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Deoxygenation of Polynuclear Metal−Oxo Anions: Synthesis, Structure, and Reactivity of the Condensed Polyoxoanion $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$

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The deoxygenation of the mixed-metal polyoxoanion $[(C_4H_9)_4N]_3NbW_5O_{19}$ with benzoyl chloride in dichloromethane forms quantitatively the condensed polyoxanion $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$, in which two polyoxoanion fragments are linked together by a Nb−O−Nb oxo bridge. The product is characterized by a strong IR band at 692 cm^{-1} assigned to a Nb−O−Nb stretch and a broad single ^{93}Nb NMR resonance at 975 ppm. Partial hydrolysis of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ to $NbW_5O_{19}O^{3-}$ in wet acetonitrile was observed by IR and ^{17}O NMR spectroscopy. The reaction of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ with a variety of alcohols and phenol forms alkoxide-derivatized polyoxoanions $[(C_4H_9)_4N]_2Nb(OR)W_5O_{18}$ (R = methyl, ethyl, isopropyl, cholesteryl, phenyl). The similarity of the IR spectra of these deriviatives suggests that functionalization occurs at the terminal NbO oxygen. A crystallographic study of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ revealed a crystallographically imposed linear Nb−O−Nb oxo bridge ($Nb-O_{bridge} = 1.887(3)$ Å) and a structure in which the terminal tungsten−oxo bonds on the adjoining polyoxoanion fragments are eclipsed. Crystal data: orthorhombic, *Cmca*; $Z = 4$, $a = 15.817(2)$ Å, $b = 17.870(2)$ Å, $c = 35.058(2)$ Å; $V = 9928.0(10)$ Å^3; $R = 5.52\%$.

Polynuclear transition metal oxo anions (polyoxoanions) are widely recognized for having interesting physical properties as well as numerous applications ranging from catalysis to pharmacology.[1] Derivatization of these compounds with organic and inorganic compounds has been investigated extensively and is a valuable means of altering polyoxoanion properties and reactivity.[2] One of the simplest polynuclear tungstates, $W_6O_{19}^{2-}$, is difficult to derivatize; however, its reactivity can be enhanced by the substitution of Nb(V) for W(VI) (Figure 1a).[1b] This substitution results in a singly substituted mixed-metal polyoxoanion in which the terminal and bridging oxygen atoms bound to niobium are significantly more nucleophilic than the corresponding oxygen atoms bound solely to tungsten.[1b,3]

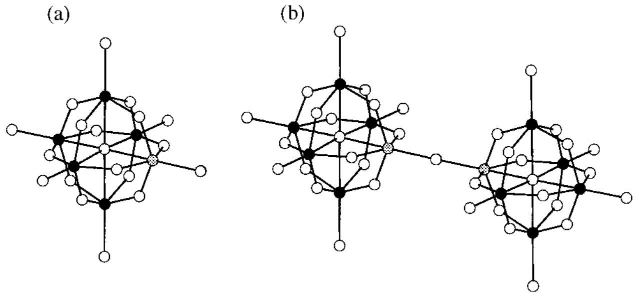

Figure 1. Structural representations of (a) the mixed-metal polyoxoanion $NbW_5O_{19}^{3-}$ and (b) its condensation product $(NbW_5O_{18})_2O^{4-}$ (W = solid, Nb = shaded, O = open spheres).

One consequence of the increase in reactivity is the self-condensation of multiply substituted niobium tungstates[4] to form larger polyoxoanions with connecting Nb−O−Nb bridges (Figure 1b). These compounds are excellent starting materials for the preparation of organic and organometallic derivatized polyoxoanions.[4] We report here that deoxygenation of the terminal NbO oxygen fragment in the singly substituted niobium tungstate $[(C_4H_9)_4N]_3NbW_5O_{19}$ with benzoyl chloride is a useful and potentially versatile method for the preparation of the condensed polyoxoanion $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ and related compounds. Condensed niobium tungstates have not been characterized crystallographically to date, possibly due to complications arising from disorder, high charge, and large size, which are common difficulties in crystallographic studies of polyoxoanions.[4a−c,5] The use of a small singly substituted niobium tungstate simplified these crystallographic problems. In addition to X-ray crystallographic studies, $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ was characterized by IR and multinuclear NMR spectroscopy and its reactions with alcohols.

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(1) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer Verlag: New York, 1983. (b) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533. (c) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (d) Pope, M. T.; Müller, A. *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity;* Kluwer Academic Publishers: Dordrecht, Netherlands, 1994. (e) Jansen, R. J. J.; van Veldhuizen, H. M.; Schwegler, M. A.; van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 115.

(2) (a) Kim, G.; Hagen, K.; Hill, C. L. *Inorg. Chem.* **1992**, *31*, 5316 and references therein. (b) Hou, Y.; Hill, C. L. *J. Am. Chem. Soc.* **1993**, *115*, 11823. (c) Zubieta, J. A. In *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity;* Pope, M. T., Muller, A., Eds.; Kluwer Academic Publishers: Dordrecht, Netherlands, 1994; p 129. (d) Strong, J. B.; Ostrander, R.; Rheingold, A. L.; Maata, E. A. *J. Am. Chem. Soc.* **1994**, *116*, 3601.

(3) (a) Schwartz, C.; Klemperer, W. G. *Inorg. Chem.* **1985**, *24*, 4459. (b) Besecker, C. J.; Klemperer, W. G.; Maltbie, D. J.; Wright, D. A. *Inorg. Chem.* **1985**, *24*, 1027. (c) Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *Organometallics* **1985**, *4*, 104.

(4) (a) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274. (b) Day, V. W.; Klemperer, W. G.; Schwartz, C. *J. Am. Chem. Soc.* **1987**, *109*, 6030. (c) Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics* **1988**, *7*, 1692. (d) Finke, R. G.; Nomiya, K.; Green, C. A.; Droege, M. W. *Inorg. Synth.* **1992**, *29*, 239.

(5) (a) Trovarelli, A.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 6034. (b) Nomiya, K.; Kaneko, M.; Kasuga, N. C.; Finke, R. G.; Pohl, M. *Inorg. Chem.* **1994**, *33*, 1469. (c) Other condensed polyoxoanions recently characterized by X-ray crystallography: (i) Wassermann, K.; Palm, R.; Lunk, H.-J.; Fuchs, J.; Steinfeld, N; Stoesser, R. *Inorg. Chem.* **1995**, *34*, 5029 and references therein. (ii) Galán-Mascarós, J. R.; Giménez-Saiz, C.; Triki, S.; Smail, T.; Gómez-Garcia, C. J.; Coronado, E.; Ouahab, L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1460.

