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Synthesis, Characterization, and Interconversion of the Niobotungstic Acid $Nb_2W_4O_{19}H^{3-}$, Its Anhydride, and Its Alkyl/Silyl Esters

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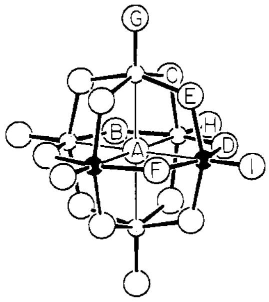
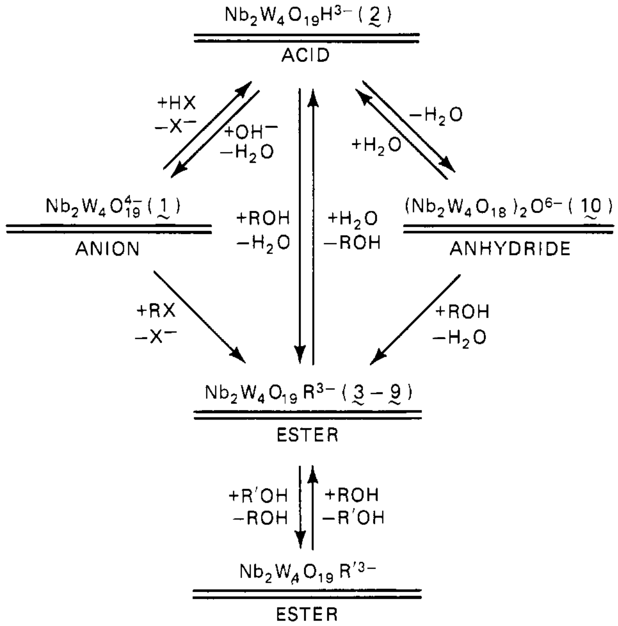
Abstract: The compounds $Nb_2W_4O_{19}R[(n\text{-}C_4H_9)_4N]_3$ (R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, $Si(CH_3)_3$, $Si(CH_3)_2[C(CH_3)_3]$, and $Si(C_6H_5)_3$) have been prepared according to the equation $Nb_2W_4O_{19}H^{3-} + ROH = Nb_2W_4O_{19}R^{3-} + HOH$ and isolated in crystalline form. For R = CH_3 and CH_2CH_3 only, the alkoxy group occupies a bridging position between two niobiums in the $Nb_2W_4O_{19}R^{3-}$ framework. The bulkier alkoxy/siloxy groups are bonded terminally to a single niobium center. Dissolution of $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ into dry CH_2Cl_2 results in the formation of the anhydride $(Nb_2W_4O_{18})_2O^{6-}$ as a tetra-*n*-butylammonium salt. Reaction of $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ with RX (R = CH_3, CH_2CH_3; X = OSO_2R) yields $Nb_2W_4O_{19}R[(n\text{-}C_4H_9)_4N]_3$ in which the $Nb_2W_4O_{19}R^{3-}$ anion exists as a mixture of five diastereomers where the R groups bind to five nonequivalent types of $Nb_2W_4O_{19}{}^{4-}$ doubly bridging oxygens. Analogous reactions of $Nb_2W_4O_{19}{}^{4-}$ with RX {R = $CH(CH_3)_2$, $Si(CH_3)_2[C(CH_3)_3]$, X = O_3SCF_3; R = $Si(CH_3)_3$, X = Cl, $NHSi(CH_3)_3$} yields $Nb_2W_4O_{19}R^{3-}$ anions where the R groups bind exclusively to a terminal ONb oxygen in $Nb_2W_4O_{19}{}^{4-}$. Protonation of the $Nb_2W_4O_{19}{}^{4-}$ ion occurs predominantly at the unique bridging ONb_2 oxygen. The structure and reactivity of the $Nb_2W_4O_{19}{}^{4-}$ ion and its derivatives are thus seen to reflect the relative labilities of different types of metal–oxygen bonds, the steric environments of different surface oxygens, and the surface charge distribution in the $Nb_2W_4O_{19}{}^{4-}$ framework. Specifically, niobium–oxygen bonds are far more labile than tungsten–oxygen bonds, bridging oxygens occupy a more sterically congested environment than terminal oxygens, bridging oxygens are more basic/nucleophilic than terminal oxygens, the ONb_2 oxygens are marginally the most basic/nucleophilic bridging oxygens, and the ONb oxygens are by far the most nucleophilic terminal oxygens.

The tremendous progress achieved in early transition-metal polyoxoanion chemistry during the past 40 years can be attributed in large part to the availability of sophisticated structural techniques capable of elucidating extremely complex metal oxide structures in the solid state (single-crystal X-ray diffraction) and solution (multinuclear NMR spectroscopy).[2] In spite of this progress, however, relatively little is understood concerning the reactivity of polyoxoanions and the pathways available for the interconversion of various structural types. Our interest in developing new synthetic routes to covalent polyoxoanion derivatives has led us to examine the relationships between polyoxoanion structure and reactivity in some detail in order to better understand how various electronic and steric factors influence the course of polyoxoanion transformations.[3] We report here a detailed study of some pathways for interconverting the C_{2v}-$Nb_2W_4O_{19}{}^{4-}$ anion[4] (see **a**), its conjugate acid $Nb_2W_4O_{19}H^{3-}$,[5] its acid anhydride $(Nb_2W_4O_{18})_2O^{6-}$, and the alkyl/silyl esters $Nb_2W_4O_{19}R^{3-}$, pathways summarized in Scheme I.



a

Scheme I



3: R = CH_3 **4**: R = CH_2CH_3 **5**: R = $CH(CH_3)_2$
6: R = $C(CH_3)_3$ **7**: R = $Si(CH_3)_3$
8: R = $Si(CH_3)_2[C(CH_3)_3]$ **9**: R = $Si(C_6H_5)_3$

The $Nb_2W_4O_{19}{}^{4-}$ system shown in Scheme I was selected for investigation with several features in mind. First, the $Nb_2W_4O_{19}{}^{4-}$ is known to be sufficiently basic to form stable organometallic derivatives[6-8] and can therefore be reasonably expected to form stable covalent organic derivatives $Nb_2W_4O_{19}R^{3-}$, where R is an

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(1) (a) Crystalytics Company and University of Nebraska. (b) University of Illinois.

(2) Pope, M. T. *Heteropoly and Isopolyoxometalates*; Springer-Verlag: Berlin, Heidelberg, 1983.

(3) Day, V. W.; Klemperer, W. G. *Science (Washington, D.C.)* **1985**, *228*, 533.

(4) (a) Dabbabi, M.; Boyer, M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1011. (b) Rocchiccioli-Deltcheff, C.; Thouvenot, R.; Dabbabi, M. *Spectrochim. Acta, Part A* **1977**, *33A*, 143. (c) Dabbabi, M; Boyer, M.; Launay, J.-P.; Jeannin, Y. *J. Electroanal. Chem.* **1977**, *76*, 153.

(5) Dabbabi, M.; Boyer, M.; Souchay, P. *C. R. Acad. Sci., Ser. C* **1974**, *278*, 1047.

(6) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125.

(7) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Inorg. Chem.* **1985**, *24*, 44.

(8) Besecker, C. J.; Klemperer, W. G.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 6158.

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alkyl or silyl group. Second, the niobium–oxygen bonds in $Nb_2W_4O_{19}^{4-}$ are known to be much more labile than the tungsten–oxygen bonds with respect to oxide exchange with water.[6] This implies that transformations involving oxide transfer should generally be feasible with retention of the $Nb_2W_4O_{19}^{4-}$ structural framework, since only three of its 19 oxygen centers are bound solely to niobium centers, O_F and O_I in **a**, and are thus likely to be removed from the structure under mild reaction conditions. Third, the d^0 $Nb_2W_4O_{19}^{4-}$ anion is a poor oxidizing agent,[4c] and redox reactions involving alcohols and alkoxide groups can be avoided, a complication more likely in d^0 vanadium or molybdenum-containing polyoxoanions. Finally, the $Nb_2W_4O_{19}^{4-}$ structure is comprised of three layers of closest packed oxygens arranged in a cubic closest packed sequence,[3] with metal centers occupying octahedral interstices, and is therefore a rigid, bulky molecular ion. As a result, steric factors are believed to influence its surface reactivity,[6] and these factors might be systematically explored by varying the steric bulk of the substituent R in the esters $Nb_2W_4O_{19}R^{3-}$.

A principal focus of the present study is the reaction of alcohols with the acid $Nb_2W_4O_{19}H^{3-}$, the anhydride $(Nb_2W_4O_{18})_2O^{6-}$, and the esters $Nb_2W_4O_{19}R'^{3-}$ to form esters $Nb_2W_4O_{19}R^{3-}$. Although these types of reactions are reported here for the first time in an early transition-metal polyoxoanion system, two of them are well-known in solid-state systems. The esterification of $Nb_2W_4O_{19}H^{3-}$ corresponds to dissociative alcohol chemisorption on a hydroxylated oxide surface, and the alcoholysis of $(Nb_2W_4O_{18})_2O^{6-}$ corresponds to dissociative alcohol chemisorption on a dehydrated oxide surface. Three of the other reaction types shown in Scheme I, namely, protonation, alkylation, and silylation, are of interest since they provide an opportunity to study the relative basicities and nucleophilicities of different types of $Nb_2W_4O_{19}^{4-}$ surface oxygens. The self-condensation of $Nb_2W_4O_{19}H^{3-}$ similarly provides a unique opportunity to examine the equilibrium governing the most fundamental growth process in polyoxoanion chemistry. Finally, some effort has been devoted to an examination of nonprotic oxide acceptor reagents that can convert the $Nb_2W_4O_{19}^{4-}$ anion directly to the $(Nb_2W_4O_{18})_2O^{6-}$ anhydride. The reagents employed all utilize carbonyl groups, in either carbon dioxide or transition-metal carbonyl clusters.

Results

The key experimental data used to characterize the new compounds and reactions shown in Scheme I will be summarized here in a selective fashion according to reaction type. A complete presentation of experimental results is given in the Experimental Section below, where data are organized when possible according to reaction products. All of the anions described below were prepared as colorless $(n\text{-}C_4H_9)_4N^+$ salts in analytically pure, crystalline form. The yields cited refer to isolated yields and are generally substantially lower than the actual yields in solution since isolation in each case involves selective precipitation and/or recrystallization.

Anion Protonation, Alkylation, and Silylation. The $Nb_2W_4O_{19}^{4-}$ anion, **1**, reacts with chloroacetic acid, alkylating agents, and silylating agents according to reaction 1 to yield the derivatives $Nb_2W_4O_{19}R^{3-}$.

$$Nb_2W_4O_{19}^{4-} \xrightarrow[-X^-]{+RX} \underset{\mathbf{2\text{-}8}}{Nb_2W_4O_{19}R^{3-}} \qquad (1)$$

2, R = H; X = $ClCH_2CO_2$
3, R = CH_3; X = CH_3OSO_3
4, R = CH_2CH_3; X = $CH_3CH_2OSO_3$
5, R = $CH(CH_3)_2$; X = CF_3SO_3
7, R = $Si(CH_3)_3$; X = $Cl/NHSi(CH_3)_3$
8, R = $Si(CH_3)_2[C(CH_3)_3]$; X = CF_3SO_3

Crystal structure analysis revealed that single crystals of **3** are composed of discrete $Nb_2W_4O_{19}CH_3^{3-}$ anions (Figure 1) and $(n\text{-}C_4H_9)_4N^+$ cations (Figure 2[9]). Final atomic coordinates and anisotropic thermal parameters for the solid-state structure of **3** are listed with estimated standard deviations in Tables I, II,[9] and III.[9] Bond lengths and angles for the anion and three independent cations are listed in Tables IV and V,[9] respectively. These data clearly show that a doubly bridging oxygen is methylated and that this oxygen is pyramidal. The polyoxoanion metal positions are disordered in the solid state with each metal site having some Nb and some W character: M_1, 50.4% W; M_2, 77.3% W; M_3, 64.2% W; M_4, 35.3% W; M_5, 76.8% W; M_6, 96.0% W. This nonstatistical distribution of the two Nb atoms among the six metal sites is the result of isomorphous cocrystallization of all or some of the 12 possible stereoisomers (seven diastereomers, five of which are chiral) obtained by methylation of the *cis*-$Nb_2W_4O_{19}^{4-}$ anion at doubly bridging oxygen sites, with the methyl group of each occupying the same lattice site. The average $M\text{-}O_B$ bond length of 2.14 (1, 6, 6, 2) Å[10] is 0.22 Å longer than the 1.92 (1, 4, 12, 22) Å average for the other doubly bridging oxygens in **3**, and each $M\text{-}O_B$ bond is ≥0.04 Å longer than the M–O bond to any nonmethylated doubly bridging oxygen. The angles at O_B are 0.8–11.2° larger than the idealized tetrahedral value of 109.5°. They sum to a value of 347° or 13° less than the idealized trigonal-planar sum of 360° but 19° greater than the tetrahedral sum of 328°.

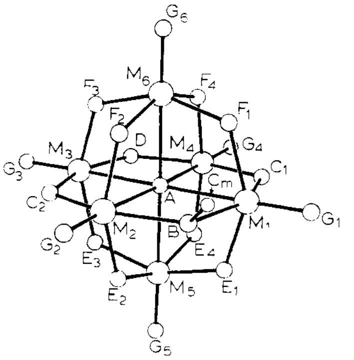

Figure 1. Persective drawing of the $Nb_2W_4O_{19}CH_3^{3-}$ anion in crystalline **3**. For purposes of clarity, metal atoms are represented by large open circles and oxygen and carbon atoms by small open circles; hydrogen atoms were not located. All six metal sites ($M_1 \rightarrow M_6$) are disordered with the following percentages of W character at each: M_1, 50.4; M_2, 77.3; M_3, 64.2; M_4, 35.3; M_5, 76.8; M_6, 96.0. Oxygen atoms are labeled only by their subscripts and the methyl carbon is labeled as C_m.

Solution ^1H NMR spectra of anion **3** prepared by reaction 1 display five major methyl resonances (see Figure 3a) as do $^{13}C\{^1H\}$ spectra of the same sample. Methylation of $Nb_2W_4O_{19}^{4-}$ with dimethyl sulfate thus yields a mixture of five distinct, diastereomeric $Nb_2W_4O_{19}CH_3^{3-}$ anions containing methoxy groups in the five possible doubly bridging sites in $Nb_2W_4O_{19}^{4-}$, namely, sites B, C, D, E, and F in **a** (see **b**–**f**).[11]

According to IR and $^{13}C\{^1H\}$ NMR spectroscopic data, the $Nb_2W_4O_{19}CH_2CH_3^{3-}$ anion, **4**, is also prepared as a mixture of five diastereomers,[11] where the ethoxy group occupies a different doubly bridging site in each isomer. IR spectra of **3** (see Figure 4c) and **4** are virtually identical in the 650–1000 cm⁻¹ metal–oxygen vibration region and C–O stretching vibrations have the expected[12] relative frequencies at 1012 and 1028 cm⁻¹ for **3** and **4**, respectively. $^{13}C\{^1H\}$ NMR spectra of **4** show five methylene resonances analogous to the five methyl resonances observed for **3**.

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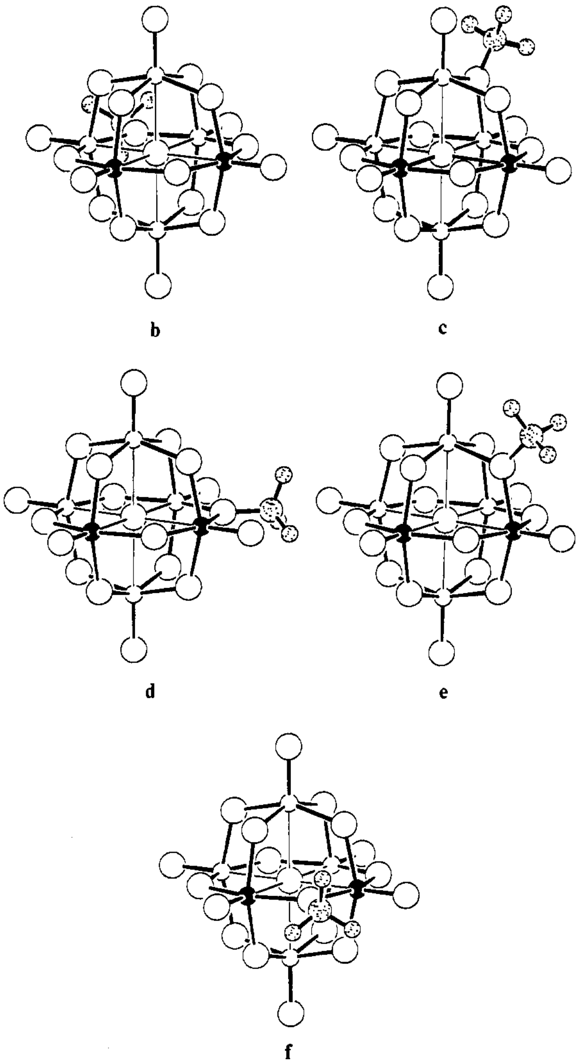
(9) See paragraph at end of paper regarding supplementary material.

(10) The first number in parentheses following an average value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the average value, respectively. The fourth number represents the number of individual measurements that are included in the average value.

(11) Rigorously, seven diastereomers are possible since the alkylated oxygen is pyramidal, not planar. Since oxygen inversion is undoubtedly rapid on the NMR time scale, only five of the diastereomers are regarded as distinct in order to simplify discussion.

(12) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3d ed.; Chapman and Hall: London, 1975; p 123.



