)	2.36(3)
W(1)–O(11)	1.97(4)	W(8)–O(33)	1.99(4)
W(1)–O(12)	2.00(4)	W(8)–O(34)	1.91(1)
W(1)–O(46)	2.45(5)	W(8)–O(35)	2.00(3)
W(2)–O(2)	1.71(4)	W(8)–O(36)	1.92(3)
W(2)–O(11)	1.88(4)	W(9)–O(9)	1.77(4)
W(2)–O(13)	1.92(2)	W(9)–O(32)	1.96(4)
W(2)–O(14)	1.90(3)	W(9)–O(35)	1.85(3)
W(2)–O(15)	1.90(4)	W(9)–O(37)	2.39(3)
W(2)–O(46)	2.34(4)	W(9)–O(38)	1.94(3)
W(3)–O(3)	1.76(4)	W(9)–O(39)	1.92(4)
W(3)–O(14)	1.97(3)	W(10)–O(10)	1.70(5)
W(3)–O(16)	1.92(1)	W(10)–O(29)	1.89(4)
W(3)–O(17)	1.99(3)	W(10)–O(37)	2.36(5)
W(3)–O(18)	1.86(3)	W(10)–O(39)	1.93(4)
W(3)–O(19)	2.37(3)	Ti(1)–O(18)	1.99(3)
W(4)–O(4)	1.77(4)	Ti(1)–O(19)	2.22(3)
W(4)–O(15)	2.02(4)	Ti(1)–O(20)	1.91(4)
W(4)–O(17)	1.91(3)	Ti(1)–O(40)	1.97(2)
W(4)–O(19)	2.31(3)	Ti(1)–O(41)	1.83(3)
W(4)–O(20)	1.89(3)	Ti(1)–O(42)	1.94(3)
W(4)–O(22)	1.90(4)	Ti(2)–O(21)	2.23(5)
W(5)–O(5)	1.75(4)	Ti(2)–O(24)	2.02(3)
W(5)–O(12)	1.93(3)	Ti(2)–O(42)	1.90(4)
W(5)–O(21)	2.32(3)	Ti(2)–O(45)	1.83(5)
W(5)–O(22)	1.93(4)	Ti(3)–O(25)	2.24(3)
W(5)–O(23)	1.94(3)	Ti(3)–O(31)	1.82(4)
W(5)–O(24)	1.83(3)	Ti(3)–O(36)	1.92(3)
W(6)–O(6)	1.74(4)	Ti(3)–O(41)	1.79(3)
W(6)–O(26)	2.37(3)	Ti(3)–O(43)	1.98(2)
W(6)–O(27)	1.95(4)	Ti(3)–O(44)	1.92(3)
W(6)–O(28)	1.90(2)	Ti(4)–O(26)	2.12(4)
W(6)–O(29)	2.03(3)	Ti(4)–O(30)	1.91(3)
W(6)–O(30)	1.87(3)	Ti(4)–O(44)	1.90(3)
W(7)–O(7)	1.71(4)	Ti(4)–O(45)	1.80(5)
W(7)–O(25)	2.32(3)	Si(1)–O(19)	1.66(3)
W(7)–O(27)	1.86(4)	Si(1)–O(21)	1.68(5)
W(7)–O(31)	1.86(3)	Si(1)–O(46)	1.59(5)
W(7)–O(32)	1.90(4)	Si(2)–O(25)	1.61(3)
W(7)–O(33)	1.92(3)	Si(2)–O(26)	1.67(4)
W(8)–O(8)	1.73(4)	Si(2)–O(37)	1.64(5)

Table IV. Distances between W, Ti, and Si Atoms (Å)[a]