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Experimental Section

Materials and Methods. All manipulations were carried out under an inert atmosphere of argon or dried nitrogen by using standard Schlenk glassware, glovebox, and vacuum line techniques.[6] Dichloromethane was distilled under argon over CaH_2 before use. $Cl_3C_2O_2H$ was purified by recrystallization in hot cyclohexane and dried on a vacuum line for 2 days at 60 °C. The starting materials $[(C_4H_9)_4N]_2WO_4$,[7] $Nb(OEt)_5$,[8a] $Ta(OEt)_5$,[8b] $K_8Nb_6O_{19}$,[9] $[(C_4H_9)_4N]_4Nb_2W_4O_{19}$,[10] $[(C_4H_9)_4N]_3NbW_5O_{19}$,[3b,11] and $[(C_4H_9)_4N]_3TaW_5O_{19}$[3b] were prepared by literature methods. ^{17}O enrichment of $[(C_4H_9)_4N]_3NbW_5O_{19}$ was accomplished by stirring a solution of $[(C_4H_9)_4N]_3NbW_5O_{19}$ in acetonitrile in the presence of a 20-fold excess of 10% ^{17}O-enriched H_2O (Enritech) for 24 h. All other compounds and solvents were used as received from the supplier without further purification.

Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN), Robertson Microlit Laboratories (Madison, NJ), or the Department of Chemistry at Columbia University with a Perkin-Elmer 2400 CHN elemental analyzer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 1600 Series FTIR spectrometer. The ^1H, ^{13}C, ^{17}O, and ^{93}Nb NMR spectra were obtained on a Varian VXR-300 spectrometer at ambient room temperature (22−23 °C). The ^{17}O NMR experiments were carried out with concentrated solutions of the polyoxoanion in 5 mm NMR tubes and were referenced to water. A 0.25 M solution of $[(C_2H_5)_4N]NbCl_6$ in CH_3CN served as an external reference for ^{93}Nb NMR spectra. Fast atom bombardment mass spectra (FAB-MS) were recorded on a JEOL JMS-DX 303 HF machine with Xe gas, 3 kV, resolution 1:1500 at 2300 *m/z*. Positive ion spectra were obtained using a 3-nitrobenzyl alcohol matrix.

Preparation of Compounds. $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$. Method 1. To a suspension of 1.312 g (0.64 mmol) of $[(C_4H_9)_4N]_3NbW_5O_{19}$ in 40 mL of CH_2Cl_2 was added excess (180 mL) benzoyl chloride under argon at room temperature. After the reaction mixture was stirred for 1 h, anhydrous diethyl ether was added, and the resulting white precipitate was isolated by filtration and washed with 5 mL of ether to give 1.151 g of product in nearly 100% yield. Anal. Calcd for $C_{64}H_{144}N_4Nb_2W_{10}O_{37}$: C, 21.43; H, 4.02; N, 1.56. Found: C, 21.72; H, 3.82; N, 1.47. IR (KBr, 500−1000 cm^{-1}): 546 (m), 587 (m), 692 (s), 812 (s) 877 (m), 974 (s), 994 (sh). ^{93}Nb NMR (74 MHz, CH_3CN): δ −975 ppm. FAB-MS, *m/z*: $[MH]^+$, 3586; $[MTBA]^+$, 3827. It is worth noting that FAB-MS of oligomeric polyoxoanions can give ambiguous results since oligomers can also be detected in the FAB-MS of the monomeric starting materials.[5a,4b] We did not observe this behavior in our FAB-MS spectra.

Method 2. To 1.312 g (0.64 mmol) of $[(C_4H_9)_4N]_3NbW_5O_{19}$ in a 250 mL Schlenk flask was added 40 mL of benzoyl chloride under argon. The mixture was stirred for approximately 5 h at room temperature before anhydrous diethyl ether was added with rapid stirring. The resulting white solid was isolated by filtration and washed with diethyl ether to give 0.956 g (83%) of the product.

$[(C_4H_9)_4N]_6(Nb_2W_4O_{18})_2O$ and $[(C_4H_9)_4N_4]_4(TaW_5O_{18})_2O$. The compounds were prepared from $[(C_4H_9)_4N]_3TaW_5O_{19}$ and $[(C_4H_9)_4N]_4Nb_2W_5O_{19}$, respectively, in excess benzoyl chloride by the same procedure as for $[(C_4H_9)_4N_4](NbW_5O_{18})_2O$ and partially characterized:

$[(C_4H_9)_4N_6](Nb_2W_4O_{18})_2O$: IR (KBr, 500−1000 cm^{-1}) 670 (s), 722 (m), 738 (m), 799 (v), 885 (sh), 912 (m), 958 (s). $[(C_4H_9)_4N_4](TaW_5O_{18})_2O$: IR (KBr, 500−1000 cm^{-1}) 554 (m), 586 (s), 699 (s), 807 (s), 878 (m), 972 (s), 993 (sh); FAB-MS *m/z* $[MH]^+$, 3763.

$[(C_4H_9)_4N]_2Nb(OR)W_5O_{18}$ (R = Methyl, Ethyl, Isopropyl, Phenyl, Cholesteryl). (i) $[(C_4H_9)_4N]_2Nb(OCH_3)W_5O_{18}$. A 0.60 g (0.17 mmol) sample of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ was stirred with 40 mL of methanol for 2 days at room temperature under argon. A suspension formed during this period. The white solid was isolated by filtration and washed with anhydrous diethyl ether to give 0.48 g (78%) of product. Anal. Calcd for $C_{33}H_{75}N_2NbW_5O_{19}$: C, 21.81; H, 4.16; N, 1.54. Found: C, 21.75; H, 4.08; N, 1.51. IR (KBr, 500−1000 cm^{-1}): 531 (m), 585 (m), 688 (m), 812 (s), 881 (m), 973 (s). ^1H NMR of anion (300 MHz, CD_3CN): δ 4.40 (s) ppm. ^{93}Nb NMR (74 MHz, CD_3CN): δ −927 ppm. FAB-MS, *m/z*: $[MH - CH_3]^+$, 1803; $[MTBA]^+$, 2044.

(ii) $[(C_4H_9)_4N]_2Nb(OCH_2CH_3)W_5O_{18}$. In a procedure analogous to the preparation of $[(C_4H_9)_4N]_2Nb(OCH_3)W_5O_{18}$, 0.35 g (0.098 mmol) of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ was stirred in ethanol at room temperature for 2 days and then precipitated with anhydrous diethyl ether to yield 0.26 g of product (73%). Anal. Calcd for $C_{34}H_{77}N_2NbW_5O_{19}$: C, 22.30; H, 4.24; N, 1.53. Found: C, 21.99; H, 4.01; N, 1.51. ^1H NMR of anion (300 MHz, CD_3CN): δ 4.58 (q, 2H), 1.10 (t, 3H) ppm. IR (KBr, 500−1000 cm^{-1}): 546 (m), 587 (m), 688 (m), 740 (m), 808 (s), 880 (m), 974 (s). FAB-MS, *m/z*: $[MH - CH_2CH_3]^+$, 1803; $[MTBA]^+$, 2044.