The IR spectra of $Nb_2W_4O_{19}H^{3-}$ (Figure 4b) and $Nb_2W_4O_{19}CH_3^{3-}$ (Figure 4c) are virtually identical in the 650–1000 cm^{-1} region, indicating that the $Nb_2W_4O_{19}^{4-}$ anion is protonated at a doubly bridging oxygen site. Comparison of the ^{17}O NMR spectra of $Nb_2W_4O_{19}^{4-}$ (**1**) in CH_3CN and $Nb_2W_4O_{19}H^{3-}$ (**2**) in CH_3CN/H_2O shows a 304 ppm upfield shift of the ONb_2 resonance in $Nb_2W_4O_{19}^{4-}$ upon protonation and a 7–27 ppm downfield shift of the resonances for the remaining $Nb_2W_4O_{19}^{4-}$ surface oxygens (see Figure 5 and Table VI). This pattern of behavior indicates that anion **2** is protonated predominantly at its ONb_2 oxygen, O_F in **a**.[3,13,14]

The IR spectrum of $Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]^{3-}$ (Figure 4e) differs significantly from the spectra of the protonated and methylated $Nb_2W_4O_{19}^{4-}$ anions (parts b and c of Figure 4), suggesting that the compounds have different structures. A single-crystal X-ray diffraction study of $\{Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]\}[(n\text{-}C_4H_9)_4N]_3$ (**8**) was therefore performed to identify the structure of the anion. Crystal structure analysis revealed that single crystals of **8** are composed of discrete $Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]^{3-}$ anions (Figure 6) and $(n\text{-}C_4H_9)_4N^+$ cations (Figure 7[9]). Final atomic coordinates and anisotropic thermal parameters for the solid-state structure of **8** are listed with estimated standard deviations in Tables VIII and IX.[9] Bond lengths and angles for the anion and three independent cations are listed in Tables X and XI,[9] respectively. These data clearly show that an oxygen terminally bonded to niobium is silylated. The four metal sites that are cis to this Nb in the solid-state structure are disordered with the following percentages of Nb character: M_1, 9.2; M_2, 27.3; M_3, 12.0; M_4, 51.5. The metal site that is trans to the Nb has 100% W character. These percentages presumably result from a nonstatistical isomorphous cocrystallization of the four rotamers that have the same orientations of the $Si(CH_3)_2$-

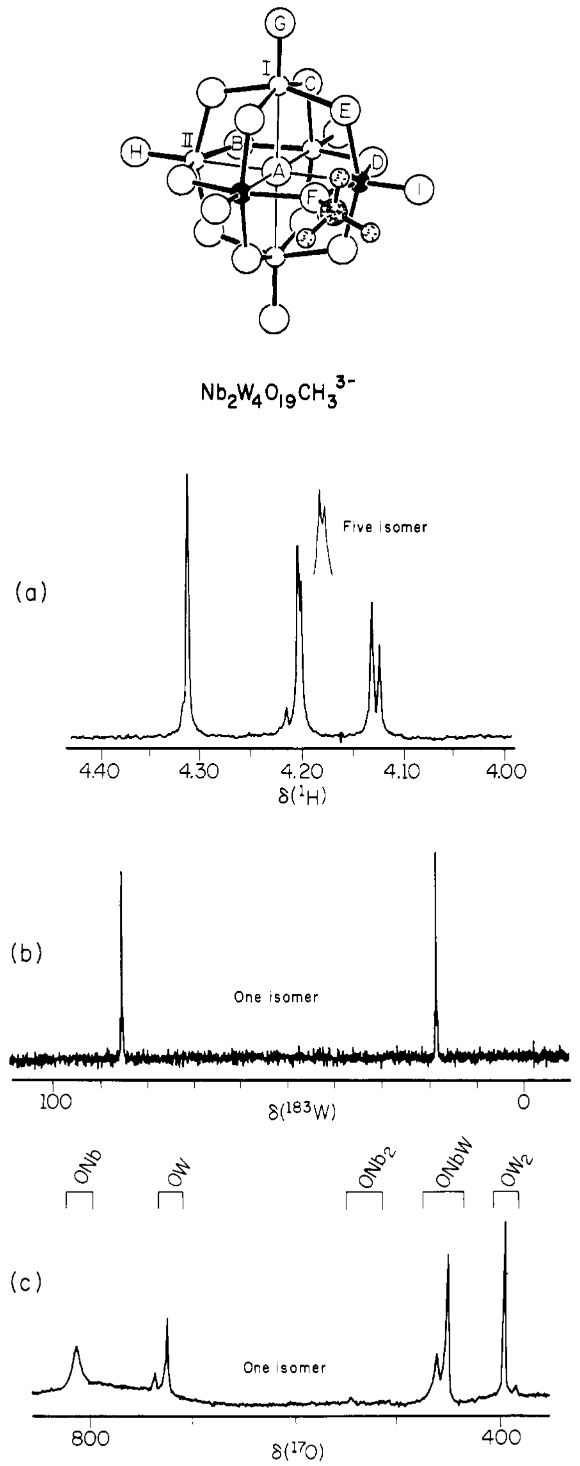


Figure 3. Top: SCHAKAL drawing of the C_{2v}-$Nb_2W_4O_{19}CH_3^{3-}$ isomer containing an ONb_2-bound methyl group. The shaded circles represent the methyl group. Small filled and small open circles represent niobium and tungsten atoms, respectively. Large open circles represent oxygen atoms. One member of each set of symmetry equivalent oxygen and tungsten atoms is labeled. (a) 360-MHz ^{1}H NMR spectrum of $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$, prepared as a five-diastereomer mixture, in acetonitrile. (b) 16.7-MHz ^{183}W NMR spectrum of $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_3$, prepared as one isomer, in acetonitrile. (c) 33.9-MHz ^{17}O NMR spectrum of $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$, prepared as one isomer, in acetonitrile. See Experimental Section and Tables VI and VII for numerical data and experimental parameters.

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[13] (a) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 3544. (b) Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 2991.

[14] Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1978**, *100*, 4891.

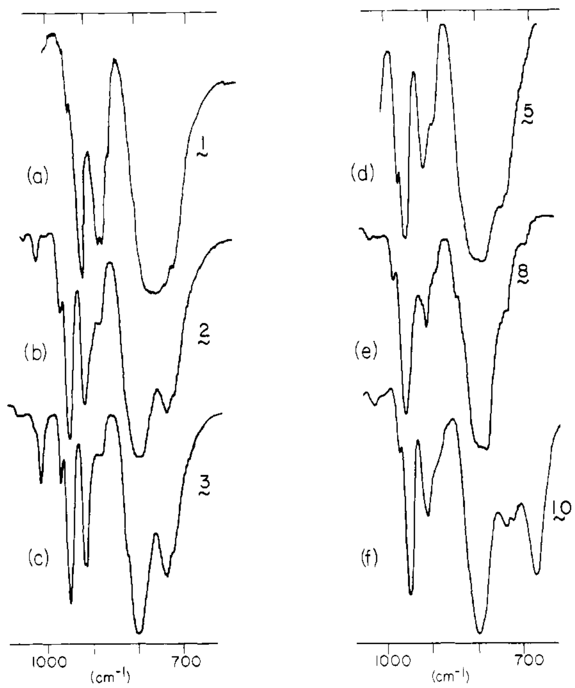

Figure 4. Infrared spectra measured from Nujol mulls of tetrabutylammonium salts of (a) *cis*-$Nb_2W_4O_{19}^{4-}$, (b) $Nb_2W_4O_{19}H^{3-}$, (c) $Nb_2W_4O_{19}CH_3^{3-}$ (five-diastereomer mixture), (d) $Nb_2W_4O_{19}CH(CH_3)_2^{3-}$, (e) $Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]^{3-}$, and (f) $(Nb_2W_4O_{18})_2O^{6-}$. For numerical data, see ref 6 for (a) and Experimental Section for (b)–(f).

$[C(CH_3)_3]$ group relative to the M_6O_{19} cage. This presumption is supported by the ^{183}W solution NMR spectrum of anion **8** (see Figure 8) that displays three resonances having relative intensities of 1:2:1. The $Nb–O_B$ bond is ≥ 0.14 Å longer than any other terminal M–O bond in **8**.

The IR spectra of $Nb_2W_4O_{19}CH(CH_3)_2^{3-}$ (**5**) shown in Figure 4d and $Nb_2W_4O_{19}Si(CH_3)_3^{3-}$ (**7**) and $Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]^{3-}$ (**8**) shown in Figure 5e are all similar in the 650–1000 cm^{-1} region, reflecting a common structure containing terminal alkoxy/siloxy groups. Tungsten-183 NMR spectra of **7** and **8** have also been measured, and they both show the expected three resonances with relative intensities 1:2:1 (see Table VII). Although these NMR data are consistent with alkoxy/siloxy groups occupying terminal niobium sites (O_I in **a**) or terminal tungsten sites (O_G or O_H in **a**), the very similar ^{183}W NMR chemical shifts observed for **7** and **8** (see Table VII) plus the independent synthesis of **5**, **7**, and **8** by esterification (see below) are consistent only with occupation of terminal niobium sites.

In summary, the $Nb_2W_4O_{19}^{4-}$ anion reacts with a variety of electrophiles to yield derivatives $Nb_2W_4O_{19}R^{3-}$, where the R group binds exclusively to a terminal ONb oxygen when R = $(CH_3)_2CH$, $(CH_3)_3Si$, and $[(CH_3)_3C](CH_3)_2Si$ and binds to bridging OM_2 oxygens, M = W and/or Nb, when R = H, CH_3, and CH_3CH_2. In the case of methylation and ethylation, all OW_2, ONbW, and ONb_2 oxygens are alkylated. In the protonated derivative, the proton binds predominantly to an ONb_2 oxygen.

Acid Esterification. Reaction of $Nb_2W_4O_{19}H^{3-}$ with excess alcohol or silanol ROH yields the esters $Nb_2W_4O_{19}R^{3-}$ according to reaction 2.

$$Nb_2W_4O_{19}H^{3-} \xrightarrow[-H_2O]{+ROH} \underset{\mathbf{3–9}}{Nb_2W_4O_{19}R^{3-}} \qquad (2)$$

3, R = CH_3
4, R = CH_2CH_3
5, R = $CH(CH_3)_2$
6, R = $C(CH_3)_3$
7, R = $Si(CH_3)_3$
8, R = $Si(CH_3)_2[C(CH_3)_3]$
9, R = $Si(C_6H_5)_3$

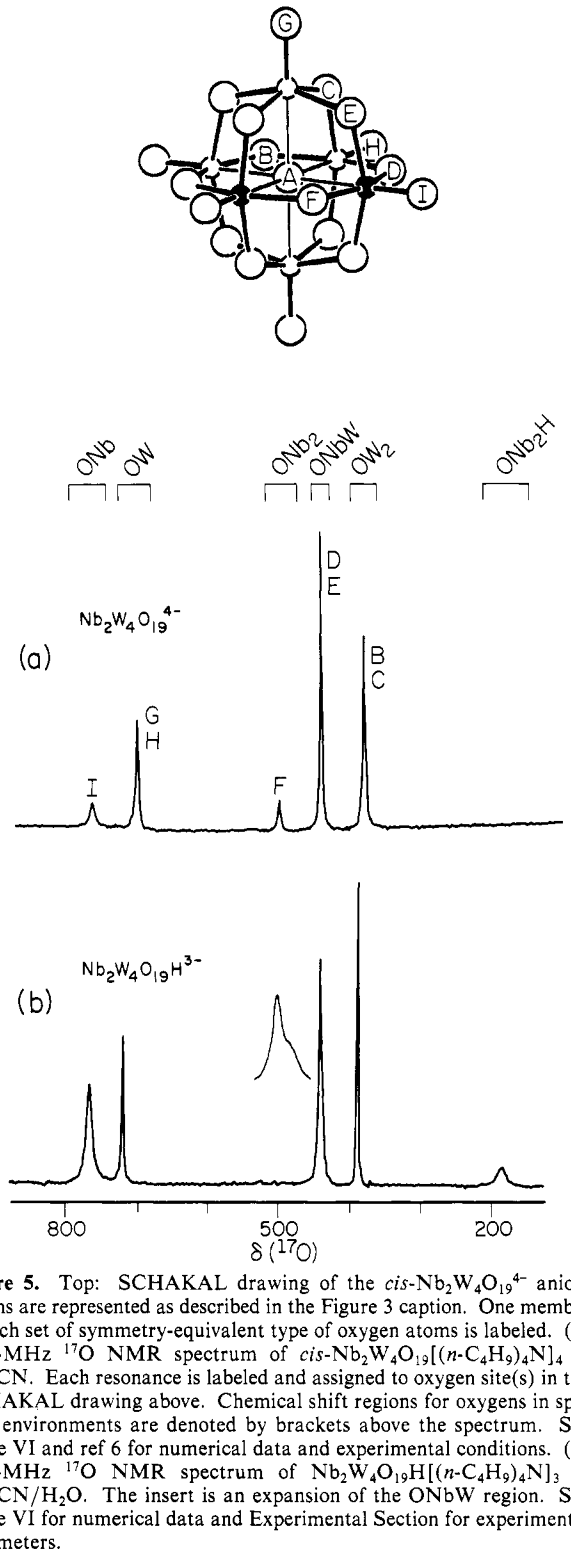

Figure 5. Top: SCHAKAL drawing of the *cis*-$Nb_2W_4O_{19}^{4-}$ anion. Atoms are represented as described in the Figure 3 caption. One member of each set of symmetry-equivalent type of oxygen atoms is labeled. (a) 33.9-MHz ^{17}O NMR spectrum of *cis*-$Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ in CH_3CN. Each resonance is labeled and assigned to oxygen site(s) in the SCHAKAL drawing above. Chemical shift regions for oxygens in specific environments are denoted by brackets above the spectrum. See Table VI and ref 6 for numerical data and experimental conditions. (b) 33.9-MHz ^{17}O NMR spectrum of $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ in CH_3CN/H_2O. The insert is an expansion of the ONbW region. See Table VI for numerical data and Experimental Section for experimental parameters.

The $Nb_2W_4O_{19}R^{3-}$ esters, R = CH_3 (**3**) and C_2H_5 (**4**), are obtained as single, isostructural isomers when prepared by esterification as opposed to alkylation. Each of these species displays only one type of alkoxy group in its ^1H and $^{13}C\{^1H\}$ NMR spectra, and the chemical shifts observed are identical with the chemical shifts observed for the alkoxy group in one of the five diastereomers obtained by alkylation of $Nb_2W_4O_{19}^{4-}$. The precise location of the bridging alkoxide group was established for the methyl ester **3** by using ^{183}W and ^{17}O NMR spectroscopy. Since the ^{183}W NMR spectrum of **3** as a single isomer shows only two resonances of equal intensity (see Figure 3b), the single $Nb_2W_4O_{19}CH_3^{3-}$ isomer must possess C_{2v} symmetry and thus be isomer **b** or **f** shown

Table I. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ (**3**)[a]

atom type[b]	10^4x	10^4y	10^4z	equiv isotropic thermal parameter,[c] B, Å^2	atom type[b]	10^4x	10^4y	10^4z	equiv isotropic thermal parameter,[c] B, Å^2
Anion									
M_1^d	2511.8 (7)	3733.2 (5)	755.4 (4)	3.02 (4)	O_{E3}	1540 (6)	3076 (5)	1977 (5)	3.1 (5)
M_2^d	661.8 (6)	3416.3 (4)	1071.4 (5)	4.11 (4)	O_{E4}	2960 (6)	3310 (5)	1734 (5)	3.8 (5)
M_3^d	1360.3 (6)	2425.7 (5)	1645.4 (5)	3.60 (4)	O_{F1}	2230 (6)	3114 (5)	393 (4)	2.7 (4)
M_4^d	3109.2 (7)	2721.7 (5)	1348.8 (5)	2.96 (5)	O_{F2}	828 (6)	2917 (6)	646 (5)	4.5 (5)
M_5^d	2025.6 (6)	3712.3 (4)	1735.6 (4)	3.28 (3)	O_{F3}	1373 (6)	2100 (5)	1116 (6)	4.0 (5)
M_6^d	1790.9 (5)	2478.0 (4)	645.4 (4)	3.42 (3)	O_{F4}	2781 (6)	2313 (5)	869 (5)	3.7 (5)
O_A	1890 (6)	3107 (5)	1171 (5)	3.2 (5)	O_{G1}	2880 (7)	4188 (6)	423 (5)	5.2 (4)
O_B	1309 (7)	3938 (5)	698 (6)	5.0 (6)	O_{G2}	−205 (7)	3698 (6)	944 (7)	7.9 (8)
O_{C1}	3348 (6)	3302 (5)	953 (5)	3.0 (5)	O_{G3}	974 (7)	1971 (5)	1969 (5)	4.9 (5)
O_{C2}	450 (6)	2857 (5)	1425 (5)	3.9 (5)	O_{G4}	3997 (7)	2444 (6)	1464 (5)	5.4 (6)
O_D	2416 (6)	2259 (4)	1683 (4)	3.0 (4)	O_{G5}	2084 (7)	4137 (6)	2115 (5)	4.9 (5)
O_{E1}	2413 (7)	4113 (5)	1256 (5)	4.2 (5)	O_{G6}	1698 (7)	2077 (7)	259 (5)	5.4 (4)
O_{E2}	1005 (7)	3873 (5)	1491 (5)	4.9 (6)	C_m	1043 (12)	4094 (9)	273 (9)	5.5 (9)
Cation 1									
N	3370 (9)	733 (7)	1530 (7)	5 (1)	C_{g1}	3142 (17)	795 (15)	282 (14)	17 (2)
C_{a1}	3275 (12)	952 (9)	1076 (8)	6 (1)	C_{g2}	5370 (14)	−5 (11)	1502 (14)	17 (2)
C_{a2}	3963 (12)	286 (8)	1520 (11)	9 (1)	C_{g3}	3876 (13)	1619 (8)	2525 (11)	11 (1)
C_{a3}	3559 (12)	1220 (8)	1810 (8)	6 (1)	C_{g4}	1286 (16)	415 (15)	1838 (18)	17 (3)
C_{a4}	2651 (10)	419 (8)	1642 (10)	7 (1)	C_{d1}	3888 (18)	881 (20)	135 (19)	22 (3)
C_{b1}	3088 (15)	559 (11)	721 (11)	11 (2)	C_{d2}	5742 (30)	7 (20)	1214 (24)	26 (4)
C_{b2}	4741 (12)	489 (10)	1404 (12)	12 (2)	C_{d3}	4019 (18)	1510 (13)	2973 (11)	12 (1)
C_{b3}	3695 (12)	1104 (10)	2235 (10)	7 (1)	C_{d4}	1024 (25)	316 (24)	2171 (16)	25 (3)
C_{b4}	1958 (12)	762 (9)	1686 (12)	11 (2)					
Cation 2									
N	−1047 (10)	1954 (8)	414 (7)	4 (1)	C_{g1}	568 (14)	868 (10)	642 (13)	13 (2)
C_{a1}	−321 (10)	1670 (9)	604 (8)	6 (1)	C_{g2}	−2582 (17)	887 (13)	805 (11)	11 (1)
C_{a2}	−1698 (11)	1524 (9)	414 (10)	8 (1)	C_{g3}	−2178 (14)	3217 (13)	882 (13)	13 (2)
C_{a3}	−1243 (12)	2451 (11)	687 (11)	9 (1)	C_{g4}	−97 (14)	2635 (12)	−567 (9)	10 (1)
C_{a4}	−911 (11)	2122 (10)	−38 (9)	6 (1)	C_{d1}	995 (16)	489 (10)	334 (14)	12 (2)
C_{b1}	13 (13)	1200 (10)	365 (10)	7 (1)	C_{d2}	−2312 (18)	340 (14)	606 (12)	10 (1)
C_{b2}	−1969 (14)	1341 (11)	857 (9)	9 (1)	C_{d3}	−2821 (14)	3540 (17)	781 (13)	15 (2)
C_{b3}	−1936 (12)	2769 (11)	567 (11)	10 (1)	C_{d4}	539 (15)	3011 (12)	−654 (11)	10 (1)
C_{b4}	−272 (10)	2528 (8)	−124 (8)	5 (1)					
Cation 3									
N	5378 (10)	3523 (7)	1990 (7)	4 (1)	C_{g1}	3862 (14)	3188 (15)	2901 (13)	15 (2)
C_{a1}	4644 (11)	3389 (9)	2244 (8)	6 (1)	C_{g2}	6474 (15)	2112 (11)	1981 (10)	10 (1)
C_{a2}	5950 (12)	3074 (9)	2055 (8)	6 (1)	C_{g3}	6585 (13)	4888 (9)	2032 (10)	9 (1)
C_{a3}	5713 (12)	4050 (9)	2164 (9)	6 (1)	C_{g4}	4776 (13)	4192 (11)	935 (11)	7 (1)
C_{a4}	5212 (10)	3574 (8)	1541 (8)	5 (1)	C_{d1}	3459 (18)	3562 (18)	2874 (15)	17 (2)
C_{b1}	4592 (15)	3315 (15)	2659 (10)	12 (2)	C_{d2}	6335 (20)	1541 (16)	1895 (16)	17 (2)
C_{b2}	5792 (14)	2503 (9)	1987 (11)	10 (1)	C_{d3}	7305 (13)	5091 (12)	1887 (11)	9 (1)
C_{b3}	6413 (12)	4295 (9)	1930 (10)	6 (1)	C_{d4}	5487 (15)	4474 (12)	784 (12)	11 (2)
C_{b4}	4725 (13)	4064 (10)	1392 (9)	5 (1)					

[a] Numbers in parentheses are the estimated standard deviation in the last significant digit. [b] Atoms are labeled in agreement with Figures 1 and 2.[9] [c] This is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor. [d] The four W and two Nb atoms appear to be disordered among the six M_i sites in the lattice with the following W percentages: M_1, 50.4; M_2, 77.3; M_3, 64.2; M_4, 35.3; M_5, 76.8; M_6, 96.0.

above. The ^{17}O NMR spectrum shown in Figure 3c resolves this ambiguity. Since no ONb_2 oxygen resonance is observed, structure **b** can be ruled out and structure **f** assigned to the compound. The ethyl analogue is assumed to be isostructural. IR spectra of **3** and **4** as single isomers are virtually identical in the 650–1000 cm^{-1} region and differ from the spectra of the same materials obtained as five-isomer mixtures only in having slightly narrower bandwidths and hence better resolution.

