1026, 805, 614, 458 cm^{-1}. Anal. Calcd for $C_{21}H_{34}OHf$: C, 52.43; H, 7.13; Hf, 37.11. Found: C, 52.31; H, 6.95; Hf, 36.99.

***cis*-{Cp^*_2HfH}$_2$(μ-OHC═CHO) (13c).** A thick-walled glass reaction vessel with a Teflon needle valve was charged with 0.30 g (0.59 mmol) of $Cp^*_2Hf(CO)_2$, 0.27 g (0.59 mmol) of $Cp^*_2HfH_2$, 10 mL of toluene, and 5 mmol (2 atm) of H_2 and stirred at 80 °C for 2 weeks. The resultant yellow solution was transferred to a frit assembly; workup with petroleum ether afforded 0.140 g (25%) of white, microcrystalline **13c**: IR 1655, 1633, 1325, 1170, 1077, 1027, 840 cm^{-1}. Anal. Calcd for $C_{21}H_{32}OHf$: C, 52.66; H, 6.73; Hf, 37.26. Found: C, 52.71; H, 6.62; Hf, 37.12.

***cis*-(Cp^*_2HfH)(Cp^*_2ZrH)(μ-OCH═CHO) (14).** In a manner analogous to **13c**, 260 mg (0.51 mmol) of **11**, 190 mg (0.51 mmol) of $Cp^*_2ZrH_2$, 10 mL of toluene, and 5 mmol (2 atm) of H_2 were stirred at 80 °C for 24 h. Workup yielded 245 mg (56.5%) of light yellow microcrystalline **14**: IR 1655, 1630, 1595, 1320, 1165, 1075, 1027, 840 cm^{-1}. Anal. Calcd for $C_{42}H_{64}O_2HfZr$: C, 57.94; H, 7.41; Hf, 20.50; Zr, 10.48. Found: C, 57.83; H, 7.31; Hf, 20.32; Zr, 10.41.

$Cp^*_2HfH(CH_2CH_3)$ (16). A solution of 0.60 g (1.25 mmol) of $Cp^*_2HfH_2$ in 15 mL of petroleum ether was stirred at room temperature under 200 torr of ethylene for 1 h. Excess ethylene was removed and the solution concentrated and cooled to −78 °C to yield 0.39 g (61%) (**16**): IR 1630, 1488, 1022, 919, 802, 778 cm^{-1}. Anal. Calcd for $C_{22}H_{36}Hf$: C, 55.15; H, 7.57; Hf, 37.76. Found: C, 55.63; H, 7.42; Hf, 37.10.

$Cp^*_2HfH(CH_2CHMe_2)$ (17). A thick-walled glass reaction vessel with a Teflon needle valve was charged with 1.0 g (2.0 mmol) of $Cp^*_2HfH_2$, 5 mL of toluene, and 8 mmol of isobutylene, and stirred at 80 °C for 2 days. Volatiles were removed in vacuo; workup with petroleum ether afforded 0.795 g (71%) of **17**: IR 1636, 1302, 1155, 1028, 805, 770 cm^{-1}. Anal. Calcd for $C_{24}H_{40}Hf$: C, 56.85; H, 7.95; Hf, 35.20. Found: C, 56.68; H, 8.12; Hf, 34.94.

$Cp^*_2HfH(CH_2CH_2Ph)$ (18). To a stirred solution of 0.41 g (0.91 mmol) of $Cp^*_2HfH_2$ in 15 mL of toluene at −78 °C was added 110 mL (0.96 mmol) of styrene via syringe under argon counterflow. The solution was warmed to room temperature and stirred an additional 30 min, toluene was removed in vacuo, and the solid residue was worked up with petroleum ether to afford 0.36 g (71%) of white crystalline **18**: IR 3060, 16.20, 1492, 1053, 1030, 975, 806, 776 cm^{-1}.

$Cp^*_2\overline{Hf(CH_2CH_2CH_2CH_2})$ (19). A thick-walled glass reaction vessel with a Teflon needle valve was charged with 1.0 g (2.22 mmol) of $Cp^*_2HfH_2$, 10 mL of toluene, and 72.6 mmol of ethylene and stirred at 80 °C for 24 h. Solvent and excess ethylene were removed, and 0.80 g (61%) of off-white **19** was crystallized from petroleum ether: IR 1490, 1022, 993 cm^{-1}. Anal. Calcd for $C_{24}H_{38}Hf$: C, 57.08; H, 7.58; Hf, 35.34. Found: C, 57.06; H, 7.59; Hf, 35.43.