(iii) $[(C_4H_9)_4N]_2Nb(OCH(CH_3)_2)W_5O_{18}$. In a procedure analogous to the preparation of $[(C_4H_9)_4N]_2Nb(OCH_3)W_5O_{18}$, the compound was isolated in 75% yield. Anal. Calcd for $C_{35}H_{79}N_2NbW_5O_{19}$: C, 22.80; H, 4.32; N, 1.52. Found: C, 23.00; H, 4.52; N, 1.28. IR (KBr, 500−1000 cm-1): 444(s), 547 (m), 585 (m), 700 (m), 809 (s), 866 (m), 974 (s). ^1H NMR of anion (300 MHz, CD_3CN): δ 4.88 (sep, 1H), 1.08 (d, 6H) ppm.

(iv) $[(C_4H_9)_4N]_2Nb(OC_6H_5)W_5O_{18}$. A suspension of 0.24 g (0.067 mmol) of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ and 0.25 g (0.27 mmol) of C_6H_5OH in dichloromethane was stirred for 3 days at room temperature. The product was isolated by adding anhydrous diethyl ether to the slightly yellow solution and collecting 0.158 g (63%) of the slightly yellow solid by filtration. Anal. Calcd for $C_{40}H_{81}N_2NbW_5O_{19}$: C, 24.30; H, 4.13; N, 1.49. Found: C, 24.45; H, 4.02; N, 1.47. IR (KBr, 500−1000 cm^{-1}): 546 (m), 588 (m), 690 (s), 812 (s), 877 (m), 972 (s).

(v) $[(C_4H_9)_4N]_2Nb(OC_{27}H_{45})W_5O_{18}$. A suspension of 0.250 g (0.65 mmol) of cholesterol and 0.22 g (0.061 mmol) of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ in dichloromethane was stirred for 5 days. The product was precipitated from the reaction mixture by adding excess anhydrous diethyl ether. It was necessary to purify the product by triturating the solid three times with anhydrous ether to yield 0.146 g (55%) of the product. Anal. Calcd for $C_{61}H_{121}N_2NbW_5O_{19}$: C, 32.63; H, 5.39; N, 1.29. Found: C, 32.85; H, 4.90; N, 1.47. IR (KBr, 500−1000 cm^{-1}): 546 (m), 588 (m), 692 (s), 816 (s), 878 (m), 974 (s). FAB-MS, *m/z*: $[MH]^+$, 2171; $[MTBA]^+$, 2412.

X-ray Crystal Study of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$. A colorless parallelepiped crystal (0.52 × 0.24 × 0.12 mm) of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ was grown in narrow (10 mm) glass tubes after 4 weeks from a mixed-solvent solution of methylene chloride and acetonitrile with anhydrous diethyl ether layered on top. The crystal was glued to a glass fiber, covered with a thin layer of epoxy cement, and examined by X-ray crystallography. Table 1 summarizes the crystal data and the data collection, solution, and refinement details. Data were collected on a Siemens P4 diffractometer at 296 K in the $\theta-2\theta$ mode with a θ scan width of 0.64° and scan speed of 5−60° θ/min using graphite-monochromated Mo Kα radiation. Some difficulty was experienced initially in obtaining constant cell dimensions for the crystal, possibly due to the loss of lattice solvent, but reproducible and reliable unit cell parameters were observed after allowing the crystal to sit for several days. Data collection and reduction were carried out by standard procedures. The structure was solved and refined using the Siemens SHELXTL PLUS (PC version) crystallographic program.[12]

The direct-methods solution of the structure with SHELXTL PLUS yielded the Nb and W atom positions as well as those of many of the O atoms. Subsequent difference Fourier maps gave all the remaining O atom positions of the anion. Difference maps also revealed two

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(6) (a) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds;* J. Wiley and Sons: New York, 1986. (b) McNally, J. P.; Leong, V. S.; Cooper, N. J. *ACS Symp. Ser.* **1987**, *357*, 6−23.

(7) Che, T. M.; Day, V. W.; Francesconi, L. C.; Fredrich, M. F.; Klemperer, W. G. *Inorg. Chem.* **1985**, *24*, 4055.

(8) (a) Bradley, D. C.; Chakravarti, B. N.; Wardlaw, W. *J. Chem. Soc.* **1956**, 2381. (b) Bradley, D. C.; Wardlaw, W.; Whitley, A. *J. Chem. Soc.* **1955**, 726.

(9) (a) Filowitz, M.; Ho, R. C. K.; Klemperer, W. G. *Inorg. Chem.* **1979**, *18*, 93. (b) Flynn, C. M., Jr.; Stucky, G. D. *Inorg. Chem.* **1969**, *8*, 178.

(10) Dabbabi, M.; Boyer, M.; Launay, J.-P. Jeannin, Y. *J. Electronanal. Chem. Interfacial Electrochem.* **1977**, *76*, 153. Preparation of the $(C_4H_9)_4N^+$ salt was done by ion exchange chromatography with Dowex 50-X 8−100 ion-exchange resin as adopted from the literature.[25b]

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

(12) Sheldrick, G. *SHELXTL/PC*; Siemens Analytical X-Ray Instrument, Inc.: Madison, WI, 1990.

Table 1. Crystallographic Information for $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$

formula	$C_{64}H_{144}N_4O_{37}Nb_2W_{10}$
fw	3586.2
crystal system	orthorhombic
space group	*Cmca*
a, Å	15.817(2)
b, Å	17.870(3)
c, Å	35.058(5)
V, Å^3	9909(3)
Z	4
D_{calcd}, g cm^{-3}	2.404
radiation	Mo Kα (0.710 73 Å)
abs cor	numerical, face-indexed
min/max transm	0.0649/0.3088
index range	$0 < h < 17$, $0 < k < 19$, $0 < l < 37$
2θ range	$3° \leq 2\theta \leq 45°$
total no. of data collected	6752
av R_m	0.046
total no. of unique data	3379
no. of unique data with $F > 4\sigma(F)$	2141
no. of variable params	186
goodness of fit	1.49
R_1[a]	0.055
R_2	0.068

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w||F_o^2| - |F_c^2||/\sum w||F_o^2|]^{1/2}$, where $w = [1/\sigma^2(F_o) + 0.0005F_o^2]$.

disordered $(C_4H_9)_4N$ cations with a refined occupancy of 55.4% (cation 1) and 44.6% (cation 2), respectively. Atom N(1) of cation 1 resides on a 2-fold axis, and atom N(2) of cation 2 is at a general position. A number of carbon atom positions in each of the two disordered cations were not discernible from difference maps, and not included in the final model. As a consequence, the largest difference peak in the final difference map was 2.03 e/Å^3. The atoms in the final full-matrix least-squares cycle were refined with anisotropic thermal parameters for the anion and a common isotropic thermal parameter of $U = 0.109$ Å^2 for the cation. The C atoms in the cation were constrained to an idealized bond distance of 1.55 Å and bond angle of 109°. The positions of the H atoms were generated from the carbon atoms to which they were attached by SHELXTL PLUS and were assigned a fixed isotropic thermal parameter of $U = 0.10$ Å^2.