By employing ^{18}O-labeled alcohol, it is possible to demonstrate that esterification of $Nb_2W_4O_{19}H^{3-}$ proceeds with retention of the alkoxy oxygen and by inference loss of polyoxoanion oxygen. Reaction of $Nb_2W_4O_{19}H^{3-}$ with $CH_3CH_2{}^{18}OH$ yields a single isomer of **4** whose IR spectrum is identical with the spectrum of material prepared from $CH_3CH_2{}^{16}OH$ in the 650–1000 cm^{-1} region but shows a C–O stretching vibration frequency of 1004 cm^{-1}, a value shifted 24 cm^{-1} from the 1028 cm^{-1} value observed for unenriched material.[15] The result is hardly surprising in light of the known lability of O–Nb bonds in $Nb_2W_4O_{19}{}^{4-}$ [6] and is assumed to hold true for the other alcohol esterification reactions described here.

All attempts to isomerize the $Nb_2W_4O_{19}CH_3{}^{3-}$ anion were unsuccessful. Refluxing acetonitrile solutions of **3** as either a single isomer or a five diastereomer mixture resulted in no net isomerization according to ^1H NMR spectroscopy, even when catalytic amounts of dimethyl sulfate or pyridine were added. Addition of 1 equiv of dimethyl sulfate to an acetonitrile solution containing 1 equiv of $Nb_2W_4O_{19}{}^{4-}$ plus 1 equiv of $Nb_2W_4O_{19}CH_3{}^{3-}$, prepared as a single isomer, yielded a product mixture whose ^1H NMR spectrum was a 1:1 superposition of **3** prepared as a five diastereomer mixture and **3** prepared as a single isomer. Equilibrium did not occur under alkylation conditions,[16] and alkylation must therefore be kinetically controlled.

The remaining alkyl esters $Nb_2W_4O_{19}R^{3-}$, R = $CH(CH_3)_2$ (**5**) and $C(CH_3)_3$ (**6**), prepared by eq 2, display almost indistinguishable IR spectra in the 650–1000 cm^{-1} region and are assumed

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(15) *cf.* Dimroth, K.; Berndt, A.; Volland, R. *Chem. Ber.* **1966**, *99*, 3040.

(16) This conclusion is made on the assumption that $[CH_3OSO_2][(n\text{-}C_4H_9)_4N]$, as byproduct of reaction, does not catalyze isomerization.

Table IV. Bond Lengths (Å) and Angles (deg) for Non-Hydrogen Atoms in the $[Nb_2W_4O_{19}CH_3]^{3-}$ Anion in Crystalline **3**[a]

parameter[b]	value	parameter[b]	value	parameter[b]	value	parameter[b]	value
			Bond Length				
M_1-O_B	2.19 (1)	M_3-O_{C2}	2.04 (1)	M_1-O_{F1}	1.96 (1)	$M_1\cdots M_2$	3.504 (2)
M_2-O_B	2.08 (1)	M_3-O_D	1.91 (1)	M_6-O_{F1}	1.90 (1)	$M_1\cdots M_4$	3.273 (1)
		M_4-O_D	1.98 (1)	M_2-O_{F2}	1.85 (2)	$M_2\cdots M_3$	3.263 (2)
O_B-C_m	1.50 (3)			M_6-O_{F2}	2.00 (1)	$M_3\cdots M_4$	3.308 (2)
		M_1-O_{E1}	1.87 (2)	M_3-O_{F3}	1.88 (2)	$M_1\cdots M_5$	3.273 (2)
M_1-O_A	2.30 (1)	M_5-O_{E1}	1.95 (2)	M_6-O_{F3}	1.92 (2)	$M_2\cdots M_5$	3.301 (2)
M_2-O_A	2.31 (1)	M_2-O_{E2}	1.85 (2)	M_4-O_{F4}	1.92 (1)	$M_3\cdots M_5$	3.327 (2)
M_3-O_A	2.43 (1)	M_5-O_{E2}	2.00 (1)	M_6-O_{F4}	1.93 (1)	$M_4\cdots M_5$	3.303 (2)
M_4-O_A	2.41 (1)	M_3-O_{E3}	1.92 (1)			$M_1\cdots M_6$	3.300 (2)
M_5-O_A	2.35 (1)	M_5-O_{E3}	1.92 (1)	M_1-O_{G1}	1.67 (1)	$M_2\cdots M_6$	3.312 (2)
M_6-O_A	2.28 (1)	M_4-O_{E4}	1.90 (1)	M_2-O_{G2}	1.72 (1)	$M_3\cdots M_6$	3.318 (2)
		M_5-O_{E4}	1.91 (1)	M_3-O_{G3}	1.66 (1)	$M_4\cdots M_6$	3.303 (2)
M_1-O_{C1}	1.91 (1)			M_4-O_{G4}	1.74 (1)		
M_4-O_{C1}	1.94 (1)			M_5-O_{G5}	1.60 (2)		
M_2-O_{C2}	1.80 (1)			M_6-O_{G6}	1.59 (2)		
			Bond Angles				
$M_1O_BC_m$	116.0 (12)	$O_BM_2O_{F2}$	82.8 (6)	$O_AM_1O_B$	74.6 (5)	$O_BM_2O_{C2}$	158.5 (5)
$M_2O_BC_m$	120.7 (11)	$O_{C2}M_2O_{E2}$	92.8 (7)	$O_AM_1O_{C1}$	79.4 (5)	$O_{E2}M_2O_{F2}$	151.6 (5)
$M_1O_BM_2$	110.3 (6)	$O_{C2}M_2O_{F2}$	91.0 (7)	$O_AM_1O_{E1}$	76.8 (5)	$O_{C2}M_3O_D$	153.7 (5)
		$O_{C2}M_3O_{E3}$	84.8 (5)	$O_AM_1O_{F1}$	74.2 (5)	$O_{E3}M_3O_{F3}$	147.5 (6)
$O_{G1}M_1O_B$	100.1 (6)	$O_{C2}M_3O_{F3}$	84.6 (6)	$O_AM_2O_B$	76.2 (5)	$O_{C1}M_4O_D$	154.3 (5)
$O_{G1}M_1O_{C1}$	105.7 (6)	$O_DM_3O_{E3}$	88.5 (5)	$O_AM_2O_{C2}$	82.2 (5)	$O_{E4}M_4O_{F4}$	149.8 (5)
$O_{G1}M_1O_{E1}$	105.8 (7)	$O_DM_3O_{F3}$	87.6 (5)	$O_AM_2O_{E2}$	77.4 (5)	$O_{E1}M_5O_{E3}$	151.0 (6)
$O_{G1}M_1O_{F1}$	102.4 (7)	$O_{C1}M_4O_{E4}$	85.6 (6)	$O_AM_2O_{F2}$	75.2 (5)	$O_{E2}M_5O_{E4}$	150.6 (6)
$O_{G2}M_2O_B$	96.4 (7)	$O_{C1}M_4O_{F4}$	84.5 (6)	$O_AM_3O_{C2}$	74.9 (5)	$O_{F1}M_6O_{F3}$	151.5 (6)
$O_{G2}M_2O_{c2}$	105.1 (7)	$O_DM_4O_{E4}$	88.7 (5)	$O_AM_3O_D$	78.8 (5)	$O_{F2}M_6O_{F4}$	151.2 (6)
$O_{G2}M_2O_{E2}$	103.4 (7)	$O_DM_4O_{F4}$	88.0 (6)	$O_AM_3O_{E3}$	74.8 (5)		
$O_{G2}M_2O_{F2}$	102.7 (8)	$O_{E1}M_5O_{E2}$	84.7 (6)	$O_AM_3O_{F3}$	72.9 (5)	$M_1O_AM_3$	174.0 (6)
$O_{G3}M_3O_{C2}$	103.5 (6)	$O_{E1}M_5O_{E4}$	86.9 (6)	$O_AM_4O_{C1}$	76.1 (4)	$M_2O_AM_4$	172.9 (7)
$O_{G3}M_3O_D$	102.8 (6)	$O_{E2}M_5O_{E3}$	85.0 (5)	$O_AM_4O_D$	78.1 (5)	$M_5O_AM_6$	176.7 (7)
$O_{G3}M_3O_{E3}$	104.7 (7)	$O_{E3}M_5O_{E4}$	88.9 (5)	$O_AM_4O_{E4}$	75.2 (5)		
$O_{G3}M_3O_{F3}$	107.6 (7)	$O_{F1}M_6O_{F2}$	85.4 (5)	$O_AM_4O_{F4}$	74.7 (5)	$M_1O_{C1}M_4$	116.3 (5)
$O_{G4}M_4O_{C1}$	102.8 (6)	$O_{F1}M_6O_{F4}$	87.5 (5)	$O_AM_5O_{E1}$	74.1 (5)	$M_2O_{C2}M_3$	116.0 (6)
$O_{G4}M_4O_D$	102.9 (6)	$O_{F2}M_6O_{F3}$	85.7 (6)	$O_AM_5O_{E2}$	73.9 (5)	$M_3O_DM_4$	116.8 (6)
$O_{G4}M_4O_{E4}$	105.7 (7)	$O_{F3}M_6O_{F4}$	87.4 (6)	$O_AM_5O_{E3}$	76.9 (5)	$M_1O_{E1}M_5$	118.6 (7)
$O_{G4}M_4O_{F4}$	104.3 (6)			$O_AM_5O_{E4}$	76.7 (5)	$M_2O_{E2}M_5$	118.0 (7)
$O_{G5}M_5O_{E1}$	105.6 (7)	$M_1O_AM_2$	98.8 (5)	$O_AM_6O_{F1}$	75.7 (5)	$M_3O_{E3}M_5$	119.8 (8)
$O_{G5}M_5O_{E2}$	103.7 (7)	$M_1O_AM_4$	88.0 (4)	$O_AM_6O_{F2}$	73.4 (5)	$M_4O_{E4}M_5$	119.9 (7)
$O_{G5}M_5O_{E3}$	103.2 (7)	$M_2O_AM_3$	86.8 (4)	$O_AM_6O_{F3}$	75.9 (5)	$M_1O_{F1}M_6$	117.5 (7)
$O_{G5}M_5O_{E4}$	105.7 (7)	$M_3O_AM_4$	86.2 (4)	$O_AM_6O_{F4}$	77.8 (5)	$M_2O_{F2}M_6$	118.6 (7)
$O_{G6}M_6O_{F1}$	101.3 (7)	$M_1O_AM_5$	89.8 (4)			$M_3O_{F3}M_6$	121.7 (6)
$O_{G6}M_6O_{F2}$	103.6 (7)	$M_2O_AM_5$	90.2 (4)	$O_AM_1O_{G1}$	173.9 (6)	$M_4O_{F4}M_6$	117.9 (6)
$O_{G6}M_6O_{F3}$	107.0 (7)	$M_3O_AM_5$	88.3 (5)	$O_AM_2O_{G2}$	172.5 (7)		
$O_{G6}M_6O_{F4}$	105.2 (6)	$M_4O_AM_5$	88.0 (5)	$O_AM_3O_{G3}$	178.3 (5)		
		$M_1O_AM_6$	92.2 (6)	$O_AM_4O_{G4}$	178.6 (7)		
$O_BM_1O_{E1}$	82.7 (6)	$M_2O_AM_6$	92.2 (5)	$O_AM_5O_{G5}$	177.6 (6)		
$O_BM_1O_{F1}$	82.8 (5)	$M_3O_AM_6$	89.5 (4)	$O_AM_6O_{G6}$	175.8 (7)		
$O_{C1}M_1O_{E1}$	92.8 (6)	$M_4O_AM_6$	89.4 (4)				
$O_{C1}M_1O_{F1}$	88.9 (5)			$O_BM_1O_{C1}$	154.0 (5)		
$O_BM_2O_{E2}$	83.4 (7)			$O_{E1}M_1O_{F1}$	150.1 (5)		

[a] Numbers in parentheses are the estimated standard deviation in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. The four W and two Nb atoms appear to be disordered among the six M_i sites in the lattice with the following W percentages: M_1, 50.4; M_2, 77.3; M_3, 64.2; M_4, 35.3; M_5, 76.8; M_6, 96.0.

Table VI. 33.9-MHz ^{17}O NMR Spectra Data for Selected Niobotungstates[a]

	chemical shifts[b] (line widths[c])					
anion	ONb	OW	ONb_2	ONbW	OW_2	ONb_2H
$Nb_2W_4O_{19}^{4-}$ (**1**)	752 (305)	691 (120)	491 (153)	434 (88)	373 (130)	
$Nb_2W_4O_{19}H^{3-}$ (**2**)	765 (274)	718 (100)		442, 441[d] (137)	388 (75)	187 (423)
$Nb_2W_4O_{19}CH_3^{3-}$ (**3**)[e]	813 (251)	732 (96), 721 (86)		458 (104[f]), 449 (58)	393 (70), 381 (89)	
$Nb_2W_4O_{19}C(CH_3)_3^{3-}$ (**6**)	784 (500)	715 (114)	527 (190)	450, 448, 444 (*g*)	385, 382 (224[h])	
$(Nb_2W_4O_{18})_2O^{6-}$	789 (554)	719 (259)	540 (128), 502 (86)	461, 456, 446 (*g*)	386 (270)	

[a] For anion **1**, spectral parameters and experimental conditions are given in ref 6. For the remaining anions, see the Experimental Section. [b] Positive chemical shifts in parts per million downfield from fresh tap water at 25 °C. Errors associated with chemical shift values are ±2 ppm for $\nu_{1/2} < 400$ Hz and ±3 ppm for $\nu_{1/2} > 400$ Hz. Assignments based on assignments given for anion **1** in ref 6. Due to the method for ^{17}O enrichment employed, the ONb_2W_4, $OCNb_2$, and OCNb oxygen resonances were not observed due to insufficient enrichment. [c] Line widths fwhm, given in hertz, are enclosed in parentheses after the chemical shift of the resonance in question. Errors associated with linewidths are ±20 Hz for $\nu_{1/2} > 100$ Hz, ±40 Hz for $100 \text{ Hz} < \nu_{1/2} < 350$ Hz, and ±15% for $\nu_{1/2} > 350$ Hz. [d] Shoulder. [e] Sample containing one isomer (see text). [f] Line width accurate to only ±50 Hz due to overlap with adjacent resonance. [g] Resonances insufficiently resolved to allow line-width measurement. [h] Combined line width of two resonances at half-height of the more intense resonance.

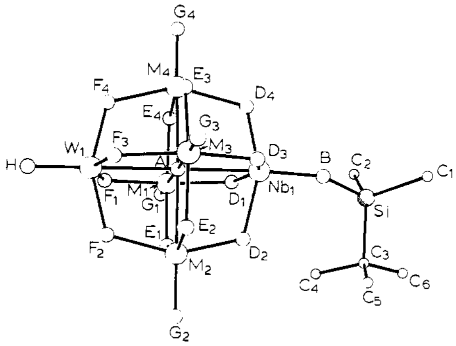

Figure 6. Perspective drawing of the $Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]^{3-}$ anion in crystalline **8**. For purposes of clarity, metal atoms are represented by large open circles, Si is represented by a medium-sized shaded circle, and oxygen and carbon atoms are represented by small open circles; hydrogen atoms were not located. Two of the metal sites are ordered (Nb_1 and W_1) while the other four ($M_1 \rightarrow M_4$) are disordered with the following percentages of W character: M_1, 90.8; M_2, 72.7; M_3, 88.0; M_4, 48.5. Oxygen atoms are labeled only by their subscripts; carbon atoms are labeled by their atomic symbol and a numeric subscript.

