of 50 kHz (16K, 6.1 Hz/data point, 0.164-s acquisition time; 32K, 3.1 Hz/data point, 0.328-s acquisition time) or 100 kHz (32K, 6.1 Hz/data point, 0.164-s acquisition time). Fluorine-19 spectra were obtained in 64–1600 scans at a spectral width of 100 kHz (16K, 12.2 Hz/data point, 0.082-s acquisition time; 32K, 6.1 Hz/data point, 0.164-s acquisition time) or 150 kHz (32K, 9.2 Hz/data point, 0.109-s acquisition time). In some instances ^{19}F free induction decays, accumulated at a spectral width of 100 kHz and in a 32K memory, were zero-filled to 64K for processing. Pulse widths corresponding to bulk magnetization tip angles, $\theta = 90°$, were 2 (^{19}F) and 22 μs (^{129}Xe). Line-broadening parameters used in exponential multiplication of the free induction decays were set equal to or less than their respective data point resolutions. In some cases, resolution was further enhanced by transforming the free induction decays from a time to a frequency domain with use of a Gaussian fit rather than the conventional Lorentzian fit. In these instances, a Gaussian broadening between 0.1 and 0.5 and a line broadening equal to the negative of the respective data point resolution were applied to the free induction decays prior to Gaussian multiplication and Fourier transformation.

The respective nuclei were referenced with respect to neat samples of $XeOF_4$ (^{129}Xe) and $CFCl_3$ (^{19}F) at 24 °C. A positive chemical shift was assigned to any resonance occurring to high frequency of the reference substance.

Raman Spectroscopy. A Coherent Model Innova 90 argon ion laser giving up to 3.5 W at 514.5 nm was used to excite the Raman spectra. The spectrometer was a Spex Industries Model 14018 double monochromator equipped with holographic gratings (1800 grooves mm^{-1}). Slit widths depended on the scattering efficiency of the sample but were typically set between 50 and 100 μm. The scanning rate used was 0.5 $cm^{-1}\ s^{-1}$. The typical laser power range used was between 0.4 and 1 W. All Raman shifts quoted are believed to be accurate to ±2 cm^{-1}. Cylindrical sample tubes were mounted vertically. The angle between the laser beam and sample tube was 45°, and Raman-scattered radiation was observed at 45° to the laser beam or 90° to the sample tube. Low-temperature spectra were recorded by mounting the sample vertically in an unsilvered Pyrex glass Dewar filled with liquid nitrogen. All spectra were obtained directly in either FEP or glass reaction vessels.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for support of this work and the Ontario Ministry of Education for the award of a scholarship (R.G.S.).

Registry No. I, 101410-65-5; II, 101470-51-3; III, 101410-66-6; IV, 101470-52-4; V, 101470-53-5; VI, 25519-01-1; VII, 119365-61-6; VIII, 119327-31-0; XeF_2, 13709-36-9; $HOIOF_4$, 34618-93-4; HF, 7664-39-3; SO_2ClF, 13637-84-8; $Xe(OTeF_5)_2$, 25005-56-5; IO_2F_3, 25402-50-0; H_5IO_6, 10450-60-9; ^{129}Xe, 13965-99-6; *cis*-$F_4OIOXeOTeF_5$, 119327-30-9; *trans*-$F_4OIOXeOTeF_5$, 119365-60-5; fluorosulfuric acid, 7789-21-1; oleum, 8014-95-7.

Contribution from the Department of Chemistry,
University of Oregon, Eugene, Oregon 97403

Polyoxoanions Derived from A-β-$SiW_9O_{34}^{10-}$: Synthesis and Crystallographic and ^{183}W NMR Characterization of $Si_2W_{18}Zr_3O_{71}H_3^{11-}$, Including Its Organic Solvent Soluble Bu_4N^+ Salt

Richard G. Finke,* Brian Rapko, and T. J. R. Weakley*,†

Received August 3, 1988

The reaction of A-β-$SiW_9O_{34}^{10-}$ and "ZrO^{2+}" ions in aqueous solution, under conditions initially designed to give "$SiW_9Zr_3O_{40}^{10-}$", instead yields the new heteropolytungstate anion $Si_2W_{18}Zr_3O_{71}H_3^{11-}$, isolated as its Bu_4N^+, Me_4N^+, and Me_3NH^+ acid salts. These have been characterized by means of elemental analysis, TGA, IR spectroscopy, ^{29}Si and ^{183}W NMR spectroscopy, and, for the Bu_4N^+ salt, FAB mass spectroscopy. Structural questions left unanswered by the solution NMR studies were answered by a single-crystal X-ray structural analysis of the Me_3NH^+ salt, $(Me_3NH)_{10}H(Si_2W_{18}Zr_3O_{71}H_3)\cdot 10H_2O$ (monoclinic, $P2_1/n$, $a = 13.452$ (3) Å, $b = 43.416$ (7) Å, $c = 18.331$ (4) Å, $\beta = 102.17$ (2)°, $Z = 4$, Mo radiation, $R = 0.055$ for 8755 independent data with $I \geq 3\sigma(I)$). The crystallographic analysis shows the anion to have the composition $[Zr_3(OH)_3(A\text{-}\beta\text{-}SiW_9O_{34})_2]^{11-}$, with approximate D_{3h} symmetry. The equatorially placed Zr atoms are linked by OH atoms. Each Zr is also bonded to two oxygens of an edge-sharing pair of WO_6 octahedra in each SiW_9O_{34} unit and each trigonal-prismatic ZrO_6 group [average Zr–O = 2.11 (4) Å] is enlarged by two long Zr–O–(Si,W) bonds [average Zr–O = 2.83 (7) Å] normal to the prism faces. Possible reasons for the formation of $Si_2W_{18}Zr_3$, rather than SiW_9Zr_3, are discussed.

Designed, high-yield synthetic pathways to heteropolyanions containing more than one metal in oxidation states ≤4 are not generally available.[1] However, the factors leading to the several possible classes of such substituted polyoxoanions and thus to their rational synthesis should become increasingly clear now that new methods for the rapid characterization of such polyoxoanions,[2] including their less widely investigated, organic solvent soluble R_4N^+ salts,[1c,2b–f,3c–e,4] are available.

As part of a program[3] aimed initially at preparing two series of triply metal-substituted polyoxoanions $SiW_9M_3O_{40}^{n-}$ and $P_2W_{15}M_3O_{62}^{m-}$ (M = V^{5+}, Nb^{5+} and Ti^{4+}, Zr^{4+}), we have investigated the synthesis and characterization of the M^{4+} = Ti and Zr members of this series. In addition to the fundamental interest in such heteropolyanions, they are of interest as possible soluble metal oxide support systems for transition-metal catalysts.[3,5]

Herein we report that synthetic conditions of $3ZrO^{2+} + SiW_9O_{34}^{10-}$, chosen initially with the goal of preparing the unknown zirconium-containing heteropolytungstate "$SiW_9Zr_3(OH_2)_3O_{37}^{4-}$" instead yield anions of the formula $Si_2W_{18}Zr_3O_{71}^{14-}$. This new, Zr-substituted polyoxoanion has been characterized as its H_2O-soluble, Me_4N^+ and Me_3NH^+ salts, by methods that include multinuclear NMR spectroscopy and a single-crystal X-ray

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† Previous address: Chemistry Department, University of Dundee, Dundee DD1 4HN, U.K.

(1) (a) For the most recent summary of this area see: Pope, M. T. *Heteropoly and Isopoly Oxometallates*; Springer-Verlag: New York, 1983. (b) This statement applies to multiple, M_x-containing, compounds possessing the Keggin ($XW_{12-x}M_xO_{40}$) and Dawson ($X_2W_{18-x}M_xO_{62}$) structures. (c) For an exception to this statement see: Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737.

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Table I. Crystallographic Data for $(Me_3NH)_{10}H[Si_2W_{18}Zr_3O_{71}H_3]\cdot 10H_2O$

formula	$(Me_3NH)_{10}H$-	*Z*	4
	$[Si_2W_{18}Zr_3O_{71}H_3]\cdot$	*T*	23 °C
	$10H_2O$	λ	0.71069 Å
fw	5560.4	ρ_{obs}	3.48 (4) g cm^{-3}
space group	$P2_1/n$ (No. 14)	ρ_{calc}	3.53 g cm^{-3}
a	13.452 (3) Å	μ	215 cm^{-1}
b	43.416 (7) Å	transmissn coeff	0.24–1.00
c	18.331 (4) Å		
β	102.17 (2)°	*R*(*F*)	0.055
V	10466 (8) Å^3	$R_w(F)$	0.066

diffraction structural analysis (Me_3NH^+ salt), and as its organic solvent soluble Bu_4N^+ salt, including a FAB mass spectrum of the Bu_4N^+ salt.