$Cp^*_2HfH(CH{=}CHCMe_3)$ (20). A 2.50-mmol sample of *tert*-butylacetylene was condensed at −195 °C onto a solution of 1 g (2.22 mmol) of $Cp^*_2HfH_2$ in 15 mL of petroleum ether, stirred for 30 min at −78 °C, and allowed to warm to room temperature. The solution was concentrated to ca. 5 mL and cooled to 78 °C to yield 0.56 g (47%) of white, crystalline **20**: IR 1624, 1560, 1490, 1360, 1232, 1218, 1204, 1064, 1026, 1005, 805 cm^{-1}. Anal. Calcd for $C_{26}H_{42}Hf$: C, 58.58; H, 7.94; Hf, 33.48. Found: C, 58.32; H, 7.89; Hf, 33.26.

$Cp^*_2Hf(CH_2CH_3)(CH{=}CHCMe_3)$ (21). A 3.0-mmol sample of ethylene was condensed at −195 °C onto a solution of 0.66 g (1.24 mmol) of **20** in 10 mL of toluene, warmed to room temperature, and stirred for 2 days. Volatiles were removed in vacuo to leave a colorless oil. Analysis of this residue by ^1H NMR indicated 95% **21**: IR 1558, 1490, 1357, 1250, 1215, 1206, 1060, 1021, 1000, 801 cm^{-1}.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE 8024869). The use of the Southern California Regional NMR Facility, supported by National Science Foundation Grant No. CHE 7916324, is also gratefully acknowledged.

Registry No. **1**, 75181-08-7; **2**, 85959-83-7; **3**, 92786-75-9; **4**, 81956-87-8; **5**, 91295-01-1; **6**, 92786-76-0; **7**, 92786-77-1; **8**, 92786-78-2; **10**, 75687-92-2; **11**, 76830-38-1; **12**, 92786-79-3; **13c**, 92935-38-1; **13t**, 92786-80-6; **14**, 92786-81-7; **15**, 92786-82-8; **16**, 92786-83-9; **17**, 92786-84-0; **18**, 92786-85-1; **19**, 92786-86-2; **20**, 92786-87-3; **21**, 92786-88-4; $HfCl_4$, 13499-05-3; $LiC_5(CH_3)_5$, 51905-34-1; BI_3, 13517-10-7; CH_3I, 74-88-4; CH_3Cl, 74-87-3; CH_3Br, 74-83-9; phenyllithium, 591-51-5; ethylene, 74-85-1; isobutylene, 115-11-7; styrene, 100-42-5; *tert*-butylacetylene, 917-92-0.

Polyoxoanion-Supported Organoactinides: The $[(C_5H_5)_3U(MW_5O_{19})_2]^{5-}$ Anions (M = Nb, Ta) and Their Thorium Analogues $[(C_5H_5)_3Th(MW_5O_{19})_2]^{5-}$†

V. W. Day,*[1a] W. G. Klemperer,*[1b] and D. J. Maltbie[1b]

Crystalytics Company, Lincoln, Nebraska 68501, Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588, and Department of Chemistry, University of Illinois, Urbana, Illinois 61801

Received August 6, 1984

The $MW_5O_{19}{}^{3-}$ anions, M = Nb and Ta, react with $(C_5H_5)_3AcCl$, Ac = Th and U, to form the $[(C_5H_5)_3Ac(MW_5O_{19})_2]^{5-}$ anions. According to a single crystal X-ray diffraction study of $(C_5H_5)_3U(NbW_5O_{19})_2[(\eta\text{-}C_4H_9)_4N]_5$ [a = 13.668 (4) Å, b = 24.172 (6) Å, c = 21.190 (6) Å, α = 98.58 (3)°, β = 98.15 (3)°, γ = 104.64 (3)°; triclinic; $P_{\bar{1}}$—C_i^1; Z = 2], IR spectroscopy, and ^{17}O NMR spectroscopy, all four complexes contain trigonal-bipyramidal actinide centers having three equatorial η^5-C_5H_5 ligands and two axial κ^1O-MW_5O_{19} ligands where the terminal OM oxygens in the MW_5O_{19} ligands coordinate to the actinide centers. The actinide–oxygen bonds in these complexes are quite labile: $[(C_5H_5)_3Th(NbW_5O_{19})_2]^{5-}$ and $[(C_5H_5)_3Th(TaW_5O_{19})_2]^{5-}$ equilibrate in CH_3NO_2 within 15 min at 25 °C to form $[(C_5H_5)_3Th(NbW_5O_{19})(TaW_5O_{19})]^{5-}$ in approximately statistical amounts.