Results and Discussion

Synthesis and Spectroscopic Characterization of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$. The compound $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ was prepared quantitatively by adding excess benzoyl chloride to a suspension of $[(C_4H_9)_4N]_3NbW_5O_{19}$ in dichloromethane (eq 1). An 83% yield was obtained when neat

$$2NbW_5O_{19}{}^{3-} \xrightarrow[-O^{2-}]{C_6H_5COCl/CH_2Cl_2} (NbW_5O_{18})_2O^{4-} \qquad (1)$$

benzoyl chloride was used. Stoichiometric quantities of benzoyl chloride gave a poor or no yield of the product. The presence of small amounts benzoic anhydride in the benzoyl chloride solution prevented unequivocal identification of the organic product of the reaction. Under the reaction conditions, ^{17}O NMR studies showed that the isotopically enriched oxygen atom in $[(C_4H_9)_4N]_3Nb(^{17}O)W_5O_{18}$ observed at 795 ppm[3b] was incorporated completely into the oxygen of the excess benzoyl chloride (487 ppm) reagent. Partial characterization of the products of the reaction of benzoyl chloride with $[(C_4H_9)_4N]_3TaW_5O_{19}$ or $[(C_4H_9)_4N]_4Nb_2W_4O_{19}$ suggested that $[(C_4H_9)_4N]_4(TaW_5O_{18})_2O$ and previously reported $[(C_4H_9)_4N]_6(Nb_2W_4O_{18})_2O$[4b] could also be prepared using this method.

Wet acetonitrile solutions of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ partially or completely hydrolyzed to $NbW_5O_{19}{}^{3-}$ as judged by IR spectroscopy. When $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ was treated with ^{17}O-enriched (10%) water, a broad resonance at 744 ppm was observed. The downfield resonance is in the chemical shift range expected for a terminal NbO oxygen in a niobium tungstate.[3b,13] The resonance is likely the result of direct oxygen atom exchange between $H_2{}^{17}O$ and $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ followed by its hydrolysis and/or oxygen atom exchange between $H_2{}^{17}O$ and the hydrolysis product $H[(C_4H_9)_4N]_2NbW_5O_{19}$, which dehydrates to $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ (eq 2). The hydrolysis of $([C_4H_9)_4N]_4(NbW_5O_{18})_2O$ is similar to

$$(NbW_5O_{18})_2O^{4-} \xrightleftharpoons[-H_2O]{H_2O} 2HNbW_5O_{19}{}^{2-} \qquad (2)$$

the reported interconversion of the anhydride $(Nb_2W_4O_{18})_2O^{6-}$ and its conjugate acid $HNb_2W_4O_{18}{}^{2-}$ in the presence of water.[4b]

Several oligomeric polyoxoanions have been prepared by self-condensation under acidic conditions[4] with the notable exception that CO_2 or transition metal carbonyl clusters can also be used as oxygen atom acceptors to deoxygenate $[(C_4H_9)_4N]_4Nb_2W_4O_{19}$ to form $[(C_4H_9)_4N]_6(Nb_2W_4O_{18})_2O$.[4b] Deoxygenation of early transition metal−oxo complexes has been accomplished by a nucleophilic substitution reaction with acid chlorides,[14] most often yielding the corresponding chloride complexes. The terminal NbO oxygen of $[(C_4H_9)_4N]_3NbW_5O_{19}$ is sufficiently nucleophilic to react with the carbonyl carbon of benzoyl chloride to form the corresponding niobium carboxylate or chloride derivatives by analogy to the mechanisms proposed for the reaction of acetyl chloride with metal oxo coordination complexes.[14b,c] These intermediates could then undergo nucleophilic substitution by another equivalent of $[(C_4H_9)_4N]_3NbW_5O_{19}$ to form $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$. The net result is deoxygenation and self-condensation of $[(C_4H_9)_4N]_3NbW_5O_{19}$ (eq 1). Attempts to demonstrate this mechanism with isotopically labeled $[(C_4H_9)_4N]_3Nb(^{17}O)W_5O_{18}$ were unsucessful due to rapid exchange of the benzoyl chloride solution with the labelled starting material, the polyoxoanion or the organic products of the reaction.

The IR spectrum of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ (Figure 2) revealed a new intense broad band at 692 cm^{-1} and the absence of the terminal Nb−O vibrational stretch at 915 cm^{-1} of the starting material.[3b,11] Other distinctive IR bands in the metal−oxygen stretching region from 500 to 1000 cm^{-1} were unchanged, indicating that the structure of the $\{NbW_5O_{18}\}^-$ fragment remains the same. The new band is characteristic of a Nb−O−Nb link between two polyoxanions and is similar to vibrational stretches of previously reported singly bridged Nb−O−Nb polyoxoanions, $(Nb_2W_4O_{18})_2O^{6-}$ (672 cm^{-1})[4b] and $(P_2Nb_3W_{15}O_{61})_2O^{16-}$ (665 cm^{-1}),[4c] and the triply bridged $Si_2Nb_6W_{18}O_{77}{}^{8-}$ (690 cm^{-1})[4a] complex.

The ^{93}Nb NMR spectrum of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ (Figure 3) exhibited a broad resonance at −975 ppm (linewidth at half-height ∼6000 Hz) compared to the narrower (∼900 Hz)

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(13) This resonance is approximately 50 ppm upfield from the terminal NbO oxygen resonance in $[(C_4H_9)_4N]_3Nb(^{17}O)W_5O_{18}$. Large upfield shifts were observed upon protonation of a Nb−O−Nb fragment in $[(C_4H_9)_4N]_6(Nb_2W_4O_{18})_2O$[4b] ($\Delta = 304$ ppm) and $H_x[(C_4H_9)_4N]_{9-x}P_2W_{15}Nb_3O_{62}$ ($\Delta = 322$ ppm) [Pohl, M.; Finke, R. G. *Organometallics* **1993**, *12*, 1453]. The relatively small upfield shift of the terminal NbO oxygen resonance observed in hydrolyzed solutions of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ is consistent with the formation of $H[(C_4H_9)_4N]_2NbW_5O_{19}$ if the proton is not bound to the terminal Nb−O oxygen but is associated with it in some way that affects its ^{17}O chemical shift. Other resonances at 399 (OW_2), 417 (OW_2), and 456 (NbOW) ppm were close to or the same as their published values.[3b]

(14) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; J. Wiley and Sons: New York, 1988; p 232. (b) Housmekerides, C. E.; Ramage, D. L.; Kretz, C. M.; Shontz, J. T.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *31*, 4453. (c) Jones, E. L.; Reynolds, J. G.; Huffman, J. C.; Christou, G. *Polyhedron* **1991**, *10*, 1817.