Experimental Section

Materials. The following materials were of reagent grade and were used as received unless otherwise indicated: Bu_4NBr (98%; Fluka); Me_4NCl, CaH_2, pyrrolidine (Aldrich); $Zr(O)(SO_4)\cdot H_2SO_4\cdot 3H_2O$ (Alfa); KCl, MeOH, CH_3CN (Baker Analyzed); CD_3CN, DMSO-d_6 (Cambridge Isotope Laboratories); Davidson 3-Å molecular sieves (Fisher). The synthesis of the lacunary heteropolytungstate A-β-$Na_9HSiW_9O_{34}\cdot 23H_2O$ has been previously reported.[2e,f] Dry CH_3CN was prepared by distillation over CaH_2 following overnight reflux under N_2 and then mixing the distillate for 48 h with ca. 30% by volume 3-Å molecular sieves, which were activated by heating at 160 °C under vacuum (≤100 μm) overnight.

Instrumentation and Analytical Procedures. The instrumentation, procedures, and conditions used for the following measurements have been described in detail:[2f] IR, FAB mass spectra,[2g,h] solution sedimentation–equilibrium ultracentrifugation molecular weight measurements, thermal gravimetric analysis (TGA), and ^1H, ^{29}Si, and ^{183}W NMR. Elemental analyses were performed by Mikroanalysches Labor Pascher, Remagen, West Germany. Water was determined by TGA weight loss from ambient temperature to 200 °C (12° min^{-1}).[6]

X-ray Crystallography (Trimethylammonium Salt). Roughly equidimensional cleaved fragments, grown as described below, were sealed into capillaries. Weissenberg photographs showed the material was monoclinic, space-group $P2_1/n$, and gave approximate cell dimensions that were subsequently refined on the diffractometer from the setting angles of 25 reflections in the range $26.3 \leq 2\theta \leq 29.7°$. Intensity data were collected at Molecular Structures Corp. and the structure analysis was carried out in this laboratory. Crystal data are summarized in Table I. Additional details of data collection and structure refinement are tabulated in the supplementary material. The standard reflections showed no significant variation during data collection. All calculations were performed by use of the TEXSAN program suite,[7] incorporating MITHRIL[8] for structure solution and DIRDIF[9] for structure expansion. Atomic scattering factors were taken from the literature.[10a] The $Si_2W_{18}Zr_3$ atom set was clearly apparent in the *E* map of highest figure of merit. An empirical absorption correction (DIFABS)[10b] was applied after isotropic refinement of the anion atoms. Subsequently, the W and Zr atoms were refined with anisotropic thermal parameters. Difference syntheses showed 9 of the 10 expected countercation C_3N units and 10 isolated atoms in the interanion spaces. The C_3N units were refined in three full-matrix least-squares cycles. Because there were only small accompanying changes in the parameters for atoms of the anion, and because the CPU time with all atoms refined approached 9 h per cycle, the C, N, and isolated atoms (the last of these treated as half-oxygens of presumably disordered water molecules) were fixed in the last cycles of refinement.

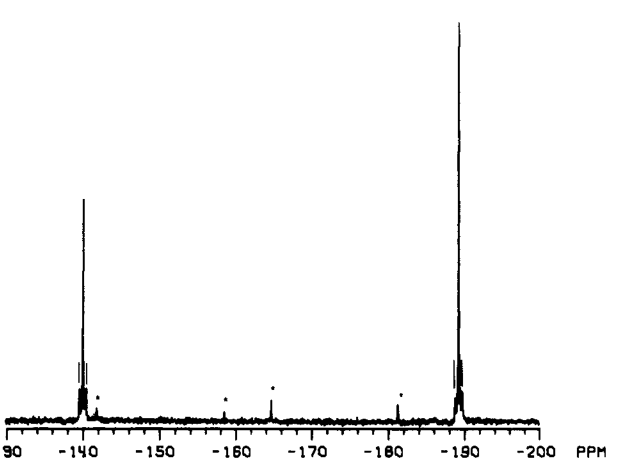

Figure 1. ^{183}W NMR spectrum of $[Si_2W_{18}Zr_3O_{71}H_x]^{x-14}$ in D_2O/HCl (pD ca. 1.8). The sample was recorded on a Nicolet NT-360 NMR spectrometer operating at 15 MHz at 21 °C using 10-mm-o.d. vertical sample tubes, and a $\pi/2$ pulse of 70 μs. The spectrum consists of 40000 pulses collected over 9 h. No apodization of the FID was employed. Chemical shifts in ppm are negative to higher field and are referenced to saturated Na_2WO_4/D_2O by using the substitution method. Asterisks note the presence of ca. 4% of a decomposition product (that slowly increases over time under the conditions of the NMR experiment; see the Experimental Section). The $^2J_{W-O-W}$ coupling constant marked with the lines at the base of the two main peaks is 14 Hz.

$(Me_4N)_{10}HSi_2W_{18}[ZrOH]_3O_{68}\cdot 15H_2O$. Nine grams (25.3 mmol) of $Zr(O)(SO_4)\cdot H_2SO_4\cdot 3H_2O$ was dissolved in 400 mL of water (pH 1.6). This initial low pH could not be adjusted due to Zr^{4+} hydrolysis in more basic solutions.[11] Next, 24 g (8.4 mmol) of A-β-$Na_9HSiW_9O_{34}\cdot 23H_2O$ was added over the course of about 1 min to the vigorously stirred zirconium solution, yielding a colorless, homogeneous, pH 1.9 solution within 5 min. Twenty grams (183 mmol) of Me_4NCl was then added to the solution followed by an additional 5 min of stirring. Next, an equal volume of methanol was added to the suspension and the precipitate isolated by suction filtration. Crystallization of the isolated white solid from a minimum of boiling, pH 1.4 water (V_{total} about 200 mL) yields 16.5 g of white needles (68% yield).

Anal. Calcd for $(Me_4N)_{10}HSi_2W_{18}[ZrOH]_3O_{68}\cdot 15H_2O$ ($C_{40}H_{154}N_{10}Si_2W_{18}Zr_3O_{86}$): C, 8.33; H, 2.66; N, 2.43; Si, 0.97; W, 57.4; Zr, 4.75; O, 23.9; Na, 0; total, 100.0; TGA weight loss for 17 H_2O = 5.29. Found: C, 7.31; H, 2.26; N, 2.17; Si, 0.92; W, 57.3; Zr, 4.68; O, 23.9; Na, <0.01; total, 99.03; TGA weight loss for 17 H_2O = 5.42. (Note that a 1.0% increase in the 1.0% low C analysis would give a total of 100.0%. Also, we have experienced several ≥1% low C analyses for Bu_4N^+ salts of polyoxoanions.) IR (KBr): 1028 (m), 1005 (w), 955 (s), 890 (s, br), 820 (w), 765 cm^{-1} (s, br).

^{29}Si NMR (1.65 mM with excess $LiClO_4$ present in D_2O/HCl (pD $\simeq$ 1.8)): singlet, $\delta = -84.2$. ^{183}W NMR (1.65 mM with excess $LiClO_4$ present in D_2O/HCl (pD $\simeq$ 1.8)) shows two lines at δ −140 (relative intensity 1.0; S/N = 104 to 1) and δ −189 (relative intensity 1.9; S/N = 224/1); $^2J_{W-O-W} = 14 \pm 1.2$ Hz as shown in Figure 1. In addition, several, minor, uncharacterized resonances at −142 (relative intensity 1), −159 (relative intensity 1), −165 (relative intensity 2), and −181 ppm (relative intensity 2) can be discerned. In Figure 1, the total intensity of these resonances comprises 4% of the combined intensity of the two major resonances at −140 and −189 ppm. The intensities of these resonances relative to those of the two major lines increases slowly over time under the acidic aqueous conditions of the NMR experiment, comprising over half of the total observed intensity following 1 week in solution at room temperature. Attempts to isolate this $H_3Si_2W_{18}Zr_3O_{71}{}^{11-}$ reaction or decomposition product were unsuccessful.