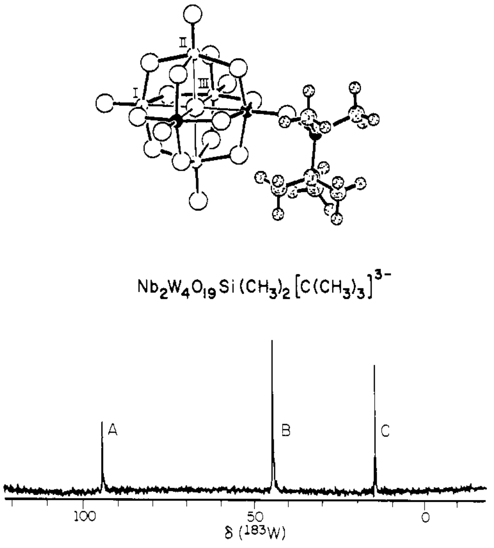

Figure 8. Top SCHAKAL drawing of the $Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]^{3-}$ anion. The shaded circles represent the organosilyl group. Other atoms are represented as described in the Figure 3 caption. One member of each set of symmetry-equivalent tungsten atoms is labeled. Bottom: 16.7-MHz ^{183}W NMR spectrum of $Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3][(n\text{-}C_4H_9)_4N]_3$. The three resonances labeled A, B, and C have integrated intensities of 1:2:1, respectively. See Table VII for numerical data and Experimental Section for experimental parameters.

Table VII. 16.7-MHz ^{183}W NMR Spectral Data for Selected Niobotungstates[a]

anion	chemical shifts[b] (integrated intensities)
$Nb_2W_4O_{19}^{4-}$ (**1**)	86.5 (2),[c] 53.4 (2)[c]
$Nb_2W_4O_{19}H^{3-}$ (**2**)	68.8 (2),[d] 17.2 (2)[d]
$Nb_2W_4O_{19}CH_3^{3-}$ (**3**)[e]	87.9 (2),[c] 21.0 (2)[c]
$Nb_2W_4O_{19}C(CH_3)_3^{3-}$ (**6**)	98.1 (1),[d] 49.0 (2),[d] 19.0 (1)[c]
$Nb_2W_4O_{19}Si(CH_3)_3^{3-}$ (**7**)	93.4 (1),[d] 43.6 (2),[d] 13.5 (1)[d]
$Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]^{3-}$ (**8**)	93.1 (1),[d] 43.9 (2),[d] 14.4 (1)[c]
$Nb_2W_4O_{19}Si(C_6H_5)_3^{3-}$ (**9**)	95.9 (1),[d] 41.4 (2),[d] 12.5 (1)[c]
$(Nb_2W_4O_{18})_2O^{6-}$ (**10**)	95.5 (1),[d] 42.4 (2),[d] 12.9 (1)[d]

[a] See Experimental Section for spectral parameters and experimental conditions. [b] Chemical shifts in ppm downfield from aqueous 2 M Na_2WO_4. [c] Satellite resonances observed, $^2J_{W-O-W} = 6$ Hz. [d] Satellite resonances obscured by $^2J_{W-O-Nb}$ line broadening. [e] Sample containing one isomer (see text).

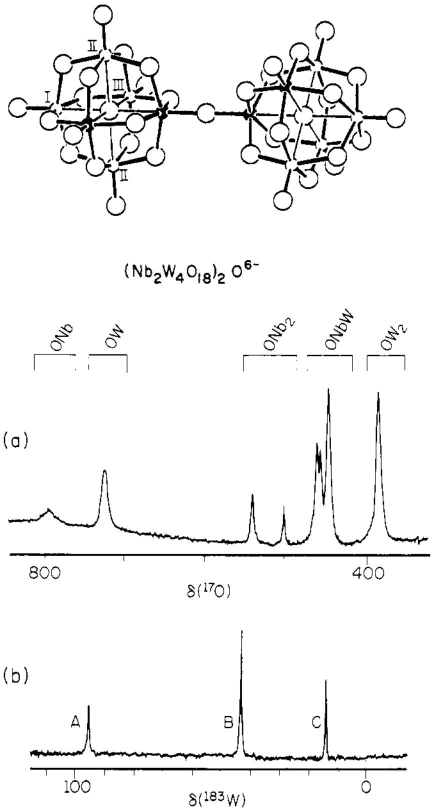

Figure 9. Top: SCHAKAL drawing of the $(Nb_2W_4O_{18})_2O^{6-}$ anion. Atoms are represented as described in the Figure 3 caption. The Nb–O–Nb angle and the conformation around the Nb–O–Nb bond have been selected arbitrarily. One member of each set of symmetry-equivalent tungsten atoms is labeled. 33.9-MHz ^{17}O NMR and 16.7-MHz ^{183}W NMR spectra are shown in (a) and (b), respectively. See Tables VI and VII for numerical data and the Experimental Section for experimental parameters.

to be isostructural. The isopropyl ester prepared in this manner is identical with material prepared by alkylation according to ^1H NMR, $^{13}C\{^1H\}$ NMR, and IR spectroscopy and therefore contains an alkyl group bonded to an ONb oxygen in $Nb_2W_4O_{19}^{4-}$ (O_I in a). The same structure was confirmed for the *tert*-butyl ester **6** using ^{183}W and ^{17}O NMR spectroscopy. The ^{183}W NMR spectrum of **6** shows three resonances with the expected 1:2:1 intensity ratios (see Table VII), and the ^{17}O NMR spectrum shows an ONb_2 resonance (see Table VI).

The silyl esters $Nb_2W_4O_{19}R^{3-}$ R = $(CH_3)_3Si$ (**7**) and $[(CH_3)_3C](CH_3)_2Si$ (**8**), prepared by esterification are identical with the materials prepared by silylation, according to ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR as well as IR spectroscopy and therefore contain siloxy groups terminally bonded to niobium. Since the triphenylsilyl ester **9** shows the same metal–oxygen IR vibrational bands in the 650–1000 cm^{-1} region, it is assumed to be isostructural. All three silyl esters **7**–**9** show the pattern of three ^{183}W NMR resonances expected for terminal siloxide groups bonded to niobium (see Table VII).

Acid Self-Condensation. By dissolving $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ into dry methylene chloride, stirring the solution for 5 min, obtaining a precipitate by addition of tetrahydrofuran, and crystallizing the resulting precipitate from dry CH_3CN, a new material is obtained whose elemental composition is very similar to $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$. According to IR and NMR spectroscopic data, the new material is the $(n\text{-}C_4H_9)_4N^+$ salt of the acid anhydride $(Nb_2W_4O_{18})_2O^{6-}$ (**10**).

The most significant spectroscopic feature of anion **10** is its ^{17}O NMR spectrum in the ONb_2 region, where two resonances are observed (see Figure 9 and Table VI). Its IR spectrum in the 650–1000 cm^{-1} region shows a strong 672 cm^{-1} band in addition to metal–oxygen vibration bands very similar to those observed for anions **5**–**9** (see Figure 4f). This extra band is in the region associated with Nb^V–O–Nb^V vibrations.[17-19] This information

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[17] (a) Buchler, J. W.; Rohbock, K. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 1073. (b) Lecomte, C.; Protas, J.; Guilard, R. *C. R. Acad. Sci, Ser. C.* **1976**, *283*, 397. (c) Johnson, J. J.; Scheidt, W. R. *J. Am. Chem. Soc.* **1977**, *99*, 294.

Table VIII. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $\{Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]\}[(n\text{-}C_4H_9)_4N]_3$ (**8**)[a]

atom type[b]	10^4x	10^4y	10^4z	equiv isotropic thermal parameter,[c] B, Å^2	atom type[b]	10^4x	10^4y	10^4z	equiv isotropic thermal parameter,[c] B, Å^2
Anion									
W_1	−483.1 (7)	5040.4 (6)	−419.7 (4)	3.28 (3)	O_{F1}	426 (9)	5138 (9)	70 (4)	3.5 (4)
Nb_1	1996.5 (14)	4866.3 (15)	−1339.1 (8)	3.39 (6)	O_{F2}	−256 (9)	6059 (6)	−603 (4)	2.3 (4)
$M_1{}^d$	1567.2 (8)	5075.3 (7)	−156.6 (4)	3.51 (3)	O_{F3}	−842 (8)	4930 (8)	−1084 (5)	2.9 (4)
$M_2{}^d$	766.1 (10)	6268.9 (6)	−982.6 (4)	2.72 (4)	O_{F4}	−256 (9)	3985 (6)	−421 (5)	2.6 (4)
$M_3{}^d$	−26.0 (8)	4823.0 (6)	−1609.8 (4)	3.01 (3)	O_{G1}	2152 (10)	5199 (9)	368 (5)	4.4 (5)
$M_4{}^d$	757.4 (13)	3632.6 (7)	−782.9 (5)	3.23 (5)	O_{G2}	741 (13)	7226 (7)	−1058 (6)	4.4 (6)
Si	4071 (6)	5105 (6)	−1764 (3)	6.6 (3)	O_{G3}	−625 (11)	4723 (9)	−2141 (5)	5.0 (6)
O_A	781 (9)	4949 (10)	−890 (4)	3.0 (4)	O_{G4}	760 (13)	2674 (7)	−708 (7)	5.4 (6)
O_B	3020 (11)	4856 (11)	−1680 (6)	6.1 (6)	O_H	−1377 (10)	5103 (11)	−80 (5)	5.0 (5)
O_{D1}	2414 (9)	4981 (11)	−657 (5)	4.1 (5)	C_1	4444 (19)	4730 (20)	−2396 (10)	9.6 (13)
O_{D2}	1736 (9)	5968 (7)	−1330 (5)	2.7 (4)	C_2	4663 (21)	4635 (18)	−1259 (12)	9.1 (13)
O_{D3}	1090 (10)	4811 (10)	−1859 (5)	4.4 (5)	C_3	4225 (28)	6185 (19)	−1715 (14)	8.6 (15)
O_{D4}	1821 (11)	3836 (9)	−1186 (5)	4.2 (5)	C_4	3937 (26)	6403 (21)	−1172 (11)	9.7 (15)
O_{E1}	1371 (10)	6121 (8)	−379 (5)	3.3 (5)	C_5	3597 (30)	6502 (19)	−2097 (13)	11.4 (17)
O_{E2}	153 (10)	5900 (7)	−1536 (5)	2.7 (4)	C_6	5111 (25)	6298 (24)	−1827 (18)	13.3 (20)
O_{E3}	88 (11)	3811 (7)	−1396 (5)	3.5 (5)					
O_{E4}	1421 (11)	3994 (8)	−223 (5)	3.5 (5)					
Cation 1									
N_1	−688 (14)	1987 (10)	−2187 (6)	3.4 (4)	C_{g1}	−2083 (20)	174 (18)	−2105 (10)	6.9 (8)
Ca_1	−1175 (19)	1292 (15)	−2368 (9)	5.4 (7)	C_{g2}	579 (23)	3318 (16)	−3094 (10)	6.7 (8)
Ca_2	−310 (19)	2295 (14)	−2683 (9)	4.5 (6)	C_{g3}	1044 (31)	937 (23)	−1509 (15)	12.1 (13)
Ca_3	35 (20)	1724 (13)	−1816 (8)	5.0 (6)	C_{g4}	−2508 (25)	3343 (19)	−1896 (12)	9.2 (10)
Ca_4	−1272 (18)	2563 (12)	−1928 (8)	3.7 (5)	C_{d1}	−2524 (20)	−203 (17)	−1659 (10)	7.2 (8)
C_{b1}	−1625 (21)	916 (16)	−1929 (10)	6.3 (8)	C_{d2}	−41 (26)	3819 (18)	−3289 (11)	8.3 (9)
C_{b2}	286 (22)	2961 (15)	−2561 (11)	6.2 (8)	C_{d3}	1824 (27)	359 (21)	−1666 (14)	11.3 (13)
C_{b3}	640 (22)	1140 (16)	−1997 (10)	6.1 (7)	C_{d4}	−3252 (27)	3682 (22)	−2206 (13)	10.7 (12)
C_{b4}	−1980 (24)	2842 (18)	−2250 (11)	7.8 (9)					
Cation 2									
N	−2350 (14)	7446 (10)	−473 (7)	3.5 (4)	C_{g1}	−539 (24)	8939 (17)	−226 (11)	7.1 (8)
C_{a1}	−1912 (21)	8173 (16)	−342 (10)	5.8 (7)	C_{g2}	−2141 (19)	6294 (15)	−1694 (9)	5.7 (7)
C_{a2}	−1983 (21)	7141 (16)	−950 (10)	5.6 (7)	C_{g3}	−2292 (21)	6412 (16)	786 (10)	6.1 (7)
C_{a3}	−2157 (19)	6837 (14)	−69 (9)	4.6 (6)	C_{g4}	−4522 (20)	8248 (15)	−855 (9)	5.6 (7)
C_{a4}	−3282 (17)	7594 (13)	−482 (8)	3.8 (5)	C_{d1}	356 (25)	8955 (19)	−140 (12)	8.6 (10)
C_{b1}	−906 (20)	8106 (15)	−254 (9)	5.3 (7)	C_{d2}	−2480 (23)	5539 (17)	−1886 (11)	7.7 (9)
C_{b2}	−2483 (21)	6450 (16)	−1141 (10)	6.1 (8)	C_{d3}	−2422 (23)	6616 (17)	1326 (10)	7.3 (8)
C_{b3}	−2475 (19)	7112 (15)	477 (9)	4.8 (6)	C_{d4}	−4848 (24)	8816 (17)	−1286 (11)	8.2 (9)
C_{b4}	−3536 (20)	8107 (15)	−926 (9)	5.2 (7)					
Cation 3									
N	3476 (18)	2166 (14)	−590 (8)	5.6 (6)	C_{g1}	1720 (31)	995 (27)	90 (17)	12.7 (15)
C_{a1}	2999 (34)	1593 (26)	−297 (16)	11.9 (14)	C_{g2}	5482 (30)	1260 (23)	−997 (14)	11.1 (12)
C_{a2}	4452 (30)	1916 (22)	−682 (13)	10.0 (11)	C_{g3}	3352 (32)	3639 (28)	468 (17)	14.8 (16)
C_{a3}	3366 (35)	2948 (31)	−353 (19)	14.2 (17)	C_{g4}	2799 (28)	2573 (21)	−1932 (13)	10.3 (11)
C_{a4}	3032 (28)	2145 (23)	−1068 (15)	10.4 (12)	C_{d1}	1747 (37)	1056 (32)	624 (20)	17.7 (20)
C_{b1}	2139 (39)	1628 (30)	−60 (18)	15.1 (17)	C_{d2}	5859 (50)	1607 (37)	−1335 (22)	26.4 (29)
C_{b2}	4555 (32)	1264 (25)	−904 (14)	11.3 (13)	C_{d3}	4106 (30)	3995 (23)	369 (14)	12.8 (13)
C_{b3}	3687 (37)	2990 (29)	23 (18)	17.4 (19)	C_{d4}	3104 (28)	2953 (22)	−2375 (14)	11.7 (13)
C_{b4}	3379 (24)	2584 (18)	−1531 (12)	8.2 (9)					

[a] Numbers in parentheses are the estimated standard deviation in the last significant digit. [b] Atoms are labeled in agreement with Figures 6 and 7.[9] [c] For non-hydrogen atoms of the anion, this is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor; for non-hydrogen atoms of the cations, it is the isotropic thermal parameter which was refined in least-squares cycles. [d] Three W and one Nb atoms appear to be disordered among the four M_i sites in the lattice with the following W percentages: M_1, 90.8; M_2, 72.7; M_3, 88.0; M_4, 48.5.

together with the ^{183}W NMR spectrum shown in Figure 9b support the structure shown in Figure 9.

Anhydride Hydrolysis. The niobotungstic acid $Nb_2W_4O_{19}H^{3-}$ (**2**) and its anhydride $(Nb_2W_4O_{18})_2O^{6-}$ (**10**) can be interconverted in acetonitrile solution as shown in (3). When the acid is dissolved

$$(Nb_2W_4O_{18})_2O^{6-} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} 2Nb_2W_4O_{19}H^{3-} \qquad (3)$$

in dry acetonitrile, it is quantitatively converted to the anhydride according to ^{17}O and ^{183}W solution NMR spectroscopy. Addition of ≥110 equiv of water/mol of Nb_2W_4 forces the equilibrium back to the acid to the extent that ^{183}W and ^{17}O resonances are observed for the acid and no other species besides the acid. In the presence of intermediate amounts of water, however, complex spectra are observed that provide evidence for rapid chemical exchange plus the existence of additional species besides anions **2** and **10**. Investigation of these solutions was considered to be beyond the scope of the present study.

Anhydride Alcoholysis. In light of the reactivity of $(Nb_2W_4O_{18})_2O^{6-}$ (**10**) toward the water hydroxyl group, it is not surprising that the anhydride also reacts readily with excess alcohol according to reaction 4 to yield the corresponding ester. In the

$$(Nb_2W_4O_{18})_2O^{6-} \xrightarrow[-H_2O]{2ROH} 2Nb_2W_4O_{19}R^{3-} \qquad (4)$$

two cases examined under controlled conditions, excess methanol and triphenylsilanol both reacted with anion **10** at ambient tem-

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(18) Illmaier, B. *Monatsh. Chem.* **1975**, *106*, 657.

(19) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274.