W(1)···W(2)	3.343(5)	W(6)···W(6^{i})	3.317(6)
W(1)···W(5)	3.715(5)	W(6)···W(10)	3.693(5)
W(2)···W(2^{i})	3.350(7)	W(6)···W(7)	3.758(4)
W(2)···W(3)	3.680(4)	W(7)···W(8)	3.323(4)
W(2)···W(4)	3.681(4)	W(7)···W(9)	3.681(4)
W(3)···W(4)	3.327(4)	W(8)···W(9)	3.693(4)
W(3)···W(3^{i})	3.783(7)	W(8)···W(8^{i})	3.767(6)
W(4)···W(5)	3.766(4)	W(9)···W(9^{i})	3.354(7)
W(5)···W(5^{i})	3.319(6)	W(9)···W(10)	3.357(5)
W(3)···Ti(1)	3.283(9)	W(6)···Ti(4)	3.24(1)
W(4)···Ti(1)	3.238(9)	W(7)···Ti(3)	3.225(9)
W(5)···Ti(2)	3.26(1)	W(8)···Ti(3)	3.263(9)
Ti(1)···Ti(3)	3.42(1)	Ti(2)···Ti(4)	3.43(2)
Ti(1)···Ti(2)	3.67(1)	Ti(3)···Ti(4)	3.67(1)
Ti(1)···Ti(1^{i})	3.76(2)	Ti(3)···Ti(3^{i})	3.76(2)
W(1)···Si(1)	3.56(3)	W(6)···Si(2)	3.56(2)
W(2)···Si(1)	3.54(2)	W(7)···Si(2)	3.543(3)
W(3)···Si(1)	3.55(2)	W(8)···Si(2)	3.53(2)
W(4)···Si(1)	3.549(3)	W(9)···Si(2)	3.58(2)
W(5)···Si(1)	3.56(2)	W(10)···Si(2)	3.60(3)
Ti(1)···Si(1)	3.45(2)	Ti(3)···Si(2)	3.40(2)
Ti(2)···Si(1)	3.45(3)	Ti(4)···Si(2)	3.41(3)

[a] Symmetry code: (i) $x, y, {}^{1}/_{2} - z$.

specific cation effects[42 a-f]) and a conclusion reinforced during a recent, international workshop on polyoxoanions.[43]

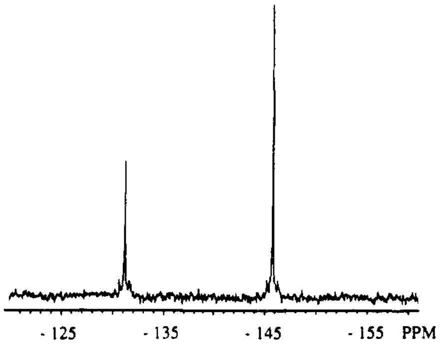

Figure 3. ^{183}W NMR spectrum of $Si_2W_{18}Ti_6O_{77}^{14-}$ in D_2O (0.1 M, metathesis to Li^+ salt, pD 3.2) at 21 °C. Chemical shifts in ppm are negative to higher field and are referenced to saturated Na_2WO_4/D_2O using the substitution method. The clean spectrum indicates the purity and the stability of the compound, while the $^{2}J_{W-O-W}$ coupling constant of 15 Hz (visible at the base of the peaks) demonstrates that an A-type $SiW_9O_{34}^{10-}$ is retained in $Si_2W_{18}Ti_6O_{77}^{14-}$.[37]

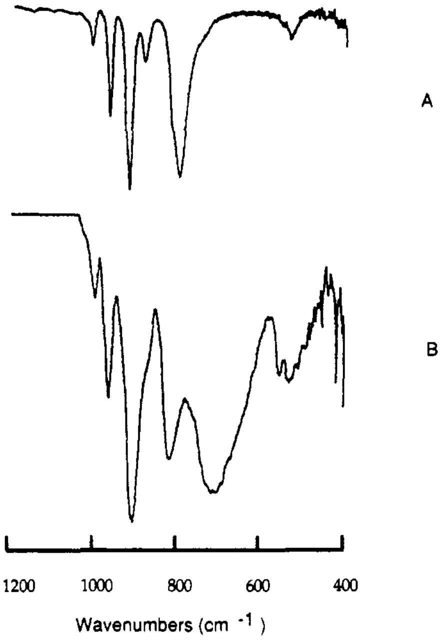

Figure 4. IR spectra of A-β-$(Bu_4N)_4SiW_{12}O_{40}$ (A) and A-β-$(Bu_4N)_{7.5}H_{6.5}$-$Si_2W_{18}Ti_6O_{77}$ (B). The new band at 700 cm^{-1} is tentatively assigned to vibrations of the Ti–O–Ti bonds linking the two "A-β-$SiW_9Ti_3O_{40}$" halves.