Introduction

Since the actinide elements are known to form stable organic[2] and polyoxoanion[3] complexes, the synthesis of polyoxoanion-supported organoactinide complexes is a reasonable objective. Polyoxoanion-supported organoactinides offer the possibility of combining several features of known organometallic complexes in a unique fashion. Large, planar ligands such as C_5H_5, C_8H_8, and $(CH_3)_5C_5$ are known to be effective as auxiliary ligands due to their

---

† Dedicated to the memory of Earl Muetterties and the standards he upheld.

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

(2) Marks, T. J. *Prog. Inorg. Chem.* **1979**, *25*, 224.

(3) Pope, M. T. "Heteropoly and Isopoly Oxometalates"; Springer-Verlag: Berlin, Heidelberg, 1983.

large steric bulk, which serves to reduce coordinative unsaturation at actinide metal centers.[2] Polyoxoanions of the early transition metals also have large steric bulk[3] and are thus likely to be effective in the same manner. Organoactinides are also known to be quite oxophilic[4] and are thus likely to form stable bonds to polyoxoanion surface oxygens. If polyoxoanion supported organoactinides are to become involved in organometallic reaction chemistry without decomposition, stable actinide–oxygen bonds are of course a prerequisite. Finally, solid oxide supported organoactinides are quite reactive toward organic molecules,[5] and their polyoxoanion-supported analogues might display similar reactivity.

Hexametalate ions $M_6O_{19}{}^{y-}$ were selected for the investigations reported here since they have been shown to have steric dimensions very similar to η^5-$(CH_3)_5C_5$ ligands when bonded in a tridentate fashion in complexes such as $\{[\eta^5\text{-}(CH_3)_5C_5]Rh(\kappa^3O\text{-}Nb_2W_4O_{19})\}^{2-}$[6] and $[(OC)_3Mn(\kappa^3O\text{-}Nb_2W_4O_{19})]^{3-}$.[7] The initial targets $[(C_5H_5)_3Ac(\kappa^3O\text{-}MW_5O_{19})]^{2-}$ (Ac = U^{IV}, Th^{IV}; M = Nb^V, Ta^V) were to be prepared according to eq 1. The products first isolated

$$(C_5H_5)_3AcCl + MW_5O_{19}{}^{3-} = [(C_5H_5)_3Ac(MW_5O_{19})]^{2-} + Cl^- \quad (1)$$

from the reaction of $MW_5O_{19}{}^{3-}$ with equimolar $(C_5H_5)_3AcCl$ in 1,2-dichloroethane/tetrahydrofuran were, however, not the desired 1:1 adducts but instead the 1:2 adducts $[(C_5H_5)_3Ac(MW_5O_{19})_2]^{5-}$. We describe here the synthesis, structure, and stability of these complexes.

Experimental Section

Reagents, Solvents, and General Procedures. The following were purchased from commercial sources and were used without further purification: $Na_2WO_4 \cdot 2H_2O$ and 30% aqueous H_2O_2 (Fisher); sulfuric acid (Mallinckrodt); $(n\text{-}C_4H_9)_4NBr$ (Aldrich); $Na_2S_2O_4 \cdot 2H_2O$ (Baker); $ThCl_4$ (Alfa).

$K_7HNb_6O_{19} \cdot 13H_2O$ was prepared according to literature procedures.[6,8] $TaW_5O_{19}[(n\text{-}C_4H_9)_4N]_3$ was prepared as previously described.[9] UCl_4,[10] $(C_5H_5)_3UCl$,[11] and $(C_5H_5)_3ThCl$[11] were synthesized by using literature procedures. Temperatures slightly higher than those specified in ref 10, ca. 110 °C, were needed to initiate the UCl_4 preparation. $(C_5H_5)_3MCl$, M = U and Th, were purified by simple extraction into toluene, not Soxhlet extraction into benzene and/or hexane washing.