Table X. Bond Lengths (Å) and Angles (deg) for Non-Hydrogen Atoms in the $Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]^{3-}$ Anion in Crystalline **8**[a]

parameter[b]	value	parameter[b]	value	parameter[b]	value	parameter[b]	value
			Bond Length Å				
Nb_1-O_B	1.86 (2)	M_1-O_{E1}	1.96 (1)	$Si-C_1$	1.92 (3)	$Nb_1\cdots M_1$	3.274 (2)
Nb_1-O_A	2.27 (1)	M_2-O_{E1}	1.90 (1)	$Si-C_2$	1.85 (3)	$Nb_1\cdots M_2$	3.290 (2)
		M_2-O_{E2}	1.89 (1)	$Si-C_3$	1.93 (3)	$Nb_1\cdots M_3$	3.276 (2)
M_1-O_A	2.34 (1)	M_3-O_{E2}	1.93 (1)			$Nb_1\cdots M_4$	3.288 (2)
M_2-O_A	2.34 (2)	M_3-O_{E3}	1.89 (1)	C_3-C_4	1.58 (5)		
M_3-O_A	2.33 (1)	M_4-O_{E3}	1.98 (1)	C_3-C_5	1.53 (6)	$W_1\cdots M_1$	3.314 (2)
M_4-O_A	2.34 (2)	M_4-O_{E4}	1.94 (1)	C_3-C_6	1.45 (6)	$W_1\cdots M_2$	3.300 (2)
W_1-O_A	2.37 (1)	M_1-O_{E4}	1.93 (1)	W_1-O_{F1}	1.90 (1)	$W_1\cdots M_3$	3.305 (2)
Nb_1-O_{D1}	1.96 (1)	M_1-O_{G1}	1.70 (1)	W_1-O_{F2}	1.94 (1)	$W_1\cdots M_4$	3.312 (2)
Nb_1-O_{D2}	1.99 (1)	M_2-O_{G2}	1.70 (1)	W_1-O_{F3}	1.92 (1)	$M_1\cdots M_2$	3.314 (2)
Nb_1-O_{D3}	2.00 (1)	M_3-O_{G3}	1.72 (1)	W_1-O_{F4}	1.97 (1)	$M_1\cdots M_4$	3.311 (2)
Nb_1-O_{D4}	1.89 (2)	M_4-O_{G4}	1.70 (1)	M_1-O_{F1}	1.91 (1)	$M_2\cdots M_3$	3.306 (2)
M_1-O_{D1}	1.90 (1)			M_2-O_{F2}	1.94 (1)	$M_3\cdots M_4$	3.301 (2)
M_2-O_{D2}	1.87 (1)	W_1-O_H	1.68 (1)	M_3-O_{F3}	1.92 (1)		
M_3-O_{D3}	1.89 (2)	$Si-O_B$	1.73 (2)	M_4-O_{F4}	1.97 (1)		
M_4-O_{D4}	2.03 (2)						
			Bond Angle, deg				
Nb_1O_BSi	153.5 (12)	$O_{G3}M_3O_{F3}$	104.6 (7)	SiC_3C_4	106 (6)	$O_AM_3O_{F3}$	75.3 (5)
		$O_{G4}M_4O_{D4}$	103.7 (8)	SiC_3C_5	104 (2)	$O_AM_4O_{D4}$	75.3 (6)
O_BSiC_1	108.8 (12)	$O_{G4}M_4O_{E3}$	104.9 (7)	SiC_3C_6	104 (3)	$O_AM_4O_{E3}$	75.5 (5)
O_BSiC_2	105.9 (13)	$O_{G4}M_4O_{E4}$	103.5 (7)	$C_4C_3C_5$	110 (3)	$O_AM_4O_{E4}$	76.1 (5)
O_BSiC_3	111.3 (15)	$O_{G4}M_4O_{F4}$	104.9 (7)	$C_4C_3C_6$	116 (3)	$O_AM_4O_{F4}$	76.1 (5)
C_1SiC_2	110.0 (15)	$O_{D1}M_1O_{E1}$	88.7 (7)	$C_5C_3C_6$	116 (3)	$O_{D1}M_1O_{F1}$	153.5 (6)
C_1SiC_3	111.3 (16)	$O_{D1}M_1O_{E4}$	86.1 (8)			$O_{E1}M_1O_{E4}$	151.8 (6)
C_2SiC_3	109.3 (16)	$O_{E1}M_1O_{F1}$	83.9 (7)			$O_{D2}M_2O_{F2}$	152.5 (5)
$O_BNb_1O_{D1}$	99.9 (7)	$O_{E4}M_1O_{F1}$	88.5 (7)	$O_HW_1O_{F1}$	104.1 (6)	$O_{E1}M_2O_{E2}$	151.9 (6)
$O_BNb_1O_{D2}$	101.3 (8)	$O_{D2}M_2O_{E1}$	88.6 (6)	$O_HW_1O_{F2}$	103.7 (8)	$O_{D3}M_3O_{F3}$	152.8 (6)
$O_BNb_1O_{D3}$	106.0 (7)	$O_{D2}M_2O_{E2}$	85.9 (6)	$O_HW_1O_{F3}$	105.6 (6)	$O_{E2}M_3O_{E3}$	152.5 (6)
$O_BNb_1O_{D4}$	103.1 (8)	$O_{E1}M_2O_{F2}$	86.7 (6)	$O_HW_1O_{F4}$	103.0 (8)	$O_{D4}M_4O_{F4}$	151.4 (6)
$O_ANb_1O_{D1}$	77.2 (5)	$O_{E2}M_2O_{F2}$	85.6 (6)	$O_AW_1O_{F1}$	75.3 (5)	$O_{E3}M_4O_{E4}$	151.6 (5)
$O_ANb_1O_{D2}$	75.9 (6)	$O_{D3}M_3O_{E2}$	84.9 (7)	$O_AW_1O_{F2}$	76.5 (6)		
$O_ANb_1O_{D3}$	76.8 (5)	$O_{D3}M_3O_{E3}$	90.5 (7)	$O_AW_1O_{F3}$	75.0 (5)	$O_AM_1O_{G1}$	177.8 (6)
$O_ANb_1O_{D4}$	79.7 (7)	$O_{E2}M_3O_{F3}$	85.7 (6)	$O_AW_1O_{F4}$	76.8 (6)	$O_AM_2O_{G2}$	179.0 (8)
$O_{D1}Nb_1O_{D2}$	87.5 (7)	$O_{E3}M_3O_{F3}$	86.2 (6)	$O_{F1}W_1O_{F2}$	87.3 (6)	$O_AM_3O_{G3}$	179.6 (8)
$O_{D1}Nb_1O_{D4}$	86.8 (7)	$O_{D4}M_4O_{E3}$	88.2 (6)	$O_{F1}W_1O_{F4}$	87.1 (6)	$O_AM_4O_{G4}$	178.9 (8)
$O_{D2}Nb_1O_{D3}$	84.8 (6)	$O_{D4}M_4O_{E4}$	84.8 (6)	$O_{F2}W_1O_{F3}$	84.7 (6)		
$O_{D3}Nb_1O_{D4}$	90.1 (7)	$O_{E3}M_4O_{F4}$	85.9 (6)	$O_{F3}W_1O_{F4}$	87.3 (6)	$Nb_1O_AW_1$	179.8 (10)
$O_ANb_1O_B$	175.9 (7)	$O_{E4}M_4O_{F4}$	87.2 (6)	$O_AW_1O_H$	179.4 (7)	$M_1O_AM_3$	178.8 (7)
$O_{D1}Nb_1O_{D3}$	154.0 (6)	$Nb_1O_{D1}M_1$	115.8 (7)	$O_{F1}W_1O_{F3}$	150.3 (6)	$M_2O_AM_4$	178.2 (7)
$O_{D2}Nb_1O_{D4}$	155.6 (7)	$Nb_1O_{D2}M_2$	116.9 (7)	$O_{F2}W_1O_{F4}$	153.3 (6)	$Nb_1O_AM_1$	90.4 (5)
$O_{G1}M_1O_{D1}$	102.5 (7)	$Nb_1O_{D3}M_3$	114.7 (6)	$O_AM_1O_{D1}$	76.6 (5)	$Nb_1O_AM_2$	90.9 (5)
$O_{G1}M_1O_{E1}$	102.6 (7)	$Nb_1O_{D4}M_4$	114.1 (8)	$O_AM_1O_{E1}$	75.5 (6)	$Nb_1O_AM_3$	90.8 (4)
$O_{G1}M_1O_{E4}$	105.6 (7)	$M_1O_{E1}M_2$	117.9 (7)	$O_AM_1O_{E4}$	76.3 (6)	$Nb_1O_AM_4$	90.9 (6)
$O_{G1}M_1O_{F1}$	103.9 (6)	$M_2O_{E2}M_3$	119.6 (7)	$O_AM_1O_{F1}$	76.9 (5)	$W_1O_AM_1$	89.4 (4)
$O_{G2}M_2O_{D2}$	104.0 (8)	$M_3O_{E3}M_4$	117.0 (7)	$O_AM_2O_{D2}$	76.3 (5)	$W_1O_AM_2$	88.9 (5)
$O_{G2}M_2O_{E1}$	104.4 (7)	$M_4O_{E4}M_1$	117.5 (7)	$O_AM_2O_{E1}$	76.5 (5)	$W_1O_AM_3$	89.4 (5)
$O_{G2}M_2O_{E2}$	103.7 (7)	$W_1O_{F1}M_1$	118.3 (6)	$O_AM_2O_{E2}$	75.3 (5)	$W_1O_AM_4$	89.3 (5)
$O_{G2}M_2O_{F2}$	103.4 (7)	$W_1O_{F2}M_2$	118.3 (6)	$O_AM_2O_{F2}$	76.3 (5)	$M_1O_AM_2$	90.0 (5)
$O_{G3}M_3O_{D3}$	102.5 (7)	$W_1O_{F3}M_3$	120.4 (7)	$O_AM_3O_{D3}$	77.6 (5)	$M_1O_AM_4$	90.0 (5)
$O_{G3}M_3O_{E2}$	105.5 (7)	$W_1O_{F4}M_4$	117.7 (6)	$O_AM_3O_{E2}$	74.9 (6)	$M_2O_AM_3$	90.0 (5)
$O_{G3}M_3O_{E3}$	102.0 (7)			$O_AM_3O_{E3}$	77.6 (6)	$M_3O_AM_4$	89.9 (5)

[a] Numbers in parentheses are the estimated standard deviation in the last significant digit. [b] Atoms aree labeled in agreement with Figure 6. The second Nb atom appears to be disordered among the four M_i sites (which are *cis* to Nb_1) in the lattice with the following W percentages: M_1, 90.8; M_2, 72.7; M_3, 88.0; and M_4, 48.5.

perature to yield esters **3** and **9**, respectively, in ≥80% yield.

Ester Hydrolysis. The sensitivity of esters $Nb_2W_4O_{10}R^{3-}$ toward water (see eq 5) is very dependent upon the nature of the substituent group R and the identity of the metals bonded to the alkoxy group.

$$Nb_2W_4O_{19}R^{3-} + H_2O = Nb_2W_4O_{19}H^{3-} + ROH \qquad (5)$$

Consider first a case where the alkoxy group is bonded only to niobium centers, i.e., the case where the RO group occupies an O_F or O_I site in **a**. The isopropyl ester reacts with ca. 5 equiv of water in acetonitrile to form the acid $Nb_2W_4O_{19}H^{3-}$ in >85% yield after less than 5 min at ambient temperature. In contrast, the *tert*-butyl and methyl esters require ca. 6 and ca. 12 h, respectively, to form the acid in >85% yield under the same conditions. The trimethyl silyl ester, however, could be recovered in >90% yield after 6 days' exposure to 5 equiv of water in acetonitrile at ambient temperature.

The relative hydrolytic stabilities of alkoxide groups bonded to tungsten and niobium centers can be evaluated from hydrolysis studies of $Nb_2W_4O_{19}CH_3^{3-}$ (**3**), prepared by alkylation of anion **1** according to reaction **1**. As described above, this material is a mixture of five diastereomers, one containing a methoxy group bonded to two niobium centers, two containing a methoxy group bonded to one niobium and one tungsten center, and two containing a methoxy group bonded to two tungsten centers (see **b–f**). After treatment of an acetonitrile solution of this material with ca. 40 equiv of water for 12 h at ambient temperature, the isomer containing a CH_3ONb_2 group (see **f**) was completely hydrolyzed but less than 5% of the isomers containing CH_3ONbW and CH_3OW_2 groups (see **b–e**) were hydrolyzed according to ^1H NMR spectroscopy.

Transesterification. Transesterification according to eq 6 has been achieved for a variety of esters containing alkoxy groups bonded only to niobium centers and requires rather forced conditions, i.e., a large excess of alcohol, elevated temperature, and long reaction times. Of the many possible interconversions of

$$Nb_2W_4O_{19}R^{3-} + R'OH = Nb_2W_4O_{19}R' + ROH \qquad (6)$$

the esters **3–9**, four have been examined under controlled conditions described in the Experimental Section. The four examined represent each of the four possible interconversions of terminally bonded alkoxy groups (site I in **a**) and/or bridging alkoxy groups (site F in **a**): *tert*-butanolysis of the isopropyl ester, a terminal to terminal conversion; methanolysis of the *tert*-butyl ester, a terminal to bridging conversion; *tert*-butanolysis of the methyl ester, a bridging to terminal conversion; ethanolysis of the methyl ester, a bridging to bridging conversion.

Because of their relative hydrolytic stabilities (see above), alkoxy groups bonded to tungsten are expected to be more resistant to alcoholysis than alkoxy groups bonded only to niobium. This expectation is borne out by product analysis of the reaction of $Nb_2W_4O_{19}CH_3^{3-}$, prepared as a five-diastereomer mixture, with neat ethanol. Material isolated after 24 h under reflux in 29% yield after crystallization from CH_3CN contained $Nb_2W_4O_{19}C_2H_5^{3-}$ as the isomer with an ethoxy group bridging two niobium centers (site F in **a**), plus the four isomers of $Nb_2W_4O_{19}CH_3^{3-}$ containing methoxy groups bridging two tungsten centers and bridging one tungsten and one niobium center (see **b–e**).

Oxide Transfer Reactions. The stoichiometric reaction of $Nb_2W_4O_{19}^{4-}$ (**1**) with protons to form $(Nb_2W_4O_{18})_2O^{6-}$ (**10**) plus water can formally be described as an oxide transfer reaction with the protons acting as oxide acceptors (eq 7). In the course of

$$2Nb_2W_4O_{19}^{4-} \xrightarrow{-O^{2-}} (Nb_2W_4O_{18})_2O^{6-} \qquad (7)$$

investigating the reactivity of the $Nb_2W_4O_{19}^{4-}$ anion toward the group VIII metal carbonyl clusters $Rh_6(CO)_{16}$, $Ir_4(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$, and $Os_3(CO)_{10}(NCCH_3)_2$, we discovered that these species are capable of converting $Nb_2W_4O_{19}^{4-}$ to $(Nb_2W_4O_{18})_2O^{6-}$, i.e., acting as oxide acceptors. Quantitative examination of carbonyl groups as oxide acceptors showed that anion **1** can be converted to the anhydride **10** in >60% yield using either $Rh_6(CO)_{16}$ or CO_2 (see Experimental Section).

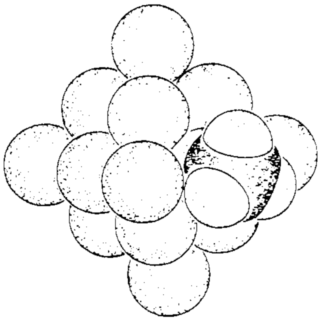
Discussion

In the Results, the synthesis, characterization, and interconversions of $Nb_2W_4O_{19}^{4-}$ (**1**), $Nb_2W_4O_{19}H^{3-}$ (**2**), $Nb_2W_4O_{19}R^{3-}$ (**3–9**), and $(Nb_2W_4O_{18})_2O^{6-}$ (**10**) were described (see Scheme I). This section is concerned with identifying the factors influencing the reactivity of the $Nb_2W_4O_{19}^{4-}$ anion and its derivatives and pointing out how these same factors influence the reactivities of related early-transition-metal polyoxoanions in solution. Overall, the reaction profile of the $Nb_2W_4O_{19}^{4-}$ anion resembles the reaction profile of organic carboxylate anions, involving protonation, alkylation/silylation, condensation, esterification, transesterification, and hydrolysis. It is far more complex, however, since the $Nb_2W_4O_{19}^{4-}$ anion has eight potentially reactive types of oxygens, labeled B-I in **a**, whereas carboxylate anions possess only one type.

Metal–Oxygen Bond Lability. The inertness of tungsten–oxygen bonds relative to niobium–oxygen bonds is manifested quite unambiguously in the relative stabilities of the five $Nb_2W_4O_{19}CH_3^{3-}$ diasteromers shown in **b–f** toward hydrolysis. Here, the methoxy group is bonded to at least one tungsten center in **b–e** but is bonded only to niobium centers in **f**. This latter isomer reacts quantitatively with water under conditions that leave the other isomers intact. Several other reactions involving niobium–oxygen but not tungsten–oxygen bond cleavage also proceed readily: esterification and self-condensation of $Nb_2W_4O_{19}H^{3-}$, hydrolysis and alcoholysis of $(Nb_2W_4O_{18})_2O^{6-}$, and transesterification of the alkyl esters $Nb_2W_4O_{19}R^{3-}$. The $Nb_2W_4O_{19}^{4-}$ anion itself can even donate a niobium-bound oxygen to such weak acids as carbon dioxide and $Rh_6(CO)_{16}$ with formation of $(Nb_2W_4O_{18})_2O^{6-}$. Overall, the $Nb_2W_4O_{19}^{4-}$ anion is seen to be comprised of labile $Nb_2O_3^{4+}$ unit firmly supported on a relatively inert $W_4O_{16}^{8-}$ framework.

The relative lability of niobium(V)–oxygen bonds relative to tungsten(VI)–oxygen bonds is not restricted to the reactions and compounds described above. The ONb and ONb_2 oxygens in $Nb_2W_4O_{19}^{4-}$ and $Nb_6O_{19}^{8-}$ undergo facile exchange with oxygen in water.[6,20] The apparent instability of the hypothetical $SiNb_3W_9O_{40}H_3^{4-}$ Keggin anion toward self-condensation in acetonitrile solution to the known $(SiNb_3W_9O_{37})_2O_3^{8-}$ ion[19] parallels the instability of $Nb_2W_4O_{19}H^{3-}$ toward $(Nb_2W_4O_{18})_2O^{6-}$ under similar conditions. In the $(SiNb_3W_9O_{37})_2O_3^{8-}$ anion, the two $SiNb_3W_9O_{37}^{-}$ subunits are believed to be linked by three ONb_2 oxygens. Attack by hydroxide ions with formation of $SiNb_3W_9O_{40}^{7-}$ is understandably facile,[19] since it involves cleavage and formation of niobium–oxygen, but not tungsten–oxygen, bonds.