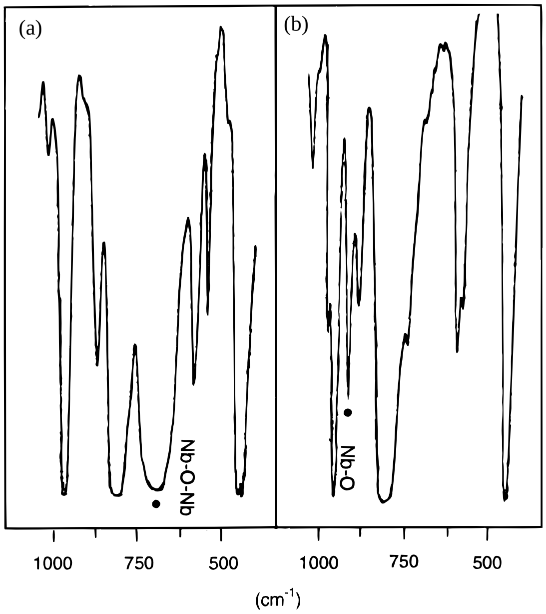

Figure 2. Infrared spectra showing the metal−oxygen stretching region (500−1000 cm^{-1}) of (a) $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ and $[(C_4H_9)_4N]_3NbW_5O_{19}$ as KBr pellets.

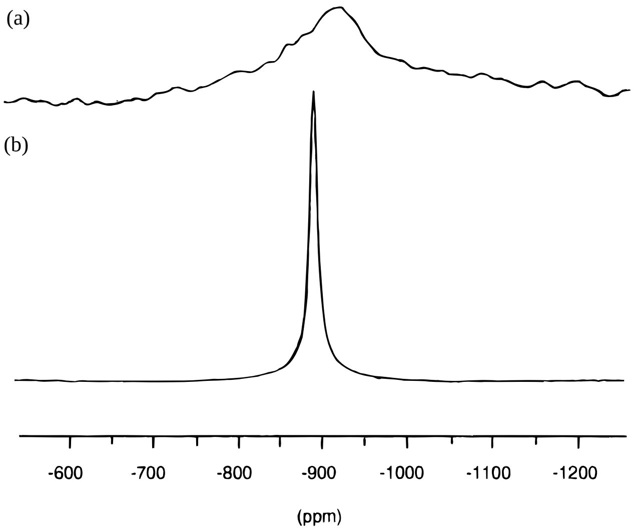

Figure 3. ^{93}Nb NMR spectra of (a) $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ and (b) $[(C_4H_9)_4N]_3NbW_5O_{19}$ in acetonitrile at 296 K.

resonance of $[(C_4H_9)_4N]_3NbW_5O_{19}$ observed at −888 ppm. Despite the good NMR sensitivity of the ^{93}Nb nucleus (0.48 vs 1 for ^{1}H), it possesses a quadrupole moment ($I = {}^{9}/_{2}$, $Q = -0.28 \times 10^{-28}$ m^{2}) that often results in broad NMR resonances.[15] We suggest that the approximate 7-fold increase in linewidth of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ compared to $[(C_4H_9)_4N]_3NbW_5O_{19}$ may be attributed to a larger correlation time for molecular rotation.[16] The linewidths of the ^{93}Nb NMR spectrum of polythioanion $Nb_6S_{17}{}^{4-}$ were ascribed to a similar effect.[17] Even broader resonances were observed for the ^{93}Nb NMR spectra of larger polyoxoanion complexes $[Cp_3M(NbW_5O_{19})_2]^{5-}$ (M = Th, ~8200 Hz; M = U, ~9900 Hz) in which two $NbW_5O_{19}{}^{3-}$ fragments are coordinated by the terminal NbO oxygen atom to the axial positions of a trigonal bipyrimidal actinide complex.[3c,18]

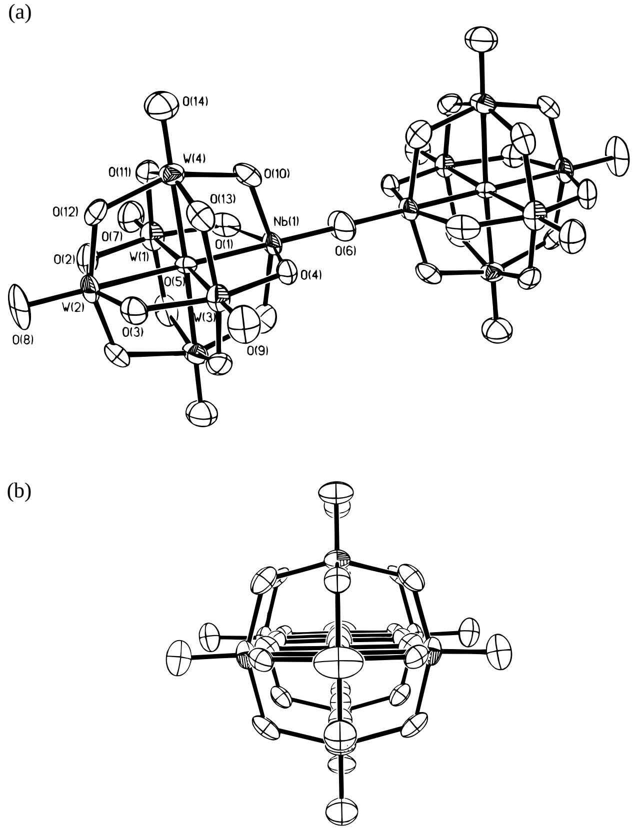

Figure 4. (a) Molecular structure of $(NbW_5O_{18})_2O^{4-}$. (b) View down the Nb−O−Nb vector.

X-ray Crystal Structure of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$. The structure of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ consists of well separated tetrabutylammonium cations and $(NbW_5O_{18})_2O^{4-}$ anions. The asymmetric unit is formed by coplanar metal and oxygen atoms on special positions capped by a $\{WO_5\}$ moiety. A crystallographically imposed linear oxo bridge connects two $\{NbW_5O_{18}\}^-$ polyoxoanion fragments (Figure 4). In each polyoxoanion fragment, four tungstens adjacent to the niobium are in equivalent positions and a unique tungsten is opposite the niobium atom, creating local C_{4v} point group symmetry. The 180° Nb−O−Nb angle and the comparatively short 1.887(3) Å Nb−O bond of the connecting oxo suggest a significant π contribution to the bonding as noted earlier in structures of oxo-bridged dinuclear niobium cyclopentadienyl complexes.[19] Multiple-bonding character in the $\{Nb-O-Nb\}^{8+}$ fragment is also supported by the D_{4h} symmetry of the $(NbW_5O_{18})_2O^{4-}$ anion,

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(15) (a) Rehder, D. In *Transition Metal Nuclear Magnetic Resonance*; Presogin, P. S., Ed.; Elsevier: Amsterdam, The Netherlands, 1991; p 45. (b) Kidd, G. R. In *NMR of Newly Accessible Nuclei;* Laszlo, P., Ed.; Academic Press: New York, 1983; pp 103−130.