Anhydrous diethyl ether (Mallinckrodt) was used from freshly opened cans. Acetonitrile (Aldrich, 99%) was stored over activated 3-Å sieves. 1,2-Dichloroethane (Fisher) and ethanol (U.S. Industrial Chemical Co.) were stored over activated 4-Å sieves. Solvents used in reactions involving actinides and those used for the preparation of ^{17}O-enriched samples were purified more thoroughly before use. Acetonitrile was distilled under N_2 from P_4O_{10} onto activated 3-Å molecular sieves (Linde). Diethyl ether, tetrahydrofuran (Aldrich), and toluene (Baker) were refluxed over sodium and benzophenone under N_2 and stored over activated 4-Å sieves. 1,2-Dichloroethane was distilled under N_2 from P_4O_{10} onto activated 4-Å sieves. CD_3CN was stored over 3-Å sieves under N_2. CD_3NO_2 was vacuum distilled from 4-Å sieves. Molecular sieves were activated by drying at 350 °C for 24 h and storing under N_2 at room temperature.

Oxygen-17 enriched samples of compounds 1–4 were prepared as described below from starting materials that were obtained in ^{17}O-enriched form using procedures described in ref 9. All manipulations of actinide complexes and ^{17}O-enriched materials were performed in a dry N_2 atmosphere.

Analytical Procedures. Elemental analyses were performed by the School of Chemical Sciences Analytical Laboratory and by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were measured from mineral oil (Nujol) mulls between KBr plates on a Perkin-Elmer 1330 spectrometer and were referenced to the 1028 cm^{-1} band of a 0.05-mm polystyrene film. ^1H NMR spectra were recorded at 360 MHz on a Nicolet spectrometer equipped with a deuterium lock. ^{17}O and ^{93}Nb NMR spectra were measured on an unlocked FTNMR system equipped with a 5.87-T Oxford Instruments magnet and a Nicolet NIC-80 data system. ^1H NMR chemical shifts were internally referenced to $(CH_3)_4Si$. ^{17}O and ^{93}Nb NMR chemical shifts were externally referenced to fresh tap water and 0.25 M $NbCl_6[(C_2H_5)_4N]$ in CH_3CN, respectively, at 25 °C using the sample replacement method. Chemical shifts for all nuclei are reported as positive numbers for resonances observed at higher frequency (lower field) than the reference. All reported line widths have been corrected for exponential line broadening. Experimental conditions, spectral parameters, and error limits for ^{17}O and ^{93}Nb NMR measurements are those given in ref 9 unless specified otherwise. A 28-μs pulse width and 20-μs preacquisition delay were used for all ^{17}O NMR measurements.

Aqueous Preparation of $NbW_5O_{19}[(n\text{-}C_4H_9)_4N]_3$.[12] The literature preparation[13] of $NbW_5O_{19}K[(CH_3)_4N]_2$ was followed by using 32.9 g (99.7 mmol) of $Na_2WO_4 \cdot 2H_2O$ and 5.48 g (4.01 mmol) of $K_7HNb_6O_{19} \cdot 13H_2O$ until just before the $(CH_3)_4NBr$ was added. At this point 20 g (62.0 mmol) of $(n\text{-}C_4H_9)_4NBr$ was added to the clear solution and a white powder precipitated. This powder was collected by suction filtration and washed with 25 mL of water, then two 25-mL portions of ethanol, and finally two 25-mL portions of ether. The white solid collected was dried in vacuo overnight. Typically, 25–30 g of material was obtained. The crude product was then stirred with 150 mL of 1,2-dichloroethane for 5 min, and the resulting slurry was gravity filtered to remove insoluble impurities. Addition of 325 mL of ether to the filtrate produced a precipitate that was collected by suction filtration and washed with two 25-mL portions of ether. The resulting white solid was dried in vacuo, yielding 20–25 g of crude material. Crystalline material was obtained by dissolving this white solid in 10–15 mL of boiling CH_3CN and gravity filtering if necessary. The solution volume was then reduced by boiling off solvent until the point of precipitation. At this point, sufficient CH_3CN was added to obtain a clear solution, and the solution was stored at −20 °C overnight. The crystals that formed were then suction filtered, washed with 25 mL of ether, and dried in vacuo to yield 12 g (5.9 mmol, 30% yield based on W) of product as a white powder. The analytical sample was recrystallized twice: IR (Nujol, 700–1000 cm^{-1}): 733 (m), 802 (s, br), 884 (m), 913 (m), 957 (s), 974 (sh) cm^{-1}. Anal. Calcd for $C_{48}H_{108}N_3NbW_5O_{19}$: C, 28.21; H, 5.33; N, 2.06; Nb, 4.55; W, 44.98. Found: C, 28.27; H, 5.40; N, 2.08; Nb, 4.68; W, 44.82.