Steric Effects. The structures adopted by the esters $Nb_2W_4O_{19}R^{3-}$ obtained by esterification of $Nb_2W_4O_{19}H^{3-}$ can be related to the steric bulk of the substituent group R. When R = CH_3 or CH_2CH_3, the alkyl group is bonded to a bridging ONb_2 oxygen (O_F in **a**), but when R = $CH(CH_3)_2$, $C(CH_3)_3$, $Si(CH_3)_3$, $Si(CH_3)_2[C(CH_3)_3]$, or $Si(C_6H_5)_3$, the alkyl/silyl group is bonded to a terminal ONb oxygen (O_I in **a**). As is evident from the space-filling representation[21] **g**, binding of a methyl group to an ONb_2 oxygen introduces no steric repulsions and electronic factors apparently favor this structure over the alternative structure involving a terminally bonded methoxide group. An ethoxide group can also be accommodated in a bridging site, as shown in **h**. Steric repulsions lead to terminally bonded alkoxide/siloxide groups, however, when bulkier substituents are introduced. The two conformers of the isopropyl ester shown in **i** and **j** nicely illustrate the steric crowding resulting from introduction of a secondary carbon center at the bridging oxygen site. This same pattern of behavior is observed upon protonating, alkylating, or silylating the $Nb_2W_4O_{19}^{4-}$ anion. Protonation, methylation, and ethylation occur preferentially at bridging oxygen sites; isopropylation, trimethylsilylation, and *tert*-butyldimethylsilylation occur at the terminal ONb oxygen site.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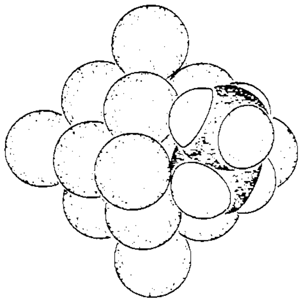
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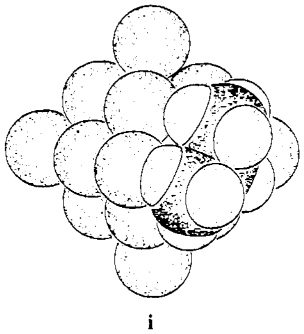
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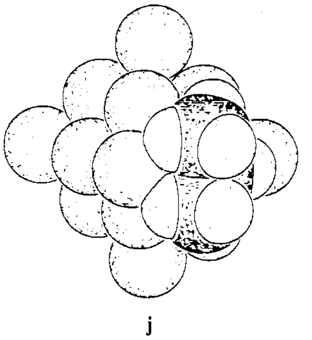
j

The balance between steric and electronic factors controlling binding site preferences in the $Nb_2W_4O_{19}R^{3-}$ anions can be discerned in other polyoxoanion systems. In a particularly clear-cut case, steric factors favor binding of the $(\eta^5\text{-}C_5H_5)_3U^+$ and $(\eta^5\text{-}C_5H_5)_3Th^+$ groups to terminal oxygens but not bridging oxygens

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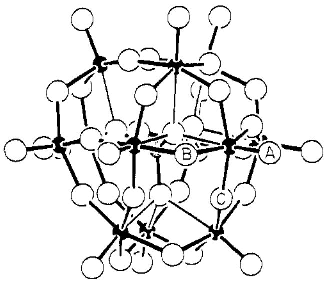
[20] Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93.

[21] Van der Waals radii for oxygen (1.4 Å), carbon (1.7 Å), and hydrogen (1.2 Å) were used in drawings **g–j**.

of $NbW_5O_{19}^{3-}$ and $TaW_5O_{19}^{3-}$ in the $[(C_5H_5)_3Ac(MW_5O_{19})_2]^{5-}$ anions, Ac = U or Th and M = Nb or Ta.[22] Similarly, steric factors presumably cause the bulky $[(CH_3)_5C_5]RhCl_2$ group to prefer $Nb_2W_4O_{19}^{4-}$ terminal oxygens over bridging oxygens in the proposed reaction intermediate $\{[(CH_3)_5C_5]RhCl_2(Nb_2W_4O_{19})\}^{4-}$.[6] Turning from hexametalate to Keggin anion systems, Knoth and Harlow have reported the alkylated $PM_{12}O_{40}R^{2-}$ anions, M = Mo or W and R = CH_3 or CH_2CH_3.[23] The T_d Keggin anions $PM_{12}O_{40}^{3-}$ have three nonequivalent types of surface oxygen atoms labeled A, B, and C in **k**, and alkylation occurs at the bridging O_B oxygen site. The O_B oxygens are therefore more nucleophilic than the O_A oxygens. The relative reactivity of the O_B and O_C oxygens is unclear, however, since the O_C is very crowded and steric factors may inhibit O_C-alkylation.



k

Electronic Effects. Since the methylation of $Nb_2W_4O_{19}^{4-}$ is kinetically controlled, the observed product distribution reflects the relative nucleophilicities of the different surface oxygens. According to ^1H NMR data, the major product is the $Nb_2W_4O_{19}CH_3^{3-}$ isomer **f** which constitutes, in situ, approximately 40% of the total product material. Most of the remaining product is distributed among the four remaining diastereomers **b**–**e** containing bridging methoxide groups. If charge were delocalized equally over all $Nb_2W_4O_{19}^{4-}$ surface oxygens, an approximately statistical product distribution would be expected, showing 6% methylation at O_B and O_F (see **a**), 11% methylation O_D, O_G, O_G, and O_I, and 22% methylation at O_C and O_E, with a bias toward the terminal O_E, O_G, and O_I oxygens on steric grounds. The observed product distribution therefore identifies the bridging oxygens as more nucleophilic than the terminal oxygens and the ONb_2 oxygen O_F as the most nucleophilic oxygen in the anion.

Observation of substantial methylation of $Nb_2W_4O_{19}^{4-}$ at all doubly bridging oxygen sites reflects substantial charge delocalization in the anion. The OW_2 oxygens in $W_6O_{19}^{2-}$ are not alkylated by dimethyl sulfate in acetonitrile even after 2 days at ambient temperature. In contrast, the OW_2 oxygens in $Nb_2W_4O_{19}^{4-}$ are alkylated in less than 5 min under the same conditions. A high degree of charge delocalization in $Nb_2W_4O_{19}^{4-}$ is also evident from the equilibrium isomer distributions for $\{Nb_2W_4O_{19}Rh[C_5(CH_3)_5]\}^{2-}$, $Nb_2W_4O_{19}Mn(CO)_3^{3-}$, and $Nb_2W_4O_{19}Re(CO)_3^{3-}$. In each case, all three possible isomers are observed where the organometallic moiety is bonded to three contiguous ONb_2, ONbW, and/or OW_2 oxygens in $Nb_2W_4O_{19}^{4-}$.[6,7]

Since the steric environments of the nonequivalent doubly bridging oxygens in $Nb_2W_4O_{19}^{4-}$ are virtually identical, the relative basicities of the different doubly bridging oxygens should parallel their relative nucleophilicities.[24] Accordingly, ^{17}O NMR spectroscopy of $Nb_2W_4O_{19}H^{3-}$ identifies the ONb_2 oxygen as the most basic surface oxygen in $Nb_2W_4O_{19}^{4-}$. The relative basicities of the remaining surface oxygens cannot be assessed, however, since the ^{17}O NMR data is obtained under conditions of fast proton exchange. Analogous patterns of behavior have been noted in polyvanadates and vanadotungstates. Protonation of $V_{10}O_{28}^{6-}$ occurs at doubly and/or triply bridging oxygen sites, not terminal oxygen sites;[13] the $V_2W_4O_{19}^{4-}$ ion is protonated predominantly at its OV_2 doubly bridging oxygen;[14] and the $SiV_3W_9O_{40}^{7-}$ ion is also protonated at one of its three symmetry-equivalent OV_2 doubly bridging oxygens.[25]

There is some evidence that methylation of $Nb_2W_4O_{19}^{4-}$ occurs not only at bridging oxygen sites but also at terminal oxygen sites, namely, the presence of a small δ 4.21 resonance in the ^1H NMR spectrum of methylated $Nb_2W_4O_{19}^{4-}$ that cannot be assigned to material alkylated at a double-bridging oxygen site (Figure 3a). With use of bulkier electrophiles, alkylation and silylation at bridging oxygen sites can be suppressed (see above), and the relative reactivities of the terminal ONb and OW oxygens can be assessed. In the cases of isopropylation, trimethylsilylation, and *tert*-butyldimethylsilylation, the products contain only ONb alkylated or silylated material. The ONb oxygens are thus markedly more nucleophilic and/or basic than the OW oxygens. Such selectivity has previously been observed or postulated for the binding of $(C_5H_5)_3U^+$ and $(C_5H_5)_3Th^+$ cations to ONb or OTa but not OW oxygens in $NbW_5O_{19}^{3-}$ and $TaW_5O_{19}^{3-}$,[22] the binding of $(C_7H_8)Rh^+$ cations to ONb but not OW oxygens in $Nb_2W_4O_{19}^{4-}$,[18] and the binding of $[(CH_3)_5C_5]RhCl_2$ to ONb but not OW oxygens in $Nb_2W_4O_{19}^{4-}$.[6]

Experimental Section

Reagents, Solvents, and General Procedures. The following were purchased from commercial sources and used, unless specified otherwise, without further purification: pyridine, carbon dioxide, *tert*-butyl alcohol, anhydrous ether, tetrahydrofuran (Baker); toluene (Fisher); 0.4 M aqueous tetrabutylammonium hydroxide, chloroacetic acid (Eastman Kodak); KOH (Mallinckrodt); ^{17}O-enriched water (Monsanto); *tert*-butyldimethylchlorosilane, chlorotrimethylsilane, hexamethyldisilazane, triphenylsilanol (Petrarch); $Rh_6(CO)_{16}$ (Stern).

$Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ (once recrystallized), $W_6O_{19}[(n\text{-}C_4H_9)_4N]_2$, $[(t\text{-}C_4H_9)(CH_3)_2SiOH]_2\cdot H_2O$, and $(CH_3)_3SiOH$ were prepared by using procedures described in ref 6, 26, 27, and 28, respectively. Oxygen-17-enriched materials were prepared from ^{17}O-enriched $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$.[6]

Unless specified otherwise, 2-propanol (Aldrich) and CD_3CN (MSD Isotopes) were distilled under N_2 from CaH_2. Acetone (Baker) was distilled over dehydrated boron oxide (dehydrated at 200 °C and allowed to cool under vacuum). Methanol (Mallinckrodt) and ethanol (U.S. Industrial Chemicals) were distilled over CaH_2. Trifluoromethanesulfonic anhydride (Aldrich) was distilled twice over P_4O_{10}. Dimethyl and diethyl sulfate were stirred over Na_2CO_3 and then vacuum distilled under nitrogen. (*tert*-Butyldimethylsilyl) trifluoromethanesulfonate (Petrarch) was twice redistilled under nitrogen. Chloroform (Fisher), methylene chloride (Fisher), and 1,2-dichloroethane (Mallinckrodt) were stored over activated molecular sieves (Linde) having the appropriate pore size.[29] Molecular sieves were activated by heating at 350 °C for at least 24 h and cooling to ambient temperature under a dynamic vacuum. Unless specified otherwise, reactions were routinely performed in a static aerobic environment. Solutions of $Nb_2W_4O_{19}R^{3-}$ alkyl esters were always handled in a nitrogen-filled drybox or glovebag.

Analytical Procedures. Elemental analyses were performed by the University of Illinois School of Chemical Sciences microanalytical laboratory and by Galbraith Laboratories, Knoxville, TN.

Compounds were routinely characterized only by infrared and, when appropriate, ^1H NMR spectroscopy unless specified otherwise. Infrared spectra were measured from mineral oil (Nujol) mulls between KBr plates on a Perkin-Elmer Model 1330 infrared spectrophotometer and were referenced to the 1028 cm^{-1} band of 0.05-mm polystyrene film. Proton and $^{13}C\{^1H\}$ NMR spectra were recorded at 360 and 94.5 MHz, respectively, on a Nicolet NT-360 NMR spectrometer. Chemical shift values were internally referenced to tetramethylsilane. All of the compounds examined were $(n\text{-}C_4H_9)_4N^+$ salts, and the ^1H and $^{13}C\{^1H\}$ resonances arising from the cation are not listed below. These resonances appeared as multiplets centered at about δ 3.2, 1.7, 1.4, and 1.0 in ^1H

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(22) Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *Organometallics* **1985**, *4*, 104.

(23) Knoth, W.; Harlow, R. *J. Am. Chem. Soc.* **1981**, *103*, 4265.

(24) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; pp 305–308.

(25) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947.

(26) Sanchez, C.; Livage, J.; Launay, J. P.; Fournier, M. *J. Am. Chem. Soc.* **1983**, *105*, 6817.

(27) Sommer, L. H.; Tyler, L. J. *J. Am. Chem. Soc.* **1954**, *76*, 1030.

(28) Owens, H. *Abstracts of Papers*, 165th National Meeting of the American Chemical Society, Dallas, Texas, April, 1973; American Chemical Society: Washington, D.C., 1973; INOR 21.

(29) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, 1980; Chapter 3.

NMR spectra and as singlets at about δ 59, 25, 21, and 14 in $^{13}C\{^1H\}$ NMR spectra.

Tungsten-183 FTNMR spectra were measured at 17 °C from CD_3CN solutions at 16.7 MHz in a 15-mm o.d. vertical spinning sample tubes on a Bruker WH-400 multinuclear NMR spectrometer. Chemical shift values were referenced to aqueous 2.0 M Na_2WO_4 by the sample replacement method and corrected due to the different lock magnetic fields between CD_3CN and D_2O. The spectra were recorded over a 4000 Hz bandwidth and digitized by using 16 384 data points.

Oxygen-17 FTNMR spectra were measured from CH_3CN solutions at 33.9 MHz in 12-mm o.d. vertical sample tubes without sample spinning on an unlocked FTNMR system equipped with a 5.87 Oxford Instruments magnet and a Nicolet NIC-80 or 1280 data processor. Chemical shift values were externally referenced to 22 °C fresh tap water by the sample replacement method. The pulse repetition rate was 5.88 Hz. A spectral bandwidth of 50 000 Hz was digitized by using 8192 data points. The pulsewidth employed, 28 μ, corresponded to a 70° pulse.

Silicon-29 FTNMR spectra were measured with ^1H decoupling from CH_3CN solutions at 49.7 MHz on the instrument described above for ^{17}O FTNMR spectroscopy. Except of the case of compound **7**, all chemical shift values were referenced internally to tetramethylsilane. The chemical shift for **7** was referenced to tetramethylsilane by using the sample replacement method.

Chemical shift values for all nuclei are reported as positive numbers for resonances observed at higher frequency (lower field) than the appropriate reference.

Fast atom bombardment mass spectra were measured at the School of Chemical Sciences Mass Spectrometer Center on a VG ZAB-SE high-resolution mass spectrometer equipped with an Ion-Teck fast atom gun. Samples were first dissolved in acetonitrile and then combined with the matrix, 3:1 dithiothreitol/dithioerythritol containing ca. 20% methanol by weight. Sample solutions were heated to remove volatiles before entry into the spectrometer.

Synthesis of $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$.[30] A 0.4 M solution of $(n\text{-}C_4H_9)_4NOH$ in water (2.8 mL, 1.1 mmol) was added to a slurry of $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ (2.0 g, 1.02 mmol) in 20 mL of water with rapid stirring. After being stirred for 15 minutes, the solution was gravity filtered and solvent was removed on a rotary evaporator at ca. 45 °C giving a pale white solid. The solid was dried in a dessicator over $CaSO_4$ for 12 h under a dynamic vacuum. This material was then dissolved into a minimum amount of 1,2-dichloroethane, the solution was gravity filtered, and 75 mL of ether was added to the filtrate, giving a product identified as $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ (1.32 g, 0.60 mmol, 59% yield based on W) by IR spectroscopy.[4b,6] ^{183}W NMR (0.3 M, CD_3CN, 27°C): see Table VII.

Synthesis of $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ (2). Method 1. A solution of chloroacetic acid (0.861 g, 9.11 mmol) in 2 mL of tetrahydrofuran was added dropwise over ca. 2 min to rapidly stirring partially dissolved, well-dispersed slurry of $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ (5.0 g, 2.28 mmol) in 70 mL of tetrahydrofuran. The white slurry was stirred rapidly for 20 min and then poured into 70 mL of THF/ether (50:50 v/v) solution over a 1-min period with rapid stirring. The white solid was collected by suction filtration and washed twice with 30 mL of tetrahydrofuran and then with 50 mL of ether to give 4.1 g of crude product which was dried in vacuo (2.1 mmol, 92% yield). Anal. Calcd for $C_{48}H_{109}N_3Nb_2W_4O_{19}$: C, 29.51; H, 5.62; N, 2.15. Found: C, 29.53; H, 5.61; N, 2.08. IR (Nujol, 600–1050 cm^{-1}): 740 (s), 805 (s), 885 (m), 920 (s), 952 (s), 973 (m), 1028 (w). ^{17}O NMR (12 mM in CH_3CN containing 110 equiv of H_2O; OW, ONbW, OW_2 oxygens ≤8 atom % ^{17}O; ONb, ONb_2H oxygens 24 atom % ^{17}O; 22 °C): see Table VI. ^{183}W NMR (0.25 M in CD_3CN containing 110 equiv of H_2O, 17 °C): see Table VII. This material could be recrystallized as follows. $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ (1.0 g) was dissolved into 1 mL of CH_3CN. After gravity filtration, 0.074 mL of H_2O was added followed by ca. 0.8 mL of ether. The solution was stored at 0 °C and after 36 h, small colorless block shaped crystals usually formed in 52% yield. If no crystals formed, the solution was agitated than let stand at 0 °C until crystals appeared.

Method 2. $(Nb_2W_4O_{18})_2O[(n\text{-}C_4H_9)_4N]_6$ (1.0 g) was dissolved in 1 mL of CH_3CN. The crystallization procedure described in method 1 was followed giving product in 52% yield.

Method 3. CD_3CN (0.4 mL) and H_2O (6 μL, 0.33 mmol) were added to $Nb_2W_4O_{19}CH(CH_3)_2[(n\text{-}C_4H_9)_4N]_3$ (**5**) (0.150 g, 0.075 mmol) at ambient temperature. The ^1H NMR spectrum of this solution measured 5 min after its preparation showed that the isopropyl ester was >95% hydrolyzed. The polyoxoanion reaction product was then recovered from solution by addition of 10 mL of ether, suction filtration, and drying in vacuo, giving 0.128 g (0.066 mmol) of $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ in 88% yield. Hydrolysis of $Nb_2W_4O_{19}C(CH_3)_3[(n\text{-}C_4H_9)_4N]_3$ (**6**) and $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ (**3**, one isomer) were accomplished by the same procedure, giving $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ in identical yield after ca. 6 and ca. 12 h, respectively.

Synthesis of $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ (3, Five-Diastereomer Mixture). $(CH_3O)_2SO_2$ (87 μL, 0.92 mmol) was added dropwise over ca. 15 s to a rapidly stirring solution of $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ (2.0 g, 0.91 mmol) in 3 mL of acetone. A white microcrystalline solid or powder formed during the course of the addition or shortly thereafter. The slurry was stirred for an additional 2–3 min and then the product collected by suction filtration. The white solid was washed with 1 mL of acetone and then four times with 7-mL portions of ether and finally dried in vacuo giving 1.65 g (0.85 mmol) of crude product in 92% yield. Crystallization was accomplished by dissolving 1.65 g of crude product into ca. 2 mL of CH_3CN, gravity filtering, and then slowly adding ether with swirling of the solution until a microcrystalline solid (0.90 g, 0.46 mmol, 51% overall yield) separated from solution. Anal. Calcd for $C_{49}H_{111}N_3Nb_2W_4O_{19}$: C, 29.91; H, 5.69; N, 2.14. Found: C, 29.74; H, 5.62; N, 2.08. IR (Nujol, 600–1050 cm^{-1}): 740 (s), 801 (s), 884 (m), 912 (s), 915 (s), 950 (s), 969 (m), 1012 (m), 1024 (w, sh). ^1H NMR (360 MHz, CD_3CN): δ 4.310, 4.200, 4.198, 4.128, 4.121. $^{13}C\{^1H\}$ NMR (94.5 MHz, CD_3CN): δ 64.2, 64.0, 63.8, 63.6, 63.1.