(16) The linewidth of a NMR resonance of a quadrupolar nucleus is directly proportional to the correlation time which is proportional to r^3, where r is the molecular radius.[15b] If $(NbW_5O_{18})_2O^{4-}$ ($r \sim 7$ Å) is 1.8 times larger than $NbW_5O_{19}{}^{3-}$ ($r \sim 4$ Å), an approximate 6-fold increase in linewidth would be expected (compared to 6.7 observed) solely on the basis of the change in molecular radius, neglecting the elliptical shape of $(NbW_5O_{18})_2O^{4-}$ and the effect of the counterions. Line broadening could also be caused equally by an electric field gradient effect. However, the electric field gradient, q, at the Nb nucleus is likely to be reduced by the formation of the Nb−O−Nb bridge compared to the multiply bonded terminal NbO. The decrease in q would have the opposite effect on the ^{93}Nb linewidth (narrower).[15b]

(17) Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1985**, 24, 1706.

(18) The thorium compound also exhibited a comparable upfield ^{93}Nb NMR shift of −943 ppm, but the shift of the uranium compound at −243 ppm, possibly a result of its paramagnetism, is markedly different.[3c]

(19) (a) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr.* **1974**, *B30*, 2290. (b) Bottomley, F.; Keizer, P. N.; White, P. S.; Preston, K. F. *Organometallics* **1990**, *9*, 1916.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(NbW_5O_{18})_2O^{4-}$

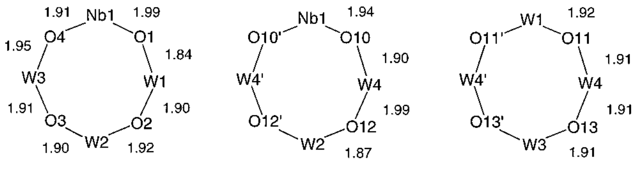
W(1)−O(1)	1.84(2)	W(1)−O(2)	1.90(3)
W(1)−O(5)	2.32(2)	W(1)−O(7)	1.70(3)
W(1)−O(11)	1.92(2)	W(2)−O(2)	1.92(3)
W(2)−O(3)	1.90(2)	W(2)−O(5)	2.39(2)
W(2)−O(8)	1.70(2)	W(2)−O(12)	1.87(1)
W(3)−O(3)	1.91(2)	W(3)−O(4)	1.95(2)
W(3)−O(5)	2.33(2)	W(3)−O(9)	1.67(3)
W(3)−O(13)	1.91(1)	W(4)−O(5)	2.326(1)
W(4)−O(10)	1.90(1)	W(4)−O(11)	1.91(2)
W(4)−O(12)	1.99(1)	W(4)−O(13)	1.91(2)
W(4)−O(14)	1.67(2)	Nb(1)−O(1)	1.99(3)
Nb(1)−O(4)	1.91(2)	Nb(1)−O(5)	2.24(2)
Nb(1)−O(6)	1.887(3)	Nb(1)−O(10)	1.94(1)
O(1)−W(1)−O(2)	153(1)	O(1)−W(1)−O(5)	76.1(9)
O(2)−W(1)−O(5)	77.0(9)	O(1)−W(1)−O(7)	103(1)
O(2)−W(1)−O(7)	104(1)	O(5)−W(1)−O(7)	179(1)
O(1)−W(1)−O(11)	88.1(5)	O(2)−W(1)−O(11)	85.3(5)
O(5)−W(1)−O(11)	75.7(5)	O(7)−W(1)−O(11)	104.4(5)
O(11)−W(1)−O(11A)	151(1)	O(2)−W(2)−O(3)	150(1)
O(2)−W(2)−O(5)	74.9(9)	O(3)−W(2)−O(5)	75.5(8)
O(2)−W(2)−O(8)	106(1)	O(3)−W(2)−O(8)	103(1)
O(5)−W(2)−O(8)	179(1)	O(2)−W(2)−O(12)	86.8(5)
O(3)−W(2)−O(12)	86.8(5)	O(5)−W(2)−O(12)	77.5(4)
O(8)−W(2)−O(12)	102.5(4)	O(12)−W(2)−O(12A)	155.0(9)
O(3)−W(3)−O(4)	151.3(9)	O(3)−W(3)−O(5)	76.7(8)
O(4)−W(3)−O(5)	74.7(8)	O(3)−W(3)−O(9)	103(1)
O(4)−W(3)−O(9)	105(1)	O(5)−W(3)−O(9)	180(1)
O(3)−W(3)−O(13)	85.8(5)	O(4)−W(3)−O(13)	87.1(5)
O(5)−W(3)−O(13)	75.6(5)	O(9)−W(3)−O(13)	104.4(5)
O(13)−W(3)−O(13A)	151(1)	O(5)−W(4)−O(10)	75.4(6)
O(5)−W(4)−O(11)	75.7(7)	O(10)−W(4)−O(11)	88.9(7)
O(5)−W(4)−O(12)	77.0(6)	O(10)−W(4)−O(12)	152.4(6)
O(11)−W(4)−O(12)	85.4(6)	O(5)−W(4)−O(13)	75.9(6)
O(10)−W(4)−O(13)	86.5(7)	O(11)−W(4)−O(13)	151.4(7)
O(12)−W(4)−O(13)	85.8(6)	O(5)−W(4)−O(14)	178.0(8)
O(10)−W(4)−O(14)	103.9(8)	O(11)−W(4)−O(14)	102.5(9)
O(12)−W(4)−O(14)	103.7(8)	O(13)−W(4)−O(14)	106.0(9)
O(1)−Nb(1)−O(4)	153.1(9)	O(1)−Nb(1)−O(5)	75.4(8)
O(4)−Nb(1)−O(5)	77.7(8)	O(1)−Nb(1)−O(6)	104.4(6)
O(4)−Nb(1)−O(6)	102.5(6)	O(5)−Nb(1)−O(6)	179.8(3)
O(1)−Nb(1)−O(10)	87.7(5)	O(4)−Nb(1)−O(10)	86.1(5)
O(5)−Nb(1)−O(10)	76.7(5)	O(6)−Nb(1)−O(10)	103.3(5)
O(10)−Nb(1)−O(10A)	153.3(9)	W(1)−O(1)−Nb(1)	117(1)
W(1)−O(2)−W(2)	119(1)	W(2)−O(3)−W(3)	120(1)
W(3)−O(4)−Nb(1)	116(1)	W(1)−O(5)−W(2)	88.7(6)
W(1)−O(5)−W(3)	177.0(9)	W(1)−O(5)−W(4)	90.2(5)
W(1)−O(5)−Nb(1)	91.5(7)	W(2)−O(5)−W(3)	88.3(6)
W(2)−O(5)−W(4)	88.6(4)	W(2)−O(5)−Nb(1)	179.7(5)
W(3)−O(5)−W(4)	89.8(5)	W(3)−O(5)−Nb(1)	91.4(7)
W(4)−O(5)−Nb(1)	91.4(4)	W(4)−O(5)−W(4A)	177.1(9)
Nb(1)−O(6)−Nb(1A)	180.0(1)	W(4)−O(10)−Nb(1)	116.4(8)
W(1)−O(11)−W(4)	118.5(8)	W(2)−O(12)−W(4)	116.9(7)
W(3)−O(13)−W(4)	118.8(8)		