Preparation of $(C_5H_5)_3U(NbW_5O_{19})_2[(n\text{-}C_4H_9)_4N]_5$ (1). A solution containing 0.31 g (0.66 mmol) of $(C_5H_5)_3UCl$ in 10 mL of THF was added with stirring to a solution of 2.03 g (0.99 mmol) of $NbW_5O_{19}[(n\text{-}C_4H_9)_4N]_3$ in 20 mL of 1,2-dichloroethane. The solution quickly turned from brown to green, and a precipitate formed. Stirring was continued for an additional 4–5 min, and the product was then collected by suction filtration. The slightly oily product was washed with 25 mL of THF followed by two 25-mL portions of ether to yield 2.3 g of light green powder. (If the $NbW_5O_{19}\{(n\text{-}C_4H_9)_4N\}_3$ used was not sufficiently pure, the product precipitated as an oil. When this occurred, the mother liquor was decanted, 25 mL of ether was added, and the oil was

---

(4) (a) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206 and references therein. (b) Duttera, M. R.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2907.

(5) He, M. Y.; Burwell, R. L.; Marks, T. J. *Organometallics* **1983**, *2*, 566.

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

(7) (a) Besecker, C. J.; Klemperer, W. G. *J. Am. Chem. Soc.* **1980**, *102*, 7598. (b) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Inorg. Chem.*, in press.

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

(9) Besecker, C. J.; Klemperer, W. G.; Maltbie, D. J.; Wright, D. A. *Inorg. Chem.*, in press.

(10) Hermann, J. A.; Suttle, J. F. *Inorg. Synth.* **1957**, *5*, 143.

(11) Marks, T. J.; Seyam, A. M.; Wachter, W. A. *Inorg. Synth.* **1976**, *16*, 147.

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

(13) Dabbabi, M.; Boyer, M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1011.

scraped with a spatula until it dried to a powder. This powder was dissolved in CH_3CN and precipitated with ether before crystallization.) Crystalline material was obtained by dissolving the crude product in 5–6 mL of CH_3CN, gravity filtering, and adding toluene until the solution was faintly cloudy. The green rods that formed overnight were collected by suction filtration, washed with 25 mL of ether, and dried in vacuo. A second crop of crystals was obtained by adding more toluene to the mother liquor. Combined yields of crystals varied from 0.4 to 0.8 g (0.1–0.2 mmol, 20–40% yield based on W). A precipitate occasionally formed immediately after toluene was added during the crystallization procedure. In this case, the solution was gravity filtered before being left to crystallize. The analytical sample was crystallized three times: IR (Nujol, 700–1000 cm^{-1}) 722 (sh), 757 (s), 805 (s), 856 (w), 880 (w), 957 (s), 965 (sh), 982 (w); ^1H NMR in addition to cation resonances at δ 3.35–3.10, 1.85–1.55, 1.45–1.20, and 1.05–0.95, one singlet due to the cyclopentadienyl protons is seen at δ −15.1 (ca. 60-Hz line width) at 25 °C in CD_3CN; ^{17}O NMR (0.003 M; 25 °C; 14 atom % ^{17}O; 80 000 acquisitions; 10.0 Hz line broadening) see Table VII; ^{93}Nb NMR (0.006 M; 25 °C; 12 000 acquisitions; 30-Hz line broadening) δ −248 (9900 Hz line width). Anal. Calcd for $C_{95}H_{195}N_5UNb_2W_{10}O_{38}$: C, 26.67; H, 4.59; N, 1.64; U, 5.56; Nb, 4.34; W, 42.98. Found: C, 26.63; H, 4.44; N, 1.59; U, 5.57; Nb, 4.28; W, 42.88.

Preparation of $(C_5H_5)_3U(TaW_5O_{19})_2[(n\text{-}C_4H_9)_4N]_5$ (2). This compound was prepared by using the procedure described for 1 by substituting 2.1 g (0.99 mmol) of $TaW_5O_{19}[(n\text{-}C_4H_9)_4N]_3$ for $NbW_5O_{19}[(n\text{-}C_4H_9)_4N]_3$. The yields of both products are comparable. The analytical sample was crystallized three times: IR (Nujol, 700–1000 cm^{-1}) 732 (sh), 758 (s), 808 (s), 868 (w), 882 (sh), 960 (s), 968 (sh), 984 (m) cm^{-1}; ^1H NMR in addition to cation resonances at δ 3.35–3.10, 1.85–1.55, 1.45–1.20, 1.05–0.95, one singlet due to the cyclopentadienyl protons is seen at δ −23.9 (ca. 244-Hz line width) at 25 °C in CD_3CN; ^{17}O NMR (0.01 M; 25 °C; 18 atom % ^{17}O; 8000 acquisitions; 5.0-Hz line broadening) see Table VII. Anal. Calcd for $C_{95}H_{195}N_5UTa_2W_{10}O_{38}$: C, 25.62; N, 1.57; H, 4.41. Found: C, 25.77; N, 1.52; H, 4.47.