Synthesis of $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ (3, One Isomer). Method 1. Methanol (10 mL) was added to $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ (4.0 g, 2.0 mmol), and the solution was stirred at ambient temperature for 48 h. Ether (40 mL) was then added to the solution, and the resulting white precipitate was collected by suction filtration and washed with ether giving 3.7 g (1.88 mmol) of crude product in 94% yield. Crystallization was accomplished by dissolving the crude product into ca. 3 mL of CH_3CN, gravity filtering, and then slowly adding ether with swirling of the solution until a microcrystalline solid separated from solution (1.9 g, 0.97 mmol, 49% overall yield). Anal. Calcd for $C_{49}H_{111}N_3Nb_2W_4O_{19}$: C, 29.91; H, 5.69; N, 2.14. Found: C, 29.96; H, 5.80; N, 2.06. IR (Nujol, 600–1050 cm^{-1}): 740 (s), 800 (s), 884 (m), 911 (s), 920 (s), 950 (s), 969 (m), 1012 (m), 1024 (w, sh). ^1H NMR (360 MHz, CD_3CN): δ 4.310. $^{13}C\{^1H\}$ NMR (78.7 MHz, CD_3CN): δ 63.96. ^{17}O NMR (13 mM, CH_3CN): OW, ONbW, OW_2 oxygens ≤10 atom % ^{17}O; ONb oxygen 36 atom % ^{17}O; CH_3ONb_2 oxygen natural abundance ^{17}O; 22 °C): see Table VI. ^{183}W NMR (0.34 M, CD_3CN, 17 °C): see Table VII.

Method 2. Methanol (0.40 mL, 9.9 mmol) was added to $(Nb_2W_4O_{18})_2O[(n\text{-}C_4H_9)_4N]_6$ (**10**) (1.2 g, 0.31 mmol). The solution was stirred for 14 h at ambient temperature, and 20 mL of ether was then added to the solution. The resulting white precipitate was collected by suction filtration and washed with ether giving 1.08 g (0.55 mmol) of $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ as one isomer in 89% yield.

Method 3. Methanol (7 mL, 270 mmol) was added to $Nb_2W_4O_{19}C(CH_3)_3[(n\text{-}C_4H_9N]_3$ (1.2 g, 0.60 mmol) and the solution stirred at 55 °C for 12 h. After the solution was cooled to ambient temperature, 40 mL of ether was added to the solution and the white precipitate collected by suction filtration giving 0.91 g (0.46 mmol) of $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ as one isomer in 77% yield.

Synthesis of $Nb_2W_4O_{19}C_2H_5[(n\text{-}C_4H_9)_4N]_3$ (4, Five-Diastereomer Mixture). This salt was prepared by exactly the same procedure used for the corresponding methyl compound except that 150 μL of $(C_2H_5O)_2SO_2$ was used, and the solution was stirred for 10 min before collecting the crude product (1.16 g, 0.59 mmol, 65% yield). Crystallization was accomplished by dissolving the crude product into 1.5 mL of CH_3CN, gravity filtering the solution into a screw-cap vial, and adding water (ca. 0.6 mL) just until a permanent precipitate appeared. The vial was capped and heated with a heat gun until the solid dissolved. The solution was allowed to cool to room temperature and then cooled to 0 °C giving 0.82 g (0.41 mmol) of colorless block shaped crystals in 45% overall yield. Anal. Calcd for $C_{50}H_{113}N_3Nb_2W_4O_{19}$: C, 30.31; H, 5.75; N, 2.12. Found: C, 30.12; H, 5.87; N, 2.17. IR (Nujol, 600–1050 cm^{-1}): 739 (s), 800 (s), 881 (m), 906 (s, sh), 914 (s), 922 (s), 952 (s), 972 (m), 1028 (m). ^1H NMR (360 MHz, CD_3CN): δ 4.64 (q), 4.42–4.57 (mult), δ 1.53 (t). $^{13}C\{^1H\}$ NMR (94.5 MHz, CD_3CN): δ 71.61, 70.87, 70.55, 70.43, 69.98 (OCH_2CH_3); δ 17.78, 16.78, 16.60 (OCH_2CH_3).

Synthesis of $Nb_2W_4O_{19}C_2H_5[(n\text{-}C_4H_9)_4N]_3$ (4, One Isomer). Method 1. Ethanol (5 mL) was added to $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ (1.5 g, 0.75 mmol) under nitrogen in a 20-mL screw-cap vial equipped with a magnetic stir bar. The vial was capped and taped and the slurry heated to 80 °C with rapid stirring. The resulting clear colorless solution was maintained at 80 °C for 12 h, allowed to cool ambient temperature, and then diluted with 25 mL of ether. The resulting white precipitate was collected by suction filtration and washed with ether giving 1.1 g of crude product (0.55 mmol, 73% yield). Crystallization was achieved in 36% yield by the procedure described above for the preparation of the five-diastereomer mixture. Anal. Calcd for $C_{50}H_{113}N_3Nb_2W_4O_{19}$: C, 30.31;

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[30] For preparative purposes, compound **1** was synthesized as described in ref 6.

H, 5.75; N, 2.12. Found: C, 30.25; H, 5.74; N, 2.21. IR (Nujol, 600–1050 cm^{-1}): 742 (s), 800 (s), 881 (m), 914 (s), 922 (s), 952 (s), 972 (m), 1028 (m). ^{1}H NMR (300 MHz, CD_3CN): δ 4.64 (q), 1.53 (t). $^{13}C\{^{1}H\}$ (94.5 MHz, CD_3CN): δ 71.60 (OCH_2CH_3), 17.73 (OCH_2CH_3).

Synthesis of $Nb_2W_4O_{19}C_2H_5[(n\text{-}C_4H_9)_4N]_3$ (4, One Isomer). Method 2. Ethanol (10 mL) was added to $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ (one isomer, prepared by method 1) (0.9 g, 0.46 mmol) in a nitrogen atmosphere. The slurry was heated at reflux for 24 h over which time the slurry dissolved into solution. After the solution was allowed to cool to room temperature, ca. 40 mL of ether was added and the whtie precipitate collected by suction filtration. Crystallization of the product was accomplished as described for the preparation of $Nb_2W_4O_{19}C_2H_5[(n\text{-}C_4H_9)_4N]_3$ (five isomer, method 1) giving 0.26 g (0.13 mmol) of crystalline product in 28% yield.

Synthesis of $Nb_2W_4O_{19}CH(CH_3)_2[(n\text{-}C_4H_9)_4N]_3$ (5). Method 1. A solution of 2-propanol (0.35 mL, 4.5 mmol) and pyridine (0.36 mL, 4.5 mmol) in 2 mL of CCl_4 was added dropwise with stirring at 0 °C to a solution of trifluoromethanesulfonic anhydride (0.75 mL, 4.5 mmol) in 2.5 mL of CCl_4 over a 2-min period.[31] An 0.80-mL portion of this solution containing ca. 1.2 mmol of isopropyl trifluoromethanesulfonate was added dropwise with stirring over a 1-min period to a solution of $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ (2.0 g, 0.91 mmol) in 10 mL of CH_2Cl_2 at 0 °C. After addition was complete, 35 mL of ether was added to the solution and the resulting white precipitate was collected by suction filtration and washed with 20 mL of ether to give 1.3 g (0.65 mmol) of crude product in 71% yield. The crude product was contaminated with a small amount of $(Nb_2W_4O_{18})_2O[(n\text{-}C_4H_9)_4N]_6$ according to IR spectroscopy. The crude product was dissolved into 1.5 mL of acetonitrile under nitrogen and gravity filtered, and ca. 5 mL of ether was added to the filtrate with stirring until a white precipitate, but no oil had formed. Addition of excess ether leads to the formation of an oily material with no significant increase in yield. The white solid was collected by suction filtration and washed with ether. This material was then crystallized by dissolving it into 1.5 mL of dry acetonitrile (distilled from P_4O_{10}) and then slowly adding ether with swirling until a microcrystalline product appeared. This purification procedure gave 0.37 g (0.19 mmol) of crystalline product in 21% overall yield. Anal. Calcd for $C_{51}H_{115}N_3Nb_2W_4O_{19}$: C, 30.69; H, 5.81; N, 2.10. Found: C, 30.60; H, 5.74; N, 2.15. IR (Nujol, 600–1050 cm^{-1}): 740 (s, sh), 785 (s), 888 (m, sh), 909 (m), 951 (s), 968 (m). ^{1}H NMR (300 MHz, CD_3CN): δ 4.67 (sep), 1.29 (d). $^{13}C\{^{1}H\}$ NMR (78.7 MHz, CD_3CN): δ 77.77, 25.93.

Method 2. 2-Propanol (7 mL) was added to $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ (1.2 g, 0.61 mmol). Acetonitrile was then added to the slurry with stirring until it became clear (ca. 2 mL) and an additional 1 mL of acetonitrile was added. The solution was stirred for 4 h at ambient temperature and then diluted with ca. 50 mL of ether. The resulting white precipitate was collected by suction filtltration and washed with ether (0.91 g, 0.45 mmol, 75% yield). Crystallization was accomplished as described in method 1 giving 0.41 g (0.21 mmol) of product in 34% overall yield. Anal. Calcd for $C_{51}H_{115}N_3Nb_2W_4O_{19}$: C, 30.69; H, 5.81; N, 2.11. Found: C, 30.47; H, 5.66; N, 2.08.

Synthesis of $Nb_2W_4O_{19}C(CH_3)_3[(n\text{-}C_4H_9)_4N]_3$ (6). Method 1. This salt was prepared by the same procedure described for preparation of the isopropyl derivative **5**, method 2, except 3.8 g (1.9 mmol) of $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ and 28 mL of *tert*-butyl alcohol were used, and 3.2 g (1.6 mmol) of crude product was obtained in 84% yield. To obtain crystalline material, the powder was dissolved into 4 mL of CH_3CN and gravity filtered into a screw-cap vial, and ca. 8 mL of ether was slowly added until a permanent precipitate appeared. The vial was then capped and the slurry heated to ca. 35 °C with swirling for 3 min over which time the powder turned into a microcrystalline solid. The microcrystalline product was collected by suction filtration and washed with two 20-mL portions of ether giving 1.94 of product in 51% overall yield. Anal. Calcd for $C_{52}H_{117}N_3Nb_2W_4O_{19}$: C, 31.07; H, 5.88; N, 2.09. Found: C, 31.15; H, 5.97; N, 2.26. IR (Nujol, 600–1050 cm^{-1}): 731 (m), 790 (s), 887 (m), 907 (m), 949 (s), 962 (m), 1015 (m). ^{1}H NMR (360 MHz, CD_3CN): δ 1.37. $^{13}C\{^{1}H\}$ NMR (94.5 MHz, CD_3CN): δ 83.3, 31.7. ^{17}O NMR (13.2 mM; CH_3CN; OCNb oxygen material abundance ^{17}O, remaining oxygen ≤10 atom % ^{17}O; 22 °C): see Table VI. ^{183}W NMR (0.29 M, CD_3CN): see Table VII.

Method 2. *tert*-Butyl alcohol (4 mL, 42.4 mmol) (dried over sodium) was added to 0.5 g (0.25 mmol) of $Nb_2W_4O_{19}CH(CH_3)_2[(n\text{-}C_4H_9)_4N]_3$ (**5**) under nitrogen. Acetonitrile (1 mL) was added to the slurry with rapid stirring until a clear solution was obtained. This solution was immersed in a 44 °C oil bath for 12 hours with rapid stirring, allowed to cool to room temperature, and then diluted with 20 mL of ether. The resulting white precipitate of $Nb_2W_4O_{19}C(CH_3)_3[(n\text{-}C_4H_9)_4N]_3$ was collected by suction filtration, washed with ether, and air-dried, giving 0.37 g of product in 73% yield.

Method 3. *t*-Butyl alcohol (4 mL, 42.4 mmol) (dried over sodium) was added to 0.5 g (0.25 mmol) of $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ (**3**, one isomer), under nitrogen. One mL of acetonitrile was added to the slurry with rapid stirring to obtain a clear solution. This solution was immersed in a 65 °C oil bath and stirred for 16 h, allowed to cool to room temperature, and then diluted with 40 mL of ether. The resulting white precipitate of $Nb_2W_4O_{19}C(CH_3)_3[(n\text{-}C_4H_9)_4N]_3$ was collected by suction filtration, washed with ether, and dried in vacuo giving 0.41 g (0.20 mmol) of product in 80% yield.

Synthesis of $Nb_2W_4O_{19}Si(CH_3)_3[(n\text{-}C_4H_9)_4N]_3$ (7). Method 1. A three-necked 50-mL round-bottom flask containing a magnetic stirring bar was purged with nitrogen and charged with $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ (4.0 g, 1.82 mmol) and 11 mL of chloroform. The system was connected to a mineral oil bubbler and kept under a continuous nitrogen flow. Pyridine (190 μL, 2.35 mmol), hexamethyldisilazane (384 μL, 1.82 mmol), and finally chlorotrimethylsilane (229 μL, 1.82 mmol) were then added to the solution with rapid stirring, resulting in the liberation of a white gas. The solution was stirred for 5 min and then diluted with 50 mL of ether. The white precipitate obtained was collected by suction filtration, washed five times with 20-mL portions of ether, and stored in a dessicator under vacuum for 12 h giving 3.2 g (1.6 mmol) of crude product in 88% yield. This crude product was dissolved into 8 mL of CH_2Cl_2, and after gravity filtration, toluene was added until the solution became saturated (ca. 4 mL). Crystals were obtained after 12–24 h slow evaporation of CH_2Cl_2 under a nitrogen flow. Rod-shaped (2.6 g, 1.3 mmol) were isolated in 71% overall yield. Anal. Calcd for $C_{51}H_{117}N_3SiNb_2W_4O_{19}$: C, 30.24; H, 5.82; N, 2.07; Si, 1.39; Nb, 9.17; W, 36.30. Found: C, 30.39; H, 5.81; N, 2.06; Si, 1.20; Nb, 8.98; W, 36.41. IR (Nujol, 600–1000 cm^{-1}): 730 (m, s), 788 (s), 842 (m), 888 (m), 911 (m), 953 (s), 977 (m). ^{1}H NMR (360 MHz, CD_2Cl_2): δ 0.196. $^{13}C\{^{1}H\}$ (94.5 MHz, CD_2Cl_2): δ 0.175. $^{29}Si\{^{1}H\}$ (0.3 M, CD_3CN, 22 °C): δ 14.7. ^{183}W NMR (0.26 M, CD_3CN): see Table VII.

Method 2. This salt was prepared by the same procedure described for the preparation of the *tert*-butyl derivative **6**, method 2, except 9 mL of freshly prepared $(CH_3)_3SiOH$ and $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ (1.2 g, 0.55 mmol) were used giving 0.94 g (0.46 mmol, 84% yield) of crude product. Crystallization was accomplished as outlined for the crystallization of the *tert*-butyl derivative (0.76 g, 0.38 mmol, 69% overall yield). Anal. Calcd for $C_{51}H_{117}N_3SiNb_2W_4O_{19}$: C, 30.24; H, 5.82; N, 2.07. Found: C, 30.04; H, 5.71; N, 2.05.

Synthesis of $Nb_2W_4O_{19}Si(t\text{-}C_4H_9)(CH_3)_2[(n\text{-}C_4H_9)_4N]_3$ (8). Method 1. A solution of $(t\text{-}C_4H_9)(CH_3)_2SiOSO_2CF_3$ (310 μL, 1.18 mmol) in 2 mL of 1,2-dichloroethane was prepared under nitrogen and added dropwise over 5 min to a rapidly stirring solution of $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ (2.0 g, 0.91 mmol) in 4 mL of 1,2-dichloroethane under nitrogen. The solution was further stirred for ca. 5 min and then heated to 45 °C for 10 min. After the solution was allowed to cool to room temperature, 50 mL of ether was added to the solution over a 1-min period. The resulting white solid or oil was dispersed by stirring and the supernatant decanted. CH_3CN (1.5 mL) was added to the oil solid, and the solution was then diluted with 50 mL of ether. This precipitation procedure was repeated (usually twice) until a white powder was obtained which was then collected by suction filtration and washed with ether, giving 0.94 g (0.45 mmol) of crude product. Infrared spectroscopy indicated that this material was contaminated with $(Nb_2W_4O_{18})_2O[(n\text{-}C_4H_9)_4N]_6$. The sample was recrystallized twice by a scaled-down version of the procedure outlined for method 2 (0.39 g crystals, 0.19 mmol, 21% overall yield). Anal. Calcd for $Nb_2W_4O_{19}SiC_{54}H_{123}N_3$: C, 31.37; H, 6.00; N, 2.03. Found: C, 31.22; H, 5.97; N, 1.98. IR (Nujol, 600–1000 cm^{-1}): 631 (w), 731 (m, sh), 786 (s), 838 (m, sh), 882 (m, sh), 902 (s), 951 (s), 976 (m). ^{1}H NMR (300 MHz, CD_3CN): δ 0.971, 0.124. $^{13}C\{^{1}H\}$ NMR (94.5 MHz, CD_3CN): δ 26.20, 20.34, −2.94. $^{29}Si\{^{1}H\}$ NMR (49.7 MHz, 0.34 M in CD_3CN, 0.0392 M $Cr(acac)_3$: δ 17.3. ^{183}W NMR (0.34 M, CD_3CN): see Table VII.

Method 2. CH_3CN (4 mL) was added to a mixture of $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ (1.52 g, 0.78 mmol) and $[(t\text{-}C_4H_9)(CH_3)_2SiOH]_2\cdot H_2O$ (0.552 g, 1.95 mmol). The slightly cloudy solution was stirred at ambient temperature for 14 h. Ether (ca. 20 mL) was then added, precipitating a white solid which was collected by suction filtration and washed twice with 15-mL portions of ether to give 1.31 g of crude product (0.63 mmol, 82% yield). Crystallization was accomplished by dissolving the crude product in 1.5 mL of CH_3CN, gravity filtering, and then adding ca. 0.8 mL of ether to the filtrate until a permanent precipitate appeared. The vial was capped and gently heated with swirling until all the solid dissolved. When the solution was cooled to ambient temperature, small crystals formed after 12 h at −20 °C and 0.55 g (0.27 mmol) of colorless

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(31) Beard, C. D.; Baum, K.; Grakauskas, V. *J. Org. Chem.* **1973**, *38*, 3673.