revealed by the “eclipsed” terminal W−O bonds on adjoining polyoxoanion fragments (Figure 4b), which maximizes the dπ−pπ interaction.[20]

The niobium and tungsten atoms in each $\{NbW_5O_{18}\}^-$ fragment reside in octahedral sites formed by close-packed oxygen atoms. In a fragment, the edge-sharing octahedra consist of bonds to terminal, bridging, and central oxygen atoms. The bond distances and angles around each metal octahedron are given in Table 2. Examination of the O−M−O bond angles involving the terminal, bridging, and central oxygens indicates a distorted octahedral coordination geometry. Each metal atom is displaced from the equatorial plane formed by the coordinated bridging oxygens toward the terminal oxygen. This distortion is due, in part, to repulsions between the close-packed terminal and bridging oxygen atoms within the coordination sphere.[21] The central oxygen atom has near-octahedral coordination geometry, and its motion is largely restricted, as suggested by its anomalously small thermal parameters. The central Nb−O bond distance of 2.24(2) Å is similar to comparable distances in other polyoxoanion niobates[22] but considerably shorter than the four symmetry-equivalent central W−O bond distances in the anion, which average 2.34 Å.

The average terminal W−O bond distance of 1.68 Å is nearly identical to those found in $W_6O_{19}^{2-}$ (1.69 Å)[23] and in multiply bonded WO complexes.[24] The bridging W−O bond lengths in $(NbW_5O_{18})_2O^{4-}$ vary from 1.84(2) to 1.99(2) Å, but their average value of 1.91 Å compares well with those found in $W_6O_{19}^{2-}$ (1.92 Å).[23] The average bridging Nb−O bond distance of 1.95 Å associated with the Nb−O−W group is similar to those of other derivatized polyoxoanions with an isostructural niobium-substituted tungstate fragment.[3bc,25] The bridging Nb−O−W angles (average 116.6°) are slightly more acute than the W−O−W angles (average 119.1°), with exception of W(2)−O(12)−W(4) (116.9(7)°). A slight canting of the terminal O(X) (X = 7, 9, 14) atom in the direction opposite the niobium center is evident from the differences between average respective O(X)···O(Y) distances (2.80 Å; Y = 1, 3, 10) and structurally corresponding O(X)···O(Z) (2.87 Å; Z = 2, 4, 12) distances. Mean deviations of no greater than 0.02 Å are observed between the three planes formed by the three metal and oxygen rings that circumscribe the central oxygen[23] or 0.09 Å for the planes of alternating layers of metal and oxygen atoms.[1b] Dihedral angles between the former planes range within 0.5° of 90° and angles for the latter planes within 1.5° of ideally coplanar.

Systematic variations or alternating long and short bond distances in bridging oxygen M−O bonds have been reported in $M_6O_{19}^{2-}$ (M = W, Mo),[23,26] $CpTiMo_5O_{19}^{3-}$,[7] and comparable substituted polyxoanions.[7,27] Three eight-membered rings of the bridging oxygen M−O bonds that circumscribe the central oxygen atom in $(NbW_5O_{18})_2O^{4-}$ are shown in the following diagram with accompanying bond distances in angstroms and an esd range of 0.01−0.03 Å. All the bonds in ring 1 are unique, while half the values in rings 2 and 3 are related to one another by a crystallographic mirror plane, as indicated by the prime notation in the schematic. Variations in the bridging oxygen−metal bond distances are exhibited by rings 1 and 2, which include the niobium atom, and, to a far less extent, by ring 3. Using the W−O 1.92 Å bond distance in $W_6O_{19}^{2-}$ for comparison,[23] deviations in ring 1 occur for Nb−O(1) (1.99(3) Å) and W(1)−O(1) (1.84(2) Å). In ring 2, the long 1.99(1) Å W(4)−O(12) bond length is the most significant deviation. All other differences in bond distances are within



ring 1 ring 2 ring 3

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[20] (a) Dunitz, J. D.; Orgel, L. E. *J. Chem. Soc.* **1953**, 2594. (b) Cotton, F. A.; Najjar, R. C. *Inorg. Chem.* **1981**, *20*, 1866.

[21] (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; J. Wiley and Sons: New York, 1988; p 156. (b) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer Verlag: New York, 1983; pp 18−21.

[22] (a) Lindqvist, I. *Ark. Kemi* **1953**, *5*, 247. (b) Bradley, D. C.; Hursthouse, M. B.; Rodesiler, P. F. *J. Chem. Soc., Chem. Commun.* **1968**, 1112. (c) Flynn, C. M.; Stuckey, G. D. *Inorg. Chem.* **1969**, *8*, 335. (d) Greaeber E. J.; Morosin, B. *Acta Crystallogr.* **1977**, *B33*, 2137.

[23] Fuchs, J. V.; Freiwald, W.; Hartl, H. *Acta Crystallogr.* **B34**, 1764.

[24] Mayer, J. *Inorg. Chem.* **1988**, *27*, 3899.

[25] (a) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 6158. (b) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125. (c) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Inorg. Chem.* **1985**, *24*, 44. (d) Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.*, **1990** *29*, 2345.