Preparation of $(C_5H_5)_3Th(NbW_5O_{19})_2[(n\text{-}C_4H_9)_4N]_5$ (3). This compound was prepared as described for 1 with the following changes. A 0.31-g (0.66-mmol) sample of $(C_5H_5)_3ThCl$ was substituted for $(C_5H_5)_3UCl$, and the reaction time was increased to 15–20 min. The yields of colorless crystals obtained were comparable to the uranium derivative. The analytical sample was crystallized three times: IR (Nujol, 700–1000 cm^{-1}) 722 (sh), 735 (sh), 760 (s), 804 (s), 860 (m), 882 (w), 957 (s), 982 (m) cm^{-1}; ^1H NMR in addition to cation resonances at δ 3.35–3.10, 1.85–1.55, 1.45–1.20, 1.05–0.95, one singlet due to the cyclopentadienyl protons is seen at δ 6.387 (ca. 1.5-Hz linewidth) at 25 °C in CD_3NO_2 and at δ 6.276 in CD_3CN; ^{17}O NMR (0.005 M; 25 °C; 14 atm % ^{17}O; 45 000 acquisitions; 5.0-Hz line broadening) see Table VII; under the same conditions but at −15 °C, δ 745 (275-Hz line width, OW), 660 (170, OThNb), 463 (124, ONbW), 397 (238, OW_2), −72 (38, $ONbW_5$); ^{93}Nb NMR (0.01 M; 25 °C; 20 000 acquisitions;20-Hz line broadening): δ −943 (8200-Hz line width). Anal. Calcd for $C_{95}H_{195}N_5ThNb_2W_{10}O_{38}$: C, 26.71; N, 1.64; H, 4.60. Found: C, 26.58; N, 1.56; H, 4.65.

Preparation of $(C_5H_5)_3Th(TaW_5O_{19})_2[(n\text{-}C_4H_9)_4N]_5$ (4). This compound was prepared as described for 2 with the following changes. A 0.31-g (0.66-mmol) sample of $(C_5H_5)_3ThCl$ was substituted for $(C_5H_5)_3UCl$, and the reaction time was increased to 15–20 min. The yields of colorless crystals were comparable to those found for the uranium derivative. The analytical sample was crystallized three times. IR (Nujol, 700–1000 cm^{-1}) 730 (s), 760 (s), 808 (s), 870 (w), 887 (sh), 958 (s), 968 (sh), 985 (w) cm^{-1}; ^1H NMR in addition to cation resonances at δ 3.35–3.10, 1.85–1.55, 1.45–1.20, and 1.05–0.95, one singlet due to the cyclopentadienyl protons is seen at δ 6.308 (ca. 1.2-Hz linewidth) at 25 °C in CD_3NO_2 and at δ 6.204 in CD_3CN; ^{17}O NMR (0.009 M; 25 °C; 14 atm % ^{17}O; 16 000 acquisitions; 5.0 Hz line broadening) see Table VII. Anal. Calcd for $C_{95}H_{195}N_5ThTa_2W_{10}O_{38}$: C, 25.65; N, 1.58; H, 4.42. Found: C, 25.71; N, 1.50; H, 4.43.

X-ray Crystallographic Study of $(C_5H_5)_3U(NbW_5O_{19})_2[(n\text{-}C_4H_9)_4N]_5$ (1).[14] After more than a dozen unsuccessful attempts to grow single crystals with other solvent systems, small, plate-shaped, green single crystals of 1 that were marginally acceptable for X-ray diffraction studies were finally grown as described above from $CH_3CN/C_6H_5CH_3$. They are, at 20 ± 1 °C, triclinic with $a = 13.668\ (4)$ Å, $b = 24.172\ (6)$ Å, $c = 21.190\ (6)$ Å, $\alpha = 98.58\ (3)°$, $\beta = 98.15\ (3)°$, $\gamma = 104.64\ (3)°$, $V = 6579\ (4)$ Å^3, and $Z = 2$ [μ_a(Mo K_α)[15a] = 10.3 mm^{-1}; $d_{calcd} = 2.16$ g/cm^3]. The choice of the centrosymmetric space group $P\bar{1}$—C_i^1 (No. 2)[16] was consistent with the values of various statistical indicators using normalized structure factors and with all stages of the subsequent structure determination and refinement.