The first step of mechanistic work is the complete characterization of *all* the products. In the present case, the crystallography and solution characterization unequivocally establish the structure of the major isolable product as the Ti–O–Ti-bridged species, $(SiW_9O_{37})_2(Ti\text{–}O\text{–}Ti)_3^{14-}$. Reasoning by strict analogy to the established chemistry[7a] of $SiW_9Nb_3O_{40}^{7-}$ and its oligomerization reaction, $2SiW_9Nb_3O_{40}^{7-} + 6H^+$ to yield $Si_2W_{18}Nb_6O_{77}^{8-} + 3H_2O$ (and the reverse reaction of $6OH^- + Si_2W_{18}Nb_6O_{77}^{8-}$ to give back $2SiW_9Nb_3O_{40}^{7-}$), it is reasonable to suggest (but still unproven) that the monomeric intermediate $[SiW_9(TiOH)_3O_{37}^{7-}]$ (or a more protonated equivalent of this intermediate, e.g. $[H_xSiW_9(TiOH)_3O_{37}^{-7+x}]$) is a key intermediate in the synthesis of $Si_2W_{18}Ti_6O_{77}^{14-}$ as eqs 1–3 illustrate (these equations are offered as a *minimum* initial mechanistic postulate only).

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(42) (a) Clare, B. W.; Kepert, D. L.; Watts, D. W. *J. Chem. Soc., Dalton Trans.* **1973**, 2481. (b) Druskovich, D. M.; Kepert, D. L. *J. Chem. Soc., Dalton Trans.* **1975**, 947. (c) Druskovich, D. M.; Kepert, D. L. *Aust. J. Chem.* **1975**, *28*, 2365. (d) Kepert, D. L.; Kyle, J. H. *J. Chem. Soc., Dalton Trans.* **1978**, 133. (e) Kepert, D. L.; Kyle, J. H. *J. Chem. Soc., Dalton Trans.* **1978**, 137. (f) Kepert, D. L.; Kyle, J. H. *J. Chem. Soc., Dalton Trans.* **1978**, 1781. (g) Kyle, J. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2609.

(43) (a) The suggestion that ion-pairing effects are an underappreciated aspect of polyoxoanion chemistry was raised during the discussion at the most recent polyoxoanion workshop: International Workshop "Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity", July 1992, Bielefeld, Germany. (b) Our own publications have noted (footnote 8a, p 1694 elsewhere[7c]) the probable importance of ion-pairing effects in polyoxometalate chemistry and have provided evidence for Na^+ ion-pairing effects for polyoxoanions in organic solvents (see p 1786 elsewhere[7d]).

$$2\,HSiW_9O_{34}^{9-} + 6\,\text{"}Ti(O)^{2+}\text{"} + 6\,H_2O \rightarrow 2\,[SiW_9(TiOH)_3O_{37}]^{7-} + 8\,H^+ \quad (1)$$

$$2\,[SiW_9(TiOH)_3O_{37}]^{7-} \rightarrow Si_2W_{18}Ti_6O_{77}^{14-} + 3\,H_2O \quad (2)$$

NET

$$2\,HSiW_9O_{34}^{9-} + 6\,\text{"}Ti(O)^{2+}\text{"} + 3\,H_2O \rightarrow Si_2W_{18}Ti_6O_{77}^{14-} + 8\,H^+ \quad (3)$$

This scheme must be quite incomplete, however, as it does not even show the (nonisolated; unknown) product(s) which account for the other *ca.* 60% of the starting $HSiW_9O_{34}^{9-}$. Clearly, additional product and then kinetic and mechanistic studies of this polyoxoanion, or virtually any other polyoxoanion which has been reported recently,[1] would be a welcome addition to the polyoxometalate literature.