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$(Me_3NH)_{10}HSi_2W_{18}[ZrOH]_3O_{68}\cdot 10H_2O$. This preparation was exactly analogous to that of the Me_4N^+ salt described above. Recrystallation from hot solution (pH 1.4) gave colorless laths (recrystallized yield: 60%). Stubbier prisms suitable for X-ray work were deposited at 20 °C from a solution saturated at about 35 °C. Anal. Calcd for $(Me_3NH)_{10}H[Si_2W_{18}Zr_3O_{71}H_3]\cdot 10H_2O$ ($C_{30}H_{124}N_{10}O_{81}Si_2W_{18}Zr_3$): C, 6.48; H, 2.25; N, 2.52; Si, 1.01; W, 59.5; Zr, 4.92. Found: C, 6.21; H, 2.25; N, 2.59; Si, 0.98; W, 59.6; Zr, 4.92.

$(Bu_4N)_7H_4Si_2W_{18}[ZrOH]_3O_{71}\cdot 7H_2O$. The procedure as described above for the preparation of the Me_4N^+ salt is repeated for the Bu_4N^+ salt, except that the addition of 30 g (93 mmol) of Bu_4NBr replaces the addition of Me_4NCl. The resulting precipitate was collected by suction filtration and dried at 60 °C, 1 atm, for 2 days. This solid was then dissolved in about 45 mL of CH_3CN and any insoluble residue removed by centrifugation. The supernatant liquid was allowed to stand in vapor contact with methylene chloride. The resulting white crystalline solid is contaminated with a yellow oil. This contaminant was removed by decanting the solution from the crystals and rinsing with 1:5 (v:v) CH_3CN/CH_2Cl_2 until the yellow oil is removed, leaving a white solid. This solid was dried at 80 °C for 4 h ($\leq$0.1 mmHg), yielding 5.75 g (21%) of white product.

Anal. Calcd for $(Bu_4N)_7H_4Si_2W_{18}[ZrOH]_3O_{71}\cdot 7H_2O$ ($C_{112}H_{273}N_7Si_2W_{18}Zr_3O_{78}$): C, 20.4; H, 4.14; N, 1.48; Si, 0.85; W, 50.1; Zr, 4.15; O, 18.9; Na, 0; total, 100.0; TGA weight loss for seven H_2O = 0.19. Found: C, 20.3; H, 4.07; N, 1.80; Si, 0.79; W, 49.9; Zr, 4.00; O, 17.1; Na, <0.05; total, 98.0; TGA weight loss for seven H_2O = 0.18.

The FAB mass spectrum was prepared by dissolving a few milligrams of sample of 100 μL of CH_3CN and adding this solution to $\approx$2 μL of liquid 5:1 dithiothretol/dithioerythritol, with spectra obtained in both positive and negative ion modes as reported previously.[2g,h]

^{183}W NMR was obtained by dissolving 2 g of the sample in 2 mL of 1:1 CH_3CN/CD_3CN at 21 °C (with 15 drops of pyrrolidine added to sharpen the otherwise very broad peaks[2d,f]). Two resonances are observed at $\delta = -130.7$ (relative intensity 1.0, $\Delta\nu_{1/2} = 11$ Hz) and $\delta = -169.4$ (relative intensity 2.3, $\Delta\nu_{1/2} = 14.6$ Hz). IR (KBr): 1035 (m), 955 (m), 900 (s), 810 (w), 750 cm^{-1} (s, br).

A low-precision weight-average molecular weight ($\bar{M}_w$) was obtained in solution (as a check on whether the $Si_2W_{18}[Zr(OH)]_3O_{68}^{11-}$ structure was retained in solution) by use of the ultracentrifugation sedimentation equilibrium method with 0.1 M Bu_4NPF_6 as electrolyte. Conditions employed are as previously described.[12] The required partial specific volume, $\bar{\nu}$, was approximated by the apparent specific molar volume and was measured as 0.4 by the method of densities: calcd for $Si_2W_{18}[Zr(OH)]_3O_{68}^{11-}$ = 4781; found = 4300 ± 600.

Attempted Metathesis of the Me_4N^+ Salt to a H_3O^+ Salt. Fifteen grams (2.6 mmol) of $(Me_4N)_{10}HSi_2W_{18}[ZrOH]_3O_{68}$ was dissolved in 3 L of water. This compound was passed through a column containing 100 g (470 mequiv) of Amberlyst 15 cation-exchange resin. The eluate was reduced to dryness by using rotary evaporation at reduced (water aspirator) pressure, while heating the solution with a steam bath. Thirteen grams of white solid was isolated. ^{183}W NMR (1 g/mL D_2O) now shows five lines at −119.7 (relative intensity 1), −120.1 (relative intensity 1), −144.9 (relative intensity 2), −147.7 (relative intensity 1), and −199.9 ppm (relative intensity 1) rather than the two-line spectrum described above for the starting compound $H_3Si_2W_{18}Zr_3O_{71}^{11-}$. The IR (KBr) spectrum shows bands at 1020 (w), 970 (m), 900 (s), and 790 cm^{-1} (s, br), indicating that the "Keggin-like" SiW_9O_{34} framework remains substantially intact.

Attempted Conversion of $Si_2W_{18}[Zr(OH)]_3O_{68}^{11-}$ + $3ZrO^{2+}$ to $SiW_9Zr_3(OH_2)_3O_{37}^{4-}$. $(Me_4N)_{10}HSi_2W_{18}[ZrOH]_3O_{68}$ (3.4 g, 0.59 mmol) was dissolved in 200 mL of water and mixed with 3.1 equiv of $Zr(O)(SO_4)\cdot H_2SO_4\cdot 3H_2O$ (0.65 g) dissolved in 100 mL water (pH of the mixture ~2). The solution was refluxed for 2.5 days, and then the total volume was concentrated to 100 mL. Addition of Me_4NCl (10 g, 90 mmol) gave an immediate precipitate. Filtration yields 1.92 g of a white paste. No ^{183}W NMR resonances (1 g/mL D_2O + excess $LiClO_4$) were discerned following >40 000 acquisitions.

Results and Discussion

Me_4N^+ and Me_3NH^+ Salts. In general, water-soluble salts of substituted heteropolyanions are much easier to crystallize than salts soluble in organic solvents. Since crystallization remains the primary means of purification for polyoxometalates (HPLC of polyoxometalates has recently been reported,[13a] however), our synthetic strategy has involved the initial preparation, crystallization, and characterization of water-soluble salts such as K^+ or Me_4N^+, followed by cation metathesis to an organic solvent soluble salt that can often be obtained as an analytically pure powder.

The white, crystalline tetramethylammonium or trimethylammonium salts are readily prepared and purified from a hot, saturated pH 1.4 HCl/H_2O solution in ca. 70% yield, according to the stoichiometry of eq 1 (rather than the stoichiometry required

$$2SiW_9O_{34}^{10-} + 3ZrO^{2+} + 3H^+ \rightarrow H_3Si_2W_{18}Zr_3O_{71}^{11-} + 3H_2O \quad (1)$$

to obtain a trisubstituted, Keggin-type heteropolytungstate, eq 2). Indeed, the stoichiometry of eq 1 was observed even if excess

$$SiW_9O_{34}^{10-} + 3ZrO^{2+} + 3H_2O \rightarrow 2\text{“}SiW_9[Zr(H_2O)]_3O_{37}^{4-}\text{”} \quad (2)$$

ZrO^{2+} ($6ZrO^{2+}/SiW_9O_{34}^{10-}$, eq 2) was present. Furthermore, attempts to "force" the formation of the $SiW_9Zr_3O_{40}^{10-}$ product by employing a higher temperature over a longer reaction time yielded no isolable product, as detailed in the Experimental Section. Comparing eq 1 vs 2 strongly suggests that less acidic conditions would favor a product with a "SiW_9Zr_3" composition, but the propensity of Zr^{4+} to hydrolyze (e.g. to ZrO_2) at high pH values[13b] and the insolubility of standard aqueous zirconium sources at higher pH have hindered such an investigation (additional experiments in this direction are possible, however, and may prove fruitful).