Intensity measurements were made on a Nicolet PI autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation for a specimen having the shape of a rectangular parallelepiped with dimensions of 0.13 × 0.38 × 0.40 mm. This crystal was sealed under N_2 in a thin-walled glass capillary and mounted on a goniometer with its longest dimension nearly parallel to the ϕ axis of the diffractometer. A total of 18 046 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 45.8° (the equivalent of 0.60 limiting Cu K$\bar{\alpha}$ spheres) were measured with scanning rates of 6°/min for those reflections having 3° < 2θ < 36° and 4°/min for all others. The data collection and reduction procedures that were used are described elsewhere.[6] In the present study, the scan width and step-off for background measurements were both 0.90° and the ratio of total background counting time to net scanning time was 0.50. The intensity data were corrected empirically for absorption effects using ψ scans for three intense reflections having 2θ between 9.8° and 19.5° (the relative transmission factors ranged from 0.260 to 1.000).

The six metals of one $NbW_5O_{19}^{3-}$ unit were located by using Patterson search techniques; the partial structural model based on these metals provided phases that were sufficiently accurate to permit location of the remaining seven metals. Counting-statistics-weighted anisotropic full-matrix least-squares refinement of the structural parameters for these 13 metals converged to R_1(unweighted, based on F)[17a] = 0.130 and R_2(weighted, based on F)[17a] = 0.172 for 7186 independent absorption-corrected reflections having 2θ(Mo K$\bar{\alpha}$) < 45.8° and $I > 3\sigma(I)$. Positions for the remaining 140 non-hydrogen atoms of the asymmetric unit appeared in subsequent difference Fourier syntheses which used phases derived from progressively more complete structural models. All of the cationic non-hydrogen atoms were located. Terminal methyl carbon atoms C_{3d} of cation 1 and C_{4d} of cation 5 each appear to be statistically disordered between two sites (C_{3d} and C'_{3d} for cation 1 and C_{4d} and C'_{4d} for cation 5); all four sites were included in the structure factor calculations as carbon atoms with occupancies of 0.50. The final cycles[14] of counter-weighted cascade block-diagonal least-squares refinement which utilized anisotropic thermal parameters for the 13 metal atoms and isotropic thermal parameters for the remaining 140 non-hydrogen atoms and 15 fixed cyclopentadienyl hydrogens gave $R_1 = 0.069$ and $R_2 = 0.063$ for 7186 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 45.8° and $I > 3\sigma(I)$. In these cycles, the cyclopentadienyl ligands were refined as rigid groups with idealized planar geometry and C–C and C–H bond lengths of 1.397 and 0.96 Å, respectively.

All structure factor calculations employed recent tabulations of atomic form factors,[15b] anomalous dispersion corrections[15c] to the scattering factors of the U, W, and Nb atoms, and a least-squares refinable extinction correction.[17b] All calculations were performed on a Data General Eclipse S-200 computer equipped with 128 K of 16-bit words, a floating point processor for 32- and 64-bit arithmetic and versions of the EXTL and SHELXTL interactive crystallographic software package as modified at Crystalytics Co.

---

[14] See paragraph at end of paper regarding supplementary material.

(15) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV; (a) pp 55–66; (b) pp 99–101; (c) pp 149–50.

(16) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol, I, p 75.

(17) (a) 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 is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$, where K is the scale factor. The weighting scheme uses $w = 1/\sigma_F 2$; for weights derived from counting statistics: $\sigma_F = \{[\sigma(F_o)]^2 + (0.01|F_o|)^2]^{-1/2}$. (b) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

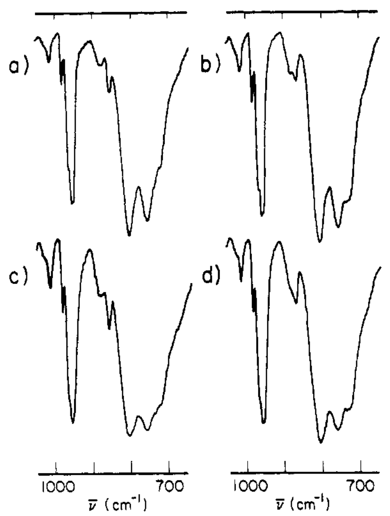


Figure 1. IR spectra of $[(C_5H_5)_3U(NbW_5O_{19})_2]^{5-}$, $[(C_5H_5)_3U(TaW_5O_{19})_2]^{5-}$, $[(C_5H_5)_3Th(NbW_5O_{19})_2]^{5-}$, and $[(C_5H_5)_3Th(TaW_5O_{19})_2]^{5-}$ as $[(n\text{-}C_4H_9)_4N]^+$ salts in Nujol mulls are shown in a–d, respectively. See Experimental Section for numerical data.