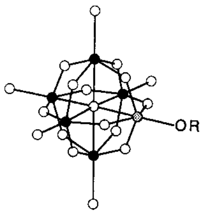
three standard deviations and are not judged to be significant. These variations are also evident from a plot of M−O ring bond distances, adopted from Fuchs,[23] provided in the Supporting Information. The accuracy of the structure determination limits the meaningfulness of the observed bond length differences in rings 1−3, but their variability is comparable to that observed in polymolybdates[2d,7,26] and substituted polytungstates.[27,28] Variations in ring bond lengths are reportedly a means of delocalizing the added negative charge evenly over all the surface atoms and relieving structural distortions imposed on the metal−oxygen framework by the substitution of a lower valent metal atom for tungsten.[7]

Alcoholysis of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$. The alcoholysis of condensed polyoxoanions, reported by Klemperer with $[(C_4H_9)_4N]_6(Nb_2W_4O_{18})_2O$,[4b] is a valuable method for the preparation of alkoxide-derivatized niobium tungstates with a variety of organic compounds. The reaction of $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ with alcohols was investigated to confirm its preparation as well as its synthetic versatility. When $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ is added to methanol, ethanol, or 2-propanol, a suspension forms, yielding the alkoxide derivative $[(C_4H_9)_4N]_2Nb(OR)W_5O_{18}$ in good yield after several days (eq 3). Phenol

$$(NbW_5O_{18})_2O^{4-} \xrightarrow[-H_2O]{ROH} 2Nb(OR)W_5O_{18}{}^{2-} \qquad (3)$$

and cholesterol derivatives, reported here for the first time, were synthesized with excess reagent in a solution of methylene chloride. ^1H NMR spectroscopy of the methoxide derivative displayed a singlet at 4.40 ppm, and the corresponding ethoxide compound showed a quartet at 4.58 ppm and a triplet at 1.10 ppm. These chemical shifts compare favorably with the 4.31 ppm singlet and 4.64 and 1.53 ppm resonances reported for the methoxide and ethoxide derivatives, respectively, of $[(C_4H_9)_4N]_3Nb_2(OR)W_4O_{18}$.[4b] The ^{93}Nb NMR spectrum of $[(C_4H_9)_4N]_2Nb(OCH_3)W_5O_{18}$ displayed a single resonance at −927 ppm. The 2-propanol, cholesterol, and phenol alkoxide derivatives $[(C_4H_9)_4N]_2Nb(OR)W_5O_{18}$ are distinguished by the downfield ^{13}C NMR shifts at 79.9, 88.7, and 170.0 ppm, respectively, of the hydroxyl bearing carbon.[29]

The IR spectrum of $[(C_4H_9)_4N]_2Nb(OCH(CH_3)_2)W_5O_{18}$ in the 500−1000 cm^{-1} region is very similar to those of the methyl and the ethyl analogs, suggesting a common structure by inference for all the derivatives reported here. Derivatization is likely to occur at the Nb−O terminal oxygen atom rather than at a bridging Nb−O−W oxygen atom since no apparent IR band due to a terminal Nb−O stretch was detected. This conclusion is supported by earlier studies in which (i) the bridging and terminal alkoxide coordination in $[(C_4H_9)_4N]_3Nb_2W_4O_{19}R$ gave distinctly different IR spectra in this region and (ii) secondary alcohols were shown to have enough steric bulk to prevent them from coordinating to bridging oxygens in $[(C_4H_9)_4N]_3Nb_2W_4O_{19}R$.[4b]



R = methyl, ethyl, isopropyl
phenyl, cholesteryl

Previous reactions of polyoxanions have often demonstrated that bridging oxygens are the most basic and labile sites. Alcoholysis of $[(C_4H_9)_4N]_6(Nb_2W_4O_{18})_2O$ with methanol was reported to yield the bridging methoxide derivative[4b] $[(C_4H_9)_4N]_3Nb_2W_4O_{19}R$. Related alkylation studies of $PM_{12}O_{40}{}^{3-}$ (M = Mo, W) revealed that derivatization of the polyoxanion occurred preferentially at bridging rather than terminal oxygens.[30] Although coordination to organometallic complexes by the terminal NbO oxygen atom of both $NbW_5O_{19}{}^{3-}$ and $Nb_2W_4O_{19}{}^{4-}$ anions is well documented,[1b,3c,25] unfavorable steric interactions may have masked the electronic effects of the polyoxoanion as suggested previously.[4b] Steric influences on the coordination of methyl and ethyl groups to polyoxoanions are absent, however, on the basis of comprehensive studies of a variety of alkoxide derivatives of $[(C_4H_9)_4N]_3Nb_2W_4O_{19}R$.[4b] For the monosubstituted niobium−tungstate featured in this study, facile and selective oxygen atom exchange of $H_2{}^{17}O$ with the terminal NbO oxygen atom of $[(C_4H_9)_4N]_3NbW_5O_{19}$ provides strong evidence for the terminal oxygen being the most labile in this compound.[3b] Alcoholysis of $[(C_4H_9)_4N]_4(NbW_4O_{18})_2O$ corroborates that the terminal oxygen atom is probably the most reactive site in $[(C_4H_9)_4N]_3NbW_5O_{19}$.

Conclusions

Condensed or oligomeric polyoxoanions are good potential starting materials for preparing polyoxoanion derivatives, and their synthetic use should continue to be explored. We have described a convenient, potentially versatile method of deoxygenation in which the terminal NbO oxygen atom is removed formally from $[(C_4H_9)_4N]_3NbW_5O_{19}$ using benzoyl chloride. This reaction forms a structurally characterized oxygen-deficient species, $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$, which can be functionalized by alcoholysis and possibly other reactions. The reactivity of polyoxoanions has been likened to that of solid-state metal oxides.[1,4] The deoxygenation methods developed for preparaing discrete molecular compounds described here and reported earlier,[4b,14] therefore, could prove useful for activating and derivatizing solid-state metal oxide surfaces by oxygen atom removal and substitution.[31]

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Note Added in Proof. An alternative preparation of $Nb(OCH_3)W_5O_{19}{}^{2-}$ and $(NbW_5O_{18})_2O^{4-}$ and the X-ray structure of the latter have been reported while this manuscript was in press.[32]

Supporting Information Available: Figures showing the asymmetric unit, a packing diagram, and a plot of MO bond distances and tables of positional and thermal parameters, bond lengths and angles, least-squares planes, and dihedral angles for $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$ (9 pages). Ordering information is given on any current masthead page.

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(26) Allcock, H. R.; Bissell, E. T.; Shawl, E. T. *Inorg. Chem.* **1973**, *12*, 2963.

(27) Mohs, T. R.; Yapp, G. P. A.; Rheingold, A. L.; Maata, E. A. *Inorg. Chem.* **1995**, *34*, 9.

(28) Iball, J.; Low, J. N.; Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1974**, 2021.

(29) Pretsch, P. D.; Seibel, J.; Simon, W.; Clerc, T. *Tables of Spectral Data for Structural Determination of Organic Compounds*; Springer-Verlag: Berlin, 1989.

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

(31) (a) Kung, H. H. *Transition Metal Oxides: Surface Chemistry and Catalysis;* Elsevier: Amsterdam, The Netherlands, 1989; Chapter 6. (b) Barteau, M. A. *J. Vac. Sci. Technol., A* **1993**, *11*, 2162.

(32) Clegg, W.; Elsegood, M. R. J.; Errington, R. J., Havelock, J. *J. Chem. Soc., Dalton Trans.* **1996**, 681.