The single line at −84.2 ppm observed in the ^{29}Si NMR spectrum for the tetramethylammonium salt indicates that a single product is obtained under the reaction conditions. The IR spectrum shows bands at ca. 1000, 950, 900, and 800 cm^{-1} as typically observed for Keggin-type tungstosilicates.[14] The elemental analysis (following overnight drying), coupled with the use of thermal gravimetric analysis to determine the number of H_2O molecules present, reveals the approximate empirical composition as $(SiW_9Zr_{1.5}O_{35\pm2})_n$ rather than $(\text{“}SiW_9Zr_3O_{40}^{10-}\text{”})_n$. However, the precision of the oxygen analysis leaves an unacceptable uncertainty in this empirical composition. Because of initial difficulty in obtaining a single crystal suitable for an X-ray diffraction study, fast atom bombardment mass spectroscopy, FAB-MS, on the Bu_4N^+ salt was utilized to demonstrate that the value of n is 2 so that the molecular formula becomes $Si_2W_{18}Zr_3O_{70\pm4}^{x-}$. Previously we concluded,[2h] from the elemental analysis and the FAB-MS alone, that the most likely molecular formula for the Bu_4N^+ salt was "$(Bu_4N)_7HSi_2W_{18}Zr_3O_{68}(H_2O)_{3x}$", where x = 1 or 2. The crystal structure analysis for the trimethylammonium salt, described next, shows that the polyoxoanion skeleton does in fact contain 71 oxygens (x = 1 above), but leaves some uncerainty in the location of the protons in the structure (a problem that typically is a difficult if not vexing one in polyoxoanion chemistry[15]). In short, the crystal structure analysis of the Me_3NH^+ salt implies that the Bu_4N^+ salt also contains a $H_3Si_2W_{18}Zr_3O_{71}^{11-}$ anion and therefore supports the deduction, from the FAB mass spectrum of the Bu_4N^+ salt, as to the anion's basic composition. This confirms the usefulness of FAB mass spectra as a tool for establishing a heteropolyanion's molecular formula when crystal structure analyses are not available.

Single-Crystal Diffraction Structural Analysis of the Trimethylammonium Salt. The anion (Figure 2; stereoview in Figure 3) contains two SiW_9O_{34} units that are linked via three equatorial Zr atoms and that have the same A-β structure as the precursor lacunary heteropolytungstate,[16] $SiW_9O_{34}^{10-}$. Atomic coordinates are given in Table II, selected bond lengths in Table III, and

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(12) Reference 2e and supplementary material therein.

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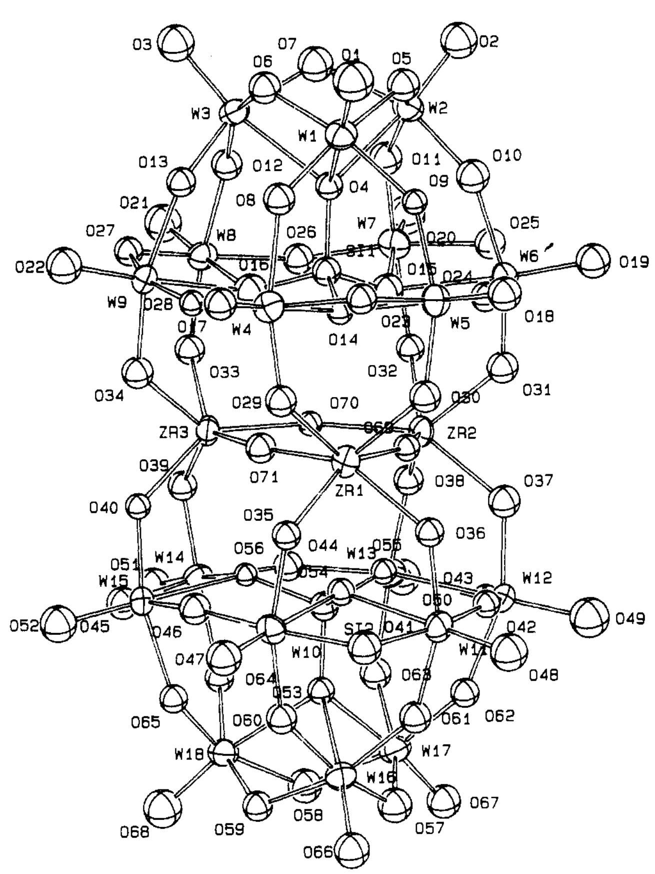

Figure 2. Structure of $Si_2W_{18}Zr_3O_{71}H_3{}^{11-}$ showing the full numbering scheme for all atoms.

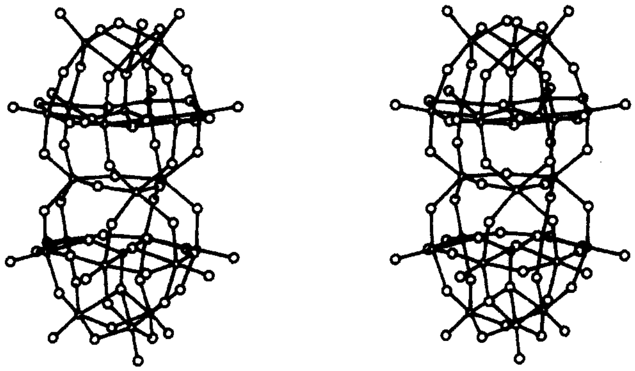

Figure 3. Stereoview of $Si_2W_{18}Zr_3O_{71}H_3{}^{11-}$.

distances between heavy atoms in Table IV. The two WO_6 octahedra in each unit linked to a given Zr atom share an edge with one another, as seen in other heteropolyanions of partial stoichiometry $(XW_9)_2M_3$, where the XW_9O_{34} moiety is of the A type, notably, $[(PW_9O_{34})_2W_3O_3(H_2O)_3]^{6-}$,[17] $[(PW_9O_{34})_2Ce_3O_3(H_2O)_3]^{12-}$,[18] and $[Cu_3(NO_3)(PW_9O_{34})_2]^{13-}$.[18,19] This is in contrast to anions containing B-type XW_9O_{33} moieties: $[(As^{III}W_9O_{33})_2W_3O_3(H_2O)_2]^{6-}$,[20] $[(As^{III}W_9O_{33})_2CoW_2O_2(H_2O)]^{8-}$,[21] $[As^{III}{}_2W_{18}Cu_3(H_2O)_3O_{66}]^{12-}$,[22] and $[(Hg_2)_2W(O)(H_2O)(As^{III}W_9O_{33})_2]^{10-}$.[23,24] The anion lacks crystallographic symmetry but has approximately D_3 inherent symmetry, the departure from D_{3h} symmetry resulting from a slight twist (ca. 2.5°) about the Si···Si axis. Coordination of the $SiW_9O_{34}{}^{10-}$ units to the Zr atom has reduced the average O···O distance between the pair of O atoms now bridged by a Zr atom to 2.77 Å compared with 3.38 Å for the same unshared atoms in the free "ligand"; this change results largely from bond angle changes, as the skeletal (W···W) distances (Table III) are little affected.

The Zr atoms are linked in the equatorial plane via oxygen atoms. The overall coordination geometry is close to trigonal prismatic, the local 3-fold axis of the ZrO_6 group lying in the equatorial plane. The Zr–O bond lengths are in the range 2.04–2.16 (2) Å, average 2.11 (4) Å. However, each Zr atom makes a long, weak contact, approximately normal to a rectangular face of the ZrO_6 group, with one oxygen atom in each of the two SiO_4 tetrahedra [2.74–2.94 (3) Å; average 2.83 (7) Å]. The algorithm derived by Brown and Altermatt recently[25] from bond lengths stored in the Inorganic Crystal Database indicates that these oxygens [O(14,15,16,54,55,56)] (Figure 2), each of which is linked to one Si and two W atoms, have valence sums in the range 1.63–1.75 average 1.70, and presumably therefore have residual bonding capacity. By contrast the valence sums for O(4) and O(53), which are linked to one Si and *three* W atoms, are 1.93 and 1.89, respectively.

We believe that the three oxygen atoms, O(69,70,71), involved in the Zr–O–Zr bridges are protonated[26] by the three H^+ ions required for charge balance, so the anion can be represented as $[(SiW_9O_{34})_2Zr_3(OH)_3]^{11-}$. It appears improbable that unprotonated oxo bridges are present at the pH (ca. 1.4) of the synthesis and crystallization, and we are unaware of any instances of diprotonated oxo bridges (i.e. water molecules) between Zr atoms. There are several examples of polynuclear hydroxo-bridged Zr complexes, e.g., $[Zr_4(OH)_4(H_2O)_{16}]^{8+}$ [27] and $[Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}]^{8+}$ (the oxo atoms in the latter[28] are tetrahedrally bonded). Support for our view comes from the bond valence sums for O(69,70,71), which are only 1.16–1.29 (average 1.21), implying considerable negative charge on these atoms if they are not protonated. By a similar argument, if the extra proton present in the three acid salts here reported does not reside on a water molecule, it could be attached to O(32), which links Zr(2) and W(7), in the Me_3NH^+ salt. The valence sum for O(32) is only 1.28, and the W(7)–O(32) bond is significantly longer, 2.03 (2) Å, than the 11 other structurally analogous bonds, average 1.84 (3) Å.