(32) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: pp (a) 55–66; (b) 99–101; (c) 149–150.

block-shaped crystals were obtained in 35% overall yield after suction filtration and washing with ether. Anal. Calcd for $C_{54}H_{123}N_3SiNb_2W_4O_{19}$: C, 31.37; H, 6.00; N, 2.03. Found: C, 31.18; H, 5.98; N, 2.05.

Synthesis of $Nb_2W_4O_{19}Si(C_6H_5)_3[(n\text{-}C_4H_9)_4N]_3$ (9). Method 1. CH_3CN (12.8 mL) CH_3CN was added to a mixture of $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ (8.1 g, 4.1 mmol) and $(C_6H_5)_3SiOH$ (5.8 g, 16.6 mmol). The resulting clear colorless solution was stirred vigorously at ambient temperature under a static nitrogen atmosphere for 24 h. The slightly cloudy solution was twice gravity filtered, and 30 mL of ether was then added to the filtrate over a 30-s period with gentle swirling until a permanent, clear, colorless oil persisted at the bottom of the flask. Gentle agitation of the oil by swirling the solution for ca. 3 min resulted in complete conversion of the oil into a microcrystalline solid. After collection by suction filtration and washing twice with 15-mL portions of ether, 7.2 g of microcrystalline product was isolated. This material was then dissolved into 4.5 mL of CH_3CN and recrystallized following the procedure just described to give 6.7 g (3.0 mmol) of product in 73% overall yield. Anal. Calcd for $C_{66}H_{123}N_2W_4O_{19}$: C, 35.84; H, 5.60; N, 1.90. Found: C, 35.74; H, 5.56; N, 1.84. IR (Nujol, 600–1050 cm^{-1}): 709 (s), 786 (s), 881 (m, sh), 904 (m), 949 (s), 966 (s), 991 (m), 1008 (m), 1032 (w). ^1H NMR (360 MHz, CD_3CN): δ 7.70–7.74 (mult, 2 H), 7.41–7.49 (mult, 3 H). $^{13}C\{^1H\}$ (94.5 MHz, CD_3CN): δ 137.30, 135.81, 130.77, 128.71. $^{29}Si\{^1H\}$ NMR (49.7 MHz, 0.39 M, CD_3CN, 0.011 M $Cr(acac)_3$): δ 19.0. ^{183}W NMR (0.32 M, CD_3CN): see Table VII.

Method 2. CH_3CN (3 mL) was added to a mixture of $(C_6H_5)_3SiOH$ (0.684 g, 2.46 mmol) and $(Nb_2W_4O_{18})_2O[(n\text{-}C_4H_9)_4N]_6$ (1.2 g, 0.31 mmol) under nitrogen. After the solution was stirred for 10 h at ambient temperature and gravity filtered, 15 mL of ether was added to the solution over a 15–30-s period. Crude product (1.1 g, 0.50 mmol, 80% yield) was isolated from solution by using a scaled down version of the crystallization procedure described above for method 1.

Synthesis of $[(Nb_2W_4O_{18})_2O][(n\text{-}C_4H_9)_4N]_6$ (10). Method 1. A solution of chloroacetic acid (0.090 g, 0.95 mmol) in 0.5 mL of CH_2Cl_2 was added to a rapidly stirring solution of $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ (2.0 g, 0.91 mmol) in 2 mL of CH_2Cl_2 over a 2-min period. After 1 min of additional stirring, 100 mL of THF was added. The resulting white precipitate was collected by suction filtration after stirring for two additional minutes, washed twice with 30-mL portions of ether, and stored in vacuo for 12 h. The crude product (1.62 g) was then dissolved in 3.5 mL of CH_3CN under nitrogen and gravity filtered. Crystallization was accomplished by slow vapor diffusion of ether into this CH_3CN solution, giving 0.92 g (0.24 mmol) of needle crystals in 52% yield. Anal. Calcd for $C_{96}H_{216}N_6Nb_4W_8O_{37}$: C, 29.65; H, 5.60; N, 2.16; Nb, 9.56; W, 37.82. Found: C, 29.65; H, 5.63; N, 2.29; Nb, 9.51; W, 37.66. IR (Nujol, 600–1000 cm^{-1}): 672 (s), 722 (m), 738 (m), 799 (v), 885 (m, sh), 912 (m), 952 (s), 972 (m). ^{17}O NMR (8.5 mM, CH_3CN, ≤15 atom % ^{17}O, 20 °C): see Table VI. ^{183}W NMR (0.15 M, CD_3CN, 17 °C): see Table VI.

Method 2. $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ (2.0 g, 1.0 mmol) was dissolved into 2 mL of dry CH_2Cl_2 (distilled from P_4O_{10}) and gravity filtered in a glovebag. Ether (125 mL) was then added to the filtrate. The white precipitate was collected by suction filtration and washed twice with 50-mL portions of ether giving 1.49 g (0.38 mmol) of crude product in 75% yield.

Method 3. $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ (0.154 g, 0.007 mmol) was added to a suspension of $Rh_6(CO)_{16}$ (0.075 g, 0.007 mmol) in 1.25 mL of CH_2Cl_2 (dried over P_4O_{10}) under nitrogen. The slurry was stirred for 3 h, and the small amount of unreacted $Rh_6(CO)_{16}$ was filtered off. Addition of 23 mL of ether to the filtrate afforded a purple solid that was extracted with 10 mL of THF. Suction filtration yielded a white solid (122 mg, 89% yield) identified as $[(Nb_2W_4O_{18})_2O][(n\text{-}C_4H_9)_4N]_6$ using IR spectroscopy. No polyoxoanion product was detected in the purple filtrate by IR spectroscopy.

Method 4. CO_2 gas was bubbled for 1 min through a rapidly stirring solution of $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ (2.0 g, 0.91 mmol) in 2 mL of dry CH_3CN (distilled from P_4O_{10}) in a dinitrogen atmosphere. The solution was stirred for one additional minute and then diluted with 35 mL of ether. The colorless oil was dispersed at the bottom of the flask with a spatula, and the supernatant was poured away. The oily solid was then washed with 4.0 mL of tetrahydrofuran, and the supernatant was decanted. The solid was finally washed with ca. 30 mL of ether. The white solid was collected by suction filtration, washed twice with 35-mL portions of ether, and then dried in a dessicator under a dynamic vacuum giving 1.12 g (0.29 mmol) of a white solid in 63% yield. Infrared spectroscopy indicated that the product was $(Nb_2W_4O_{18})_2O[(n\text{-}C_4H_9)_4N]_6$.

Hydrolysis of $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$, Five-Diastereomer Mixture. $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ as a five-diastereomer mixture (0.05 g, 0.030 mmol) was dissolved into 0.4 mL of CD_3CN. D_2O (23 μL, 1.27 mmol) was added to the solution. After 12 h at ambient temperature, ^1H NMR spectroscopy indicated that one of the five isomers (δ 4.310) was completely hydrolyzed while the remaining isomers were present in >95% of their original concentrations.

Attempted Hydrolysis of $Nb_2W_4O_{19}Si(CH_3)_3[(n\text{-}C_4H_9)_4N]_3$. H_2O (44 μL, 2.4 mmol) was added to a solution of $Nb_2W_4O_{19}Si(CH_3)_3[(n\text{-}C_4H_9)_4N]_3$ (1.0 g, 0.49 mmol) in 0.5 mL of CH_3CN. The solution was stored at 22 °C for 6 days. Nearly quantitative precipitation of the original salt (0.92 g), identified by IR spectroscopy, was accomplished by addition of excess ether to the solution.

Ethanolysis of $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$, Five-Diastereomer Mixture. Ethanol (10 mL, 0.13 mmol) was added to a five-isomer mixture of $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ (1.0 g 0.51 mmol). The slurry was heated at reflux for 24 h during which time the solid dissolved into solution. Crude (0.71 g, 71% yield) and crystalline (0.29 g, 29% yield) products were isolated from solution as described for the preparation of $Nb_2W_4O_{19}C_2H_5[(n\text{-}C_4H_9)_4N]_3$ (one isomer, method 1). ^1H NMR (360 MHz, CD_3CN): δ 4.64 (q), 4.200, 4.198, 4.128, 4.121. The same spectrum was observed for crude and recrystallized material.

Attempted Alkylation of $W_6O_{19}[(n\text{-}C_4H_9)_4N]_2$. $(CH_3O)_2SO_2$ (1 μL, 0.011 mmol) was added to a solution of $W_6O_{19}[(n\text{-}C_4H_9)_4N]_2$ (3 mg, 0.0016 mmol) in 0.4 mL of CD_3CN. The solution was monitored by ^1H NMR spectroscopy and showed no indication of reaction after 2 days at ambient temperature.

Mass Spectrometry. Fast atom bombardment mass spectra were measured in both the positive and negative ion detection modes for $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_3$ (2) and $(Nb_2W_4O_{18})_2O[(n\text{-}C_4H_9)_4N]_6$ (10) in an inconclusive attempt to support their formulations. Only ions corresponding to nonfragmented hexametalate polyoxoanion units will be reported here. For compound **2**, the major cations observed could be assigned to $\{Nb_2W_4O_{19}H_2[(n\text{-}C_4H_9)_4N]_3{\cdot}CH_3CN\}^+$ and $Nb_2W_4O_{19}H[(n\text{-}C_4H_9)_4N]_4{}^+$; minor cations observed included $\{[(Nb_2W_4O_{18})_2O]H_2[(n\text{-}C_4H_9)_4N]_5\}^+$. The anions $\{Nb_2W_4O_{19}H_{(x+1)}[(n\text{-}C_4H_9)_4N]_{(2-x)}\}^-$ (x = 0, 2) were observed as peaks with intensities only about twice the base-line noise. For compound **10**, the anions $\{[(Nb_2W_4O_{18})_2O]H_x[(n\text{-}C_4H_9))_4N]_{(5-x)}\}^-$ (x = 1, 2, 3, 5) and $\{Nb_2W_4O_{19}H_{(x+1)})[(n\text{-}C_4H_9)_4N]_{(2-x)}\}^-$ (x = 0–2) were observed with intensities about twice the base-line noise. No cations measured from a sample of **10** were observed which could be assigned to a nonfragmented hexametalate polyoxoanion unit.

X-ray Crystallographic Studies[9] of $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ (3) and $\{Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]\}[(n\text{-}C_4H_9)_4N]_3$ (8). Large well-shaped colorless single crystals of $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ (**3**), obtained as described above from the five-isomer mixture, and $\{Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]\}[(n\text{-}C_4H_9)_4N]_3$ (**8**), obtained by cooling a hot, saturated acetone solution to ambient temperature, were suitable for X-ray diffraction studies. At 20 ± 1 °C, crystals of both compounds are orthorhombic, with a = 17.643 (3) Å, b = 24.089 (5) Å, c = 32.273 (6) Å, V = 13716 (5) Å^3, and Z = 8 [$\mu_a(\mathrm{Mo}\ K\bar{\alpha})^{32a} = 7.20\ mm^{-1}$; d_{calcd} = 1.906 g cm^{-3}] for **3** and a = 15.756 (3) Å, b = 17.620 (4) Å, c = 26.850 (6) Å, V = 7454 (2) Å^3, and Z = 4 [$\mu_a(\mathrm{Mo}\ K\bar{\alpha})^{32a} = 6.64\ mm^{-1}$; d_{calcd} = 1.843 g cm^{-3}] for **8**. Space groups for both compounds are uniquely determined by the systematically absent reflections: centrosymmetric $Pbca$—D_{2h}^{15}, No. 61,[33a] for **3** and noncentrosymmetric $P2_12_12_1$—D_2^4, No. 19,[33b] for **8**.

Intensity measurements were made for both compounds on a computer-controlled Nicolet autodiffractometer using full [0.90° (**3**) or 1.00° (**8**) wide] ω scans and graphite-monochromated Mo $K\bar{\alpha}$ radiation for rectangular parallelepiped-shaped specimens having dimensions of 0.30 mm × 0.58 mm × 0.66 mm (**3**) and 0.34 mm × 0.44 mm × 0.56 mm (**8**). Both crystals were glued with epoxy to the inside of sealed thin-walled glass capillaries and mounted on a goniometer with their longest edge nearly parallel to the ϕ axis of the diffractometer. Totals of 7853 (**3**) and 5641 (**8**) independent reflections having $3° < 2\theta_{MoK\bar{\alpha}} < 43°$ (**3**) or 45.8° (**8**) [the equivalent of 0.50 (**3**) or 0.60 (**8**) Cu $K\bar{\alpha}$ limiting spheres] were measured for both compounds with scanning rates of 6°/min or 3°/min. The intensity data for both compounds were corrected empirically for variable absorption effects by using ψ scans for four reflections of **3** having 2θ between 10.5° and 30.5° or five reflections of **8** having 2θ between 7.6° and 28.5° (the relative transmission factors ranged from 0.216 to 1.000 for **3** and 0.453 to 1.000 for **8**). The data collection and reduction procedures that were used are described elsewhere.[6]

The six crystallographically independent metal atoms in the asymmetric units of both **3** and **8** were located by using (SHELXTL) "direct methods" techniques. Refinement of the structural parameters for these six metals in **3** (all modeled as anisotropic W atoms with occupancies of 0.851) gave R_1 (unweighted, based on F)[34] = 0.157 for 3541 independent

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(33) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I: p (a) 150; (b) 105.

absorption-corrected reflections having $I > 3\sigma(I)$ and $2\theta_{\mathrm{MoK}\bar{\alpha}} < 43°$. Refinement of the six metals in **8** (one as 100% Nb, one as 100% W, and four as W with occupancies of 0.889) gave $R_1 = 0.143$ for 3806 independent absorption-corrected reflections having $I > 3\sigma(I)$ and $2\theta_{\mathrm{MoK}\bar{\alpha}} < 45.8°$. Significant variation in the resulting equivalent isotropic thermal parameters for the W atoms with occupancies <1.00 indicated nonstatistical disordering in the solid state of the two cis Nb atoms over all six metal sites in **3** and one Nb over four metal sites in **8**.

Difference Fourier syntheses for both structures based on the respective model containing six (**3**) or four (**8**) anisotropic partial-occupancy W atoms revealed the remaining 71 (**3**) and 77 (**8**) non-hydrogen atoms of the asymmetric unit. Inclusion of these atoms into the model with isotropic thermal parameters and occupancies of 1.00 gave $R_1 = 0.078$ for 3541 reflections of **3** and $R_1 = 0.060$ for 3806 reflections of **8**. Idealized positions for methylene hydrogens of the $(n\text{-}C_4H_9)_4N^+$ cations in **3** werethen calculated by assuming sp^3 hybridization of the carbons and a C–H bond length of 0.96 Å; these hydrogen atoms were included in all subsequent structure factor calculations with fixed coordinates and isotropic thermal parameters which were fixed at 1.2 times the value of the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded. The occupancies (as W atoms for disordered sites) of the six anisotropic metal atoms in the anions of **3** and **8** were then allowed to vary in least-squares refinement cycles; the refined occupancies corresponded to normalized W percentages of 50.4 for M_1, 77.3 for M_2, 64.2 for M_3, 35.3 for M_4, 76.8 for M_5, and 96.0 for M_6 in **3** and 90.8 for M_1, 72.7 for M_2, 88.0 for M_3, and 48.5 for M_4 in **8** (the two remaining metal sites in **8** appeared to be 100% W or Nb). All subsequent structure factor calculations for both compounds employed a least-squares refineable extinction correction[35] and "whole" atoms at these disordered metal positions whose scattering factors and anomalous dispersion corrections had these percentages of Nb and W character.

The final cycles[9] of counter-weighted[36] cascade block-diagonal least-squares refinement which employed anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for the fixed methylene hydrogen atoms in the cations of **3** give $R_1 = 0.051$ and R_2 (weighted, based on F)[34] = 0.039 for 3541 independent absorption-corrected reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$. Similar refinement cycles for **8** in which all metal, Si, C and O atoms of the anion were modeled with anisotropic thermal parameters and the N and C atoms of the cations were modeled with isotropic thermal parameters gave $R_1 = 0.046$ and $R_2 = 0.041$ for 3806 independent absorption-corrected reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 45.8°$ and $I > 3\sigma(I)$.

All structure factor calculations for both compounds employed recent tabulations of atomic form factors[32b] and anomalous dispersion corrections[32c] to the scattering factors of the Nb, W, and Si atoms. All calculations were performed on a Data General Eclipse S-200 or S-230 computer equipped with 256K of 16-bit words, a floating-point processor for 32- and 64-bit arithmetic, and versions of the Nicolet EXTL and SHELXTL interactive crystallographic software packages as modified at Crystalytics Company.

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Registry No. **1**·$[(n\text{-}C_4H_9)_4N]_4$, 75005-92-4; **2**·$[(n\text{-}C_4H_9)_4N]_3$, 109765-30-2; **3f**·$[(n\text{-}C_4H_9)_4N]_3$, 109800-66-0; **4f**·$[(n\text{-}C_4H_9)_4N]_3$, 109800-68-2; **5**·$[(n\text{-}C_4H_9)_4N]_3$, 109800-70-6; **6**·$[(n\text{-}C_4H_9)_4N]_3$, 109800-72-8; **7**·$[(n\text{-}C_4H_9)_4N]_3$, 109800-74-0; **8**·$[(n\text{-}C_4H_9)_4N]_3$, 109800-76-2; **9**·$[(n\text{-}C_4H_9)_4N]_3$, 109800-78-4; **10**·$[(n\text{-}C_4H_9)_4N]_6$, 109862-62-6; $Rh_6(CO)_{16}$, 28407-51-4; CO_2, 124-38-9; $W_6O_{19}[(n\text{-}C_4H_9)_4N]_2$, 12329-10-1.

Supplementary Material Available: Crystal structure report for $Nb_2W_4O_{19}CH_3[(n\text{-}C_4H_9)_4N]_3$ (**3**), Table II (anisotropic thermal parameters for **3**), Table III (fractional atomic coordinates for methylene hydrogen atoms in **3**), Table V (bond lengths and angles for cations in **3**), Figure 2 (ORTEP drawings of cations in **3**), crystal structure report for $\{Nb_2W_4O_{19}Si(CH_3)_2[C(CH_3)_3]\}[(n\text{-}C_4H_9)_4N]_3$ (**8**), Table IX (anisotropic thermal parameters for **8**), Table XI (bond lengths and angles for cations in **8**), Figure 7 (ORTEP drawings of cations in **8**) (25 pages); structure factor amplitude tables for **3** and **8** (33 pages). Ordering information is given on any current masthead page.

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(34) The R values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, where $w = (\sigma_F)^{-2}$ is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$, where K is the scale factor.

(35) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

(36) For counter weights: $\sigma_F = \{[\sigma(F_o)]^2 + (p|F_o|)^2\}^{1/2}$ where the "ignorance factor", p, has the value of 0.01 in this case.