Summary. The reaction of TiO^{2+} precursors with the lacunary polyoxoanion A-β-$SiW_9O_{34}^{10-}$ gives rise to the previously unknown A-β-$Si_2W_{18}Ti_6O_{77}^{14-}$ in up to *ca.* 41% yields. The compound has been unambiguously characterized in the solid state by X-ray single-crystal structural analysis and in solution by IR, ^{183}W NMR, and solution molecular weight measurements. Hence, the relatively new subclass of polyoxoanions of general formula $X_2W_{18}M_6O_{77}^{n-}$ discovered earlier[7a] can now be said to be firmly established, an important point since others had expressed some skepticism about their existence.[44]

Finally, it is worth noting that at least the $Si_2W_{18}Nb_6O_{77}^{8-}$ member of this new subclass of polyoxoanions exhibits a relatively rich chemistry, being cleaved by[45] H_2O_2 to yield an allylic alcohol oxygenation precatalyst,[21a] being cleaved by 3.0 equiv of OH^- to yield the soluble-oxide support system $SiW_9Nb_3O_{40}^{7-}$,[7a] and being cleaved by reagents such as primary and secondary amines or bifunctional alcohol amines such as $HOCH_2CH_2NH_2$.[7a,46] Hence, and to the extent species like A-β-$Si_2W_{18}Ti_6O_{77}^{14-}$ mimic the reactivity of $Si_2W_{18}Nb_6O_{77}^{8-}$, the new subclass of $X_2W_{18}M_6O_{77}^{n-}$ polyoxoanions may be of interest for their relatively rich reaction chemistry (i.e. in comparison to traditional polyoxoanions). Such reactivity studies, as well as further product, kinetic, and mechanistic studies of the formation and degradation of these and other polyoxoanions, should prove of interest.

Acknowledgment. Thermal gravimetric analysis was obtained with assistance from Mr. Chris Grant and Professor William J. Randall. Y.L. thanks Professor A. Tézé for valuable discussions during his sabbatical leave in Eugene. Support was provided by the NSF, Grant CHE-8313345, during the early phases of this research and then by the Department of Energy, Chemical Sciences Division, Office of Basic Energy, Grant DOE FG06-089ER13998.

Supplementary Material Available: Five yield optimization experiments for $Si_2W_{18}Ti_6O_{77}^{14-}$ including experimental details, results (Table A), and discussion, ^{183}W NMR peak patterns for A-type Keggin polyoxoanions and their M–O–M-bridged $X_2M_{18}M'_6O_{77}^{n-}$ analogs (Table B), plots of the ultracentrifuge molecular weight determinations in H_2O for $K_{12}H_2$-$Si_2W_{18}Ti_6O_{77}$ and in CH_3CN for $(Bu_4N)_{7.5}H_{6.5}Si_2W_{18}Ti_6O_{77}$ (Figures A and B), and details of the data collection and structure refinement, bond angles, anisotropic thermal parameters, bond distances, symmetry operators, least-squares planes, and dihedral angles (Tables C-G) (20 pages). Ordering information is given on any current masthead page.

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[44] Day, V. W.; Klemperer, W. G.; Schwartz, C. *J. Am. Chem. Soc.* **1987**, *109*, 6030 (see the statement on the top of p 6039).

[45] Interestingly in this regard is the fact that Ti peroxides such as $Ti(O_2)(C_2O_4)_2^{2-}$ are well-known: (a) Nour, E. M.; Morsy, S. *Inorg. Chim. Acta* **1986**, *117*, 45. (b) Mühlebach, J.; Müller, K.; Schwarzenbach, G. *Inorg. Chem.* **1970**, *9*, 2381. (c) Griffith, W. P. *J. Chem. Soc.* **1964**, 5248. (d) Patel, C. C.; Jere, G. V. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1155.

[46] Droege, M. Ph.D. Thesis, University of Oregon, 1984.