The $[Si_2W_{18}Zr_3O_{71}H_3]^{11-}$ anion resembles two $SiW_9Zr_3O_{40}$ Keggin-like units with the Zr atoms in common; the (6 + 2) coordination number and the unusual coordination geometry for the zirconium atoms represent a compromise enabling these atoms to adapt simultaneously to both Keggin units. The Zr atoms all lie close to the anion axis and are roughly equidistant (average 2.39 Å) from it. In this respect the anion differs from all other

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(24) (a) In addition, the structure $As^{III}{}_2W_{20}Zn(H_2O)O_{68}{}^{8-}$,[24b] which only has two $(WO)^{4+}$ units bridging B-$As^{III}W_9O_{33}$ fragments, has been determined by ^{183}W NMR to possess the same connectivity as mentioned above between the bridging $(WO)^{4+}$ units and the AsW_9O_{33} fragments. (b) Contant, R.; Hervé, G.; Thouvenot, R. *Abstracts*, Polyoxometalate Workshop, St. Lambert-des-Bois, France, July 1983.

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(26) One formalism useful for describing the charge distribution and surface charge density of Keggin-type heteropolyanions is to consider these compounds as inorganic clathrates surrounding the central, charged $XO_4{}^{n-}$ tetrahedron that contains the heteroatom.[26b] For example, $PW_{12}O_{40}{}^{3-}$ can be rewritten as $(PO_4{}^{3-})(W_{12}O_{36}{}^0)$ and $P_2W_{18}O_{62}{}^{6-}$ can be rewritten as $(PO_4{}^{3-})_2(W_{18}O_{56}{}^0)$. Applying this formalism to the zirconium-containing heteropolytungstate skeleton $Si_2W_{18}Zr_3O_{68}{}^{8-}$ (containing Zr^{4+}) yields $(SiO_4{}^{4-})_2(W_{18}Zr_3O_{60}{}^0)$, indicating the absence of significant surface charge density. However, the presence of $Zr(O)^{2+}$ bridges in $Si_2W_{18}(ZrO)_3O_{68}{}^{14-}$ yields $(SiO_4{}^{4-})_2(W_{18}Zr_3O_{63}{}^{6-})$, indicating that appreciable surface electron density will be present, with concomitant protonation of the ZrO bonds until Zr(OH) and/or $Zr(OH_2)$ are formed. (b) Barcza, L.; Pope, M. T. *J. Phys. Chem.* **1973**, *77*, 1795.

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Table II. Atomic Coordinates ($\times 10^4$; W, $\times 10^5$) and Isotropic Thermal Parameters (Å^2) (Equivalent Isotropic Parameters (Å^2), $B_{eq} = {}^1/_3\sum_i\sum_j B_{ij}a_ia_j\mathbf{a}^*_i\cdot\mathbf{a}^*_j$, for W and Zr)

atom	x	y	z	B
W(1)	74853 (12)	13332 (3)	16737 (8)	2.86 (6)
W(2)	97230 (11)	10172 (4)	24111 (8)	2.90 (6)
W(3)	76131 (12)	5870 (3)	21425 (7)	2.71 (6)
W(4)	56927 (11)	15300 (3)	28481 (8)	2.64 (6)
W(5)	77872 (11)	19231 (3)	31296 (8)	2.65 (6)
W(6)	102449 (11)	15490 (3)	40402 (8)	2.57 (6)
W(7)	102805 (11)	8029 (3)	43599 (8)	2.70 (6)
W(8)	78786 (11)	3516 (3)	40926 (7)	2.50 (6)
W(9)	57533 (11)	6900 (3)	33242 (7)	2.49 (6)
W(10)	40477 (11)	18935 (3)	50849 (8)	2.54 (6)
W(11)	72008 (11)	22732 (3)	63381 (8)	2.75 (6)
W(12)	96244 (11)	18741 (3)	72056 (8)	2.63 (6)
W(13)	96160 (11)	11315 (3)	76010 (7)	2.65 (6)
W(14)	71530 (11)	6993 (3)	72064 (7)	2.38 (6)
W(15)	50261 (11)	10489 (3)	64316 (7)	2.44 (6)
W(16)	62275 (12)	20178 (3)	79511 (8)	2.85 (6)
W(17)	83855 (11)	16496 (3)	87192 (8)	2.82 (6)
W(18)	61656 (11)	12655 (3)	83535 (8)	2.73 (6)
Zr(1)	6696 (2)	1765 (1)	4745 (2)	2.47 (12)
Zr(2)	9416 (2)	1344 (1)	5719 (2)	2.32 (11)
Zr(3)	6729 (2)	843 (1)	5250 (2)	2.34 (12)
Si(1)	7972 (7)	1133 (2)	3586 (5)	2.36 (17)
Si(2)	7273 (7)	1492 (2)	6843 (5)	2.52 (17)
O(1)	7152 (20)	1497 (6)	795 (14)	4.9 (6)
O(2)	10789 (18)	970 (5)	2047 (12)	3.8 (5)
O(3)	7309 (18)	273 (6)	1537 (13)	3.9 (5)
O(4)	8186 (15)	1046 (4)	2765 (10)	2.1 (4)
O(5)	8907 (17)	1248 (5)	1671 (12)	3.1 (5)
O(6)	7188 (17)	911 (5)	1410 (11)	3.0 (5)
O(7)	8967 (18)	647 (6)	1995 (12)	3.9 (5)
O(8)	6328 (16)	1341 (5)	2008 (11)	2.7 (4)
O(9)	8004 (15)	1674 (4)	2304 (10)	1.9 (4)
O(10)	10036 (17)	1360 (5)	2990 (12)	3.3 (5)
O(11)	10089 (17)	774 (5)	3338 (11)	3.2 (5)
O(12)	8138 (17)	390 (5)	3090 (11)	2.9 (4)
O(13)	6401 (17)	671 (5)	2453 (11)	2.8 (4)
O(14)	7317 (15)	1455 (5)	3518 (10)	2.3 (4)
O(15)	9071 (16)	1177 (5)	4132 (11)	2.9 (5)
O(16)	7368 (17)	851 (5)	3866 (12)	3.2 (5)
O(17)	4514 (17)	1608 (5)	2341 (12)	3.3 (5)
O(18)	8080 (17)	2270 (5)	2822 (18)	3.5 (5)
O(19)	11239 (18)	1788 (5)	3970 (12)	3.7 (5)
O(20)	11289 (19)	549 (6)	4618 (13)	4.4 (6)
O(21)	8244 (19)	−33 (6)	4205 (13)	4.0 (5)
O(22)	4587 (18)	544 (5)	2911 (12)	3.7 (5)
O(23)	6404 (16)	1898 (5)	2665 (11)	2.6 (4)
O(24)	9110 (16)	1806 (5)	3640 (11)	2.5 (4)
O(25)	11037 (17)	1177 (5)	4274 (12)	3.2 (5)
O(26)	9227 (15)	531 (5)	4420 (11)	2.4 (4)
O(27)	6531 (15)	314 (5)	3613 (11)	2.3 (4)
O(28)	5468 (15)	1110 (5)	3110 (10)	2.1 (4)
O(29)	5567 (16)	1690 (5)	3748 (11)	2.7 (4)
O(30)	7388 (16)	2027 (5)	4001 (11)	2.8 (4)
O(31)	10177 (17)	1591 (5)	5008 (12)	3.2 (5)
O(32)	10262 (16)	964 (5)	5398 (10)	2.4 (4)
O(33)	7488 (16)	445 (5)	4958 (11)	2.8 (4)
O(34)	5657 (17)	720 (5)	4331 (12)	3.2 (5)
O(35)	5350 (16)	1852 (5)	5054 (11)	2.5 (4)
O(36)	7178 (16)	2182 (5)	5335 (11)	2.7 (4)
O(37)	9978 (17)	1726 (5)	6354 (12)	3.1 (5)
O(38)	9975 (16)	1095 (5)	6695 (11)	2.7 (4)
O(39)	7096 (15)	580 (5)	6246 (10)	2.4 (4)
O(40)	5322 (15)	884 (5)	5600 (10)	2.2 (4)
O(41)	5757 (17)	2275 (5)	6077 (12)	3.4 (5)
O(42)	8550 (15)	2130 (5)	6673 (10)	2.4 (4)
O(43)	10339 (15)	1531 (5)	7761 (11)	2.9 (4)
O(44)	8496 (16)	835 (5)	7398 (11)	2.5 (4)
O(45)	5678 (17)	704 (5)	6995 (11)	3.0 (5)
O(46)	4837 (17)	1458 (5)	6081 (11)	2.8 (4)
O(47)	3809 (18)	2017 (6)	5779 (12)	3.8 (5)
O(48)	7447 (19)	2659 (6)	6353 (13)	4.4 (6)
O(49)	10542 (20)	2147 (6)	7491 (14)	5.0 (6)
O(50)	10543 (18)	912 (5)	8157 (12)	3.7 (5)
O(51)	7332 (17)	355 (5)	7666 (12)	3.3 (5)
O(52)	3773 (18)	927 (6)	6373 (12)	3.9 (5)
O(53)	7076 (16)	1574 (5)	7678 (11)	2.4 (4)
O(54)	6770 (16)	1764 (5)	6249 (11)	2.5 (4)
O(55)	8491 (15)	1465 (4)	6892 (10)	1.9 (4)
O(56)	6707 (14)	1153 (4)	6601 (10)	1.7 (4)
O(57)	7438 (17)	1991 (5)	8726 (12)	3.5 (5)
O(58)	7424 (18)	1384 (5)	9055 (12)	3.5 (5)
O(59)	5659 (16)	1676 (5)	8402 (11)	2.6 (4)
O(60)	5278 (16)	1918 (5)	7066 (11)	2.9 (4)
O(61)	6998 (16)	2222 (5)	7352 (11)	2.9 (4)
O(62)	8970 (16)	1884 (5)	8054 (11)	2.5 (4)
O(63)	8983 (17)	1292 (5)	8586 (11)	3.1 (5)
O(64)	6967 (15)	942 (5)	8068 (11)	2.4 (4)
O(65)	5213 (16)	1236 (5)	7448 (11)	2.6 (4)
O(66)	5631 (19)	2320 (6)	8314 (13)	4.0 (5)
O(67)	9235 (18)	1708 (5)	9557 (12)	3.6 (5)
O(68)	5576 (19)	1087 (6)	8959 (13)	4.5 (6)
O(69)	8226 (15)	1647 (5)	5214 (10)	2.1 (4)
O(70)	8263 (14)	999 (4)	5544 (10)	1.8 (4)
O(71)	6398 (15)	1308 (5)	4902 (10)	2.4 (4)
OW(1)	1858 (18)	671 (6)	6253 (12)	3.7 (5)
OW(2)	2217 (30)	865 (9)	9371 (21)	12 (1)
OW(3)	7233 (30)	2676 (9)	4148 (21)	12 (1)
OW(4)	2880 (30)	256 (9)	2065 (21)	12 (1)
OW(5)	9375 (30)	189 (10)	948 (21)	13 (1)
OW(6)	1802 (32)	2985 (10)	5015 (22)	16 (1)
OW(7)	2810 (33)	1700 (11)	1244 (23)	17 (1)
OW(8)	6388 (33)	18 (11)	196 (23)	16 (1)
OW(9)	1415 (35)	452 (11)	1011 (24)	19 (1)
OW(10)	0 (37)	4910 (12)	520 (25)	24 (2)
OW(11)	6366 (34)	3268 (11)	4193 (24)	18 (1)
N(1)	4490 (32)	441 (10)	7996 (22)	6.8 (10)
N(2)	8627 (28)	788 (9)	9469 (19)	5.8 (9)
N(3)	8802 (28)	2529 (9)	8617 (19)	5.4 (8)
N(4)	9762 (28)	1934 (9)	1741 (20)	5.7 (9)
N(5)	8394 (36)	3311 (11)	2493 (26)	8.9 (13)
N(6)	9817 (48)	4086 (15)	6024 (33)	13 (2)
N(7)	2812 (32)	1170 (10)	3850 (23)	6.4 (10)
N(8)	28 (30)	24 (9)	3171 (20)	5.7 (9)
N(9)	505 (36)	2585 (11)	5438 (24)	7.8 (11)
C1)	4095 (46)	174 (15)	7446 (32)	10 (2)
C(2)	5180 (49)	326 (15)	8606 (35)	10 (2)
C(3)	3642 (50)	639 (15)	8132 (33)	10 (2)
C(4)	9067 (38)	512 (12)	9173 (27)	6.9 (13)
C(5)	9369 (39)	986 (12)	0 (26)	7.2 (13)
C(6)	7787 (47)	679 (14)	9811 (32)	9 (2)
C(7)	8960 (35)	2742 (11)	8031 (24)	6.1 (11)
C(8)	9677 (50)	2437 (15)	9174 (34)	9 (2)
C(9)	8020 (51)	2690 (16)	9022 (35)	11 (2)
C(10)	312 (35)	2127 (11)	2306 (24)	5.7 (11)
C(11)	9037 (44)	2118 (14)	1195 (30)	9 (2)
C(12)	438 (44)	1754 (13)	1334 (30)	8 (2)
C(13)	7558 (40)	3432 (12)	1811 (28)	7.4 (13)
C(14)	8224 (36)	2988 (11)	2593 (24)	5.8 (11)
C(15)	8189 (61)	3492 (19)	3186 (43)	14 (3)
C(16)	9648 (53)	3786 (17)	5421 (38)	12 (2)
C(17)	8788 (57)	4054 (17)	6354 (38)	13 (2)
C(18)	9957 (72)	4305 (23)	5497 (51)	18 (3)
C(19)	3485 (43)	1386 (14)	4443 (30)	8 (2)
C(20)	2822 (57)	1292 (18)	3133 (41)	13 (2)
C(21)	891 (44)	142 (13)	2821 (30)	8 (2)
C(22)	9405 (45)	−223 (14)	2660 (32)	9 (2)
C(23)	484 (44)	−161 (14)	3937 (31)	8 (2)
C(24)	3057 (64)	872 (21)	3875 (45)	17 (3)
C(25)	285 (58)	2706 (18)	6143 (41)	13 (2)
C(26)	−420 (63)	2428 (19)	4955 (43)	15 (3)
C(27)	1315 (59)	2283 (19)	5574 (40)	15 (2)

anions of the $(XW_9)_2M_3$ skeletal type, where two M atoms are either distinctly further from or distinctly closer ($[P_2W_{21}O_{71}(H_2O)_3]^{6-}$) to the anion axis than the third atom. *Also, the structure analysis shows no terminal oxygen atom on any Zr atom; here the present anion shows its most striking difference from the $[(PW_9O_{34})_2Ce_3O_3(H_2O)_2]^{12-}$ anion, which it otherwise most closely resembles.* In the latter, the two Ce atoms further from the anion axis (2.69 Å) are 7-coordinate and each bears a

Table III. Bond Lengths in the Anion (Å)

W(1)–O(1)	1.73 (2)	W(4)–O(28)	1.93 (2)
W(1)–O(8)	1.79 (2)	W(4)–O(8)	2.08 (2)
W(1)–O(6)	1.92 (2)	W(4)–O(14)	2.29 (2)
W(1)–O(9)	1.92 (2)	W(5)–O(18)	1.68 (2)
W(1)–O(5)	1.95 (2)	W(5)–O(30)	1.84 (2)
W(1)–O(4)	2.38 (2)	W(5)–O(23)	1.88 (2)
W(2)–O(2)	1.72 (2)	W(5)–O(24)	1.90 (2)
W(2)–O(10)	1.83 (2)	W(5)–O(9)	1.93 (2)
W(2)–O(5)	1.85 (2)	W(5)–O(14)	2.28 (2)
W(2)–O(7)	1.97 (2)	W(6)–O(19)	1.72 (2)
W(2)–O(11)	1.97 (2)	W(6)–O(31)	1.80 (2)
W(2)–O(4)	2.30 (2)	W(6)–O(24)	1.91 (2)
W(3)–O(3)	1.75 (2)	W(6)–O(25)	1.93 (2)
W(3)–O(13)	1.87 (2)	W(6)–O(10)	2.06 (2)
W(3)–O(7)	1.91 (2)	W(6)–O(15)	2.29 (2)
W(3)–O(12)	1.93 (2)	W(7)–O(20)	1.73 (2)
W(3)–O(6)	1.94 (2)	W(7)–O(11)	1.84 (2)
W(3)–O(4)	2.35 (2)	W(7)–O(26)	1.87 (2)
W(4)–O(17)	1.69 (2)	W(7)–O(25)	1.94 (2)
W(4)–O(29)	1.83 (2)	W(7)–O(32)	2.03 (2)
W(4)–O(23)	1.93 (2)	W(7)–O(15)	2.27 (2)
W(8)–O(21)	1.74 (2)	W(11)–O(54)	2.28 (2)
W(8)–O(33)	1.82 (2)	W(12)–O(49)	1.71 (3)
W(8)–O(27)	1.85 (2)	W(12)–O(37)	1.84 (2)
W(8)–O(12)	1.95 (2)	W(12)–O(42)	1.92 (2)
W(8)–O(26)	1.95 (2)	W(12)–O(43)	1.94 (2)
W(8)–O(16)	2.29 (2)	W(12)–O(62)	1.94 (2)
W(9)–O(22)	1.71 (2)	W(12)–O(55)	2.33 (2)
W(9)–O(34)	1.88 (2)	W(13)–O(50)	1.72 (2)
W(9)–O(28)	1.89 (2)	W(13)–O(38)	1.83 (2)
W(9)–O(27)	1.95 (2)	W(13)–O(63)	1.95 (2)
W(9)–O(13)	1.98 (2)	W(13)–O(44)	1.96 (2)
W(9)–O(16)	2.30 (2)	W(13)–O(43)	1.98 (2)
W(10)–O(47)	1.72 (2)	W(13)–O(55)	2.29 (2)
W(10)–O(35)	1.84 (2)	W(14)–O(51)	1.71 (2)
W(10)–O(41)	1.90 (2)	W(14)–O(39)	1.82 (2)
W(10)–O(46)	1.93 (2)	W(14)–O(44)	1.86 (2)
W(10)–O(60)	1.94 (2)	W(14)–O(45)	1.94 (2)
W(10)–O(54)	2.33 (2)	W(14)–O(64)	1.96 (2)
W(11)–O(48)	1.71 (3)	W(14)–O(56)	2.28 (2)
W(11)–O(36)	1.88 (2)	W(15)–O(52)	1.75 (2)
W(11)–O(42)	1.89 (2)	W(15)–O(40)	1.80 (2)
W(11)–O(41)	1.90 (2)	W(15)–O(46)	1.89 (2)
W(11)–O(61)	1.95 (2)	W(15)–O(45)	1.92 (2)
W(15)–O(65)	2.00 (2)	Zr(1)–O(69)	2.12 (2)
W(15)–O(56)	2.26 (2)	Zr(1)–O(30)	2.14 (2)
W(16)–O(66)	1.74 (2)	Zr(1)–O(36)	2.14 (2)
W(16)–O(61)	1.88 (2)	Zr(1)–O(29)	2.14 (2)
W(16)–O(60)	1.89 (2)	Zr(1)–O(54)	2.74 (3)
W(16)–O(57)	1.93 (2)	Zr(1)–O(14)	2.89 (3)
W(16)–O(59)	1.93 (2)	Zr(2)–O(37)	2.07 (2)
W(16)–O(53)	2.35 (2)	Zr(2)–O(38)	2.09 (2)
W(17)–O(67)	1.73 (2)	Zr(2)–O(31)	2.11 (2)
W(17)–O(62)	1.88 (2)	Zr(2)–O(69)	2.13 (2)
W(17)–O(63)	1.91 (2)	Zr(2)–O(70)	2.13 (2)
W(17)–O(58)	1.93 (2)	Zr(2)–O(32)	2.16 (2)
W(17)–O(57)	1.96 (2)	Zr(2)–O(55)	2.73 (3)
W(17)–O(53)	2.33 (2)	Zr(2)–O(15)	2.94 (3)
W(18)–O(68)	1.68 (3)	Zr(3)–O(34)	2.04 (2)
W(18)–O(65)	1.88 (2)	Zr(3)–O(39)	2.12 (2)
W(18)–O(64)	1.91 (2)	Zr(3)–O(40)	2.13 (2)
W(18)–O(59)	1.92 (2)	Zr(3)–O(70)	2.13 (2)
W(18)–O(58)	1.97 (2)	Zr(3)–O(33)	2.13 (2)
W(18)–O(53)	2.34 (2)	Zr(3)–O(71)	2.13 (2)
Zr(1)–O(35)	2.04 (2)	Zr(3)–O(56)	2.82 (3)
Zr(1)–O(71)	2.06 (2)	Zr(3)–O(16)	2.85 (3)
Si(1)–O(15)	1.61 (2)	Si(2)–O(55)	1.63 (2)
Si(1)–O(16)	1.61 (2)	Si(2)–O(53)	1.65 (2)
Si(1)–O(4)	1.63 (2)	Si(2)–O(54)	1.65 (2)
Si(1)–O(14)	1.64 (2)	Si(2)–O(56)	1.67 (2)

terminal aquo ligand. The smaller Zr atoms appear well shielded from ligation by solvent.

Table IV. Distances between Heavy Atoms (Å)

W(1)···W(2)	3.325 (3)	W(10)···W(11)	3.276 (3)
W(1)···W(3)	3.347 (3)	W(10)···W(15)	3.758 (3)
W(2)···W(3)	3.346 (3)	W(11)···W(12)	3.739 (3)
W(1)···W(4)	3.655 (3)	W(12)···W(13)	3.305 (3)
W(1)···W(5)	3.659 (3)	W(13)···W(14)	3.743 (3)
W(2)···W(6)	3.723 (3)	W(14)···W(15)	3.285 (3)
W(2)···W(7)	3.614 (3)	W(10)···W(16)	3.658 (3)
W(3)···W(8)	3.662 (3)	W(11)···W(16)	3.649 (3)
W(3)···W(9)	3.666 (3)	W(12)···W(17)	3.657 (3)
W(4)···W(5)	3.242 (3)	W(13)···W(17)	3.665 (3)
W(4)···W(9)	3.747 (3)	W(14)···W(18)	3.677 (3)
W(5)···W(6)	3.745 (3)	W(15)···W(18)	3.656 (3)
W(6)···W(7)	3.289 (3)	W(16)···W(17)	3.353 (3)
W(7)···W(8)	3.723 (3)	W(16)···W(18)	3.353 (3)
W(8)···W(9)	3.257 (3)	W(17)···W(18)	3.362 (3)
W(4)···Zr(1)	3.599 (5)	W(10)···Zr(1)	3.541 (5)
W(5)···Zr(1)	3.635 (5)	W(11)···Zr(1)	3.612 (5)
W(6)···Zr(2)	3.600 (5)	W(12)···Zr(2)	3.534 (5)
W(7)···Zr(2)	3.780 (5)	W(13)···Zr(2)	3.525 (5)
W(8)···Zr(3)	3.583 (5)	W(14)···Zr(3)	3.565 (5)
W(9)···Zr(3)	3.558 (5)	W(15)···Zr(3)	3.581 (5)
Zr(1)···Zr(2)	4.144 (6)	Zr(2)···Zr(3)	4.149 (6)
Zr(1)···Zr(3)	4.105 (6)		

The ^{183}W NMR in D_2O shows a two-line spectrum (Figure 1) at −140 and −189 ppm of 1:2 intensity, establishing that the overall (average) symmetry of the heteropolytungstate in solution is D_{3h}. Furthermore, the 14-Hz $^2J_{W-O-W}$ coupling constant is indicative of corner coupling between the tungsten octahedra in the "cap" and the tungsten octahedra in the "belt"[2a–e,3,29] and requires that the A-$SiW_9O_{34}^{10-}$ structure of the starting material,[16] confirmed by the structural analysis in the solid state, is maintained in solution.

Bu_4N^+ Salt. Precipitation of the zirconium-substituted heteropolytungstate from the initial reaction solution with Bu_4NBr yields the Bu_4N^+ salt. This compound is soluble in polar organic solvents such as CH_3CN, DMF, or DMSO but can be crystallized in modest yield from CH_3CN/CH_2Cl_2 by use of vapor-diffusion techniques. The compound shows the same IR characteristics as the Me_4N^+ salt described above, and elemental analysis again indicates the same composition $(SiW_9Zr_{1.5}O_{35\pm2})_n$.

The composition of the heteropolyanion (with its two SiW_9O_{34} units) was established by a FAB mass spectrum and verified in solution by an ultracentrifugation molecular weight measurement. The FAB negative ion spectrum shows peaks assignable to $[(Bu_4N)_{6-n}H_{1+n}Si_2W_{18}Zr_3O_{68}]^-$, $n = 0$–6, with losses due to O ($m/e = 16$), ZrO_2 ($m/e = 123$), and WO_3 ($m/e = 232$) as reported previously.[2h] The positive ion spectrum also shows peaks assignable to $[(Bu_4N)_{8-n}H_{1-n}Si_2W_{18}Zr_3O_{68}]^+$, where $n = 0$–3, as well as intervening ZrO_2 peaks. Since oxygen present as H_2O in the structure can be readily lost during the FAB-MS (or oxygens can be protonated by H^+ generated from the FAB matrix during the FAB process[30] and then lost as H_2O), there is always uncertainty between the peaks seen in the FAB-MS and structures of the same overall charge but differing in the elements of H_2O (e.g., between $Si_2W_{18}Zr_3O_{68}^{8-}$ and $H_6Si_2W_{18}Zr_3O_{71}^{8-}$). Because of this, we previously concluded the structure $[Si_2W_{18}Zr(OH_2)_3]_xO_{68}^{8-}$ ($x = 1$ or 2), was most likely. The $x = 1$ case, rewritten as $H_3Si_2W_{18}(ZrOH)_3O_{71}^{8-}$, can now be selected as consistent with all of the available data. A low-precision solution molecular weight (calcd 4781, found $\bar{M}_w = 4300 \pm 600$), confirms that the $Si_2W_{18}Zr_3$ composition persists even under the dilute (10^{-5}–10^{-6} M) concentrations of this molecular weight measurement.

A ^{183}W NMR spectrum in dry CD_3CN shows only broad, ill-defined resonances. Such situations have been previously observed and studied in detail; they are characteristic of certain heteropolyanions under conditions in which slow exchange of H^+ occurs.[2d,f,15,31] Consistent with such an interpretation, addition

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of pyrrolidine reveals the expected spectrum for D_{3h} symmetry, with two lines of approximate 2:1 intensity at −169.4 and −130.7 ppm, respectively. Unfortunately, the increased line widths often observed in organic solvents[2f] prevented determination of the $^2J_{W-O-W}$ coupling constant for the anion in these organic solvents.

Summary. The significant features of the reaction of A-β-$SiW_9O_{34}^{10-}$ with ZrO^{2+} in acidic, aqueous solution may be summarized as follows:

1. The chemical behavior observed appears much more similar to that reported for A-α-$PW_9O_{34}^{9-}$ with M^{2+} or M^{4+} species, in that products of the composition $X_2W_{18}M_3$ are formed (at least under the acidic conditions of the present synthesis) rather than the XW_9M_3 (Keggin-like) structures that have been observed for M = V^{5+},[2b,2f] Mo^{6+},[1a] W^{6+},[1a] and Ti^{4+}.[3e]

2. The product $Si_2W_{18}[ZrOH]_3O_{68}^{11-}$ exhibits characteristics similar to those reported for $P_2W_{18}[CeO]_3O_{68}^{14-}$, formed by the reaction of A-α-$PW_9O_{34}^{9-}$ with Ce^{4+}. These include (a) retention of the isomeric form of the lacunary heteropolytungstate upon complexation with these M^{4+} ions and (b) the presence of an extra "belt" comprised of M–O–M (M = Ce) or M–OH–M (M = Zr) units—a feature peculiar to only these two $X_2W_{18}M_3$ systems.

3. The absence of any coordinating water or terminal M═O bonds in the $Si_2W_{18}[ZrOH]_3O_{68}^{11-}$ anion is a feature unique to this $X_2W_{18}M_3$ molecule and can be explained by the steric effects of the SiW_9O_{34} fragments on the relatively small zirconium atoms, "tucking" the Zr_3O_3 belt into the center of the structure and thereby "protecting" them from OH_x coordination despite the high oxophilicity of zirconium.

4. The "$Si_2W_{18}Zr_3$" composition and structure are retained in solution as demonstrated by multinuclear NMR, solution molecular weight measurements, and FAB mass spectrometry.

Acknowledgment. Support during the course of this work from NSF Grant CHE-8313459 and from Dreyfus Teacher-Scholar, Alfred P. Sloan, and Guggenheim (1985–1986) Fellowships to R.G.F. is gratefully acknowledged. The fast atom bombardment mass spectra were obtained as previously described[2h] on a VG analytical ZAB-HF ultrahigh-resolution 8-kV mass spectrometer with a Model 11250 data system at the University of Illinois at Urbana-Champaign with the assistance of Dr. J. C. Cook and Professor K. S. Suslick. T.J.R.W. thanks the University of Oregon for a visiting Associate Professorship during his sabbatical year (1987–1988).

Supplementary Material Available: Tables of crystal parameters and data collection and refinement details, anisotropic parameters, bond lengths and angles in the cations, and intramolecular bond angles in the $Si_2W_{18}Zr_3O_{71}^{14-}$ anion (12 pages); listings of observed vs calculated structure factors (59 pages). Ordering information is given on any current masthead page.

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Contribution from GTE Laboratories Incorporated, Waltham, Massachusetts 02254, and the Departments of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121, and Brandeis University, Waltham, Massachusetts 02254

Structural and Magnetic Studies of Electrochemically Crystallized Halides of 1,4,5,8-Tetraselenonaphthalene (TSeN)

Lewis A. Acampora,[†] Boris S. Elman,[†] Daniel J. Sandman,[*,†] Susan Jansen,[‡,§] M. Thomas Jones,[‡]
Raymond D. Rataiczak,[‡,∥] and Bruce M. Foxman[⊥]

Received August 22, 1988

Experimental conditions are described for the growth of single crystals by anodic electrocrystallization of the isomorphous 1:1 chloride and bromide of 1,4,5,8-tetraselenonaphthalene (TSeN). A structural study was performed on the chloride for reasons of crystal quality, while physical studies were carried out on the more plentiful bromide, which was found to have a polycrystalline resistivity of 10^3–10^4 Ω cm. The chloride of TSeN, $[C_{10}H_4Se_4]Cl$, is an orthorhombic crystal of space group *Cmca* (D_{2h}^{18}; No. 64) with a = 19.110 (4) Å, b = 8.574 (2) Å, c = 13.437 (3) Å, V = 2201.6 Å^3, and Z = 8. The structure, solved by Patterson and difference-Fourier syntheses, is comprised of dimers of parallel TSeN cation radicals rather than infinite chains. Curie law behavior was observed in both static magnetic susceptibility and electron spin resonance studies of the bromide. The ESR spectral envelope is an example of an orthorhombic **g**-tensor system for which the intrinsic line width and the hyperfine anisotropy are much smaller than that of the **g** tensor. The line width of the solution ESR spectrum of the TSeN cation radical and the isotropic g value show a small solvent effect.

Introduction

We recently reported the synthesis, purification, and crystal and molecular structure of the organoselenium π-donor 1,8:4,5-bis(diseleno)naphthalene (tetraselenonaphthalene, TSeN, **1**).[1] Cyclic voltammetry and the solution electron spin resonance (ESR) spectrum of the cation radical revealed the electron-transfer properties of TSeN. We now focus our attention on the structure and properties of the solid ion-radical salts, in particular the chloride and bromide of TSeN, our motivation for undertaking the synthesis of TSeN.[1]

We[2] and others[3] have attempted the synthesis of TSeN ion-radical salts by solution charge transfer. This experimentation to date has led to neither highly conductive solids nor to any crystals whose structures have been determined.[4] Since our initial hope was to prepare the solids $(TSeN)_2X$ and since electrocrystallization is the technique of choice for the superconducting tetrachalcogenofulvalene salts of this stoichiometry,[5] experimentation along these lines was initiated.

Electrocrystallization experiments were attempted with a variety of anions under many different conditions, but experimentally

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[†] GTE Laboratories.
[‡] University of Missouri—St. Louis.
[§] Present address: Department of Chemistry, Temple University, Philadelphia, PA 19122.
[∥] Permanent address: Department of Chemistry, Muskingum College, New Concord, OH 43762.
[⊥] Brandeis University.

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(4) Very recently, solution charge-transfer experiments at the University of Missouri—St. Louis have led to single crystals of a solid of the composition (by elemental analysis) $(TSeN)I_2$. Additionally, samples of a chloride and bromide of TSeN different (by X-ray powder diffraction) from those described herein have been obtained as well as a new trifluoroacetate. The electrical, magnetic, and structural properties of these solids will be discussed separately.
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