Results and Discussion

Synthesis and Characterization. All four title anions, prepared as $(n\text{-}C_4H_9)_4N^+$ salts according to eq 2, were

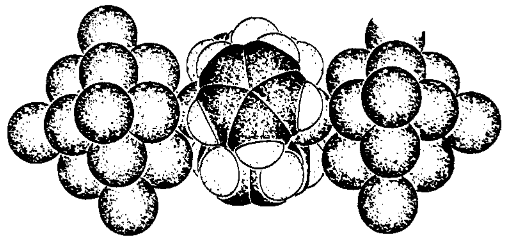
$$\begin{gathered}(C_5H_5)_3AcCl + 2(MW_5O_{19})[(n\text{-}C_4H_9)_4N]_3 = \\ [(C_5H_5)_3Ac(MW_5O_{19})_2][(n\text{-}C_4H_9)_4N]_5 + (n\text{-}C_4H_9)_4NCl \\ \mathbf{1},\ Ac = U,\ M = Nb \\ \mathbf{2},\ Ac = U,\ M = Ta \\ \mathbf{3},\ Ac = Th,\ M = Nb \\ \mathbf{4},\ Ac = Th,\ M = Ta\end{gathered} \qquad (2)$$

formulated by using elemental analytical data and ^1H NMR spectroscopic data given in the Experimental Section. The IR spectra of compounds **1**–**4** are extremely similar in the 650–1000 cm^{-1} region (see Figure 1), strongly suggesting a common structure for the four anions. A single-crystal X-ray diffraction study of **1** was undertaken to determine this structure.

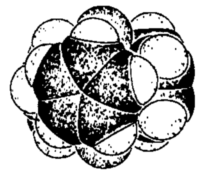
Solid-State Structure of $[(C_5H_5)_3U(NbW_5O_{19})_2][(n\text{-}C_4H_9)_4N]_5$ (1).[14] X-ray structural analysis revealed that single crystals of **1** are composed of discrete $[(C_5H_5)_3U(NbW_5O_{19})_2]^{5-}$ anions (Figure 2) and $(n\text{-}C_4H_9)_4N^+$ cations (Figure 3).[14] Final atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms of **1** are given with estimated standard deviations in Tables I and II,[14] respectively, and idealized coordinates for cyclopentadienyl hydrogen atoms are given in Table III.[14] Average bond lengths and angles for the $[(C_5H_5)_3U(NbW_5O_{19})_2]^{5-}$ anion are given in Table IV. Detailed bond lengths and angles for non-hydrogen atoms of the $[(C_5H_5)_3U(NbW_5O_{19})_2]^{5-}$ anion and the five crystallographically independent $[(n\text{-}C_4H_9)_4N]^+$ cations are given in Tables V[14] and VI,[14] respectively.

The coordination geometry at uranium in **1** is trigonal bipyramidal (see Figure 2), where η^5-C_5H_5 ligands occupy equatorial sites and κ^1O-NbW_5O_{19} ligands, using their ONb terminal oxygens, occupy axial sites. The average bond lengths and angles given in Table IV have values similar to those observed in the closely related trigonal-bipyramidal complexes $[(C_5H_5)_3U(NCS)(NCCH_3)]$,[18] $[(C_5H_5)_3U(NCS)_2]^-$,[19] and $[(C_5H_5)_3U(NCCH_3)_2]^+$,[20] where average U–C bond distances vary between 2.74 and 2.76 Å and U–NCS bond distances vary between 2.41 and 2.50 Å. The 2.36-Å average U–O distance observed here is similar to the 2.370- and 2.342-Å values observed in $[(CH_3)_5C_5]_2U\{OC[N(CH_3)_2]\}_2$[4a] but significantly longer than the 2.046-Å value observed in $\{[(CH_3)_5C_5]_2U(OCH_3)\}_2PH$.[4b] Within the NbW_5O_{19} ligands, average bond lengths and angles closely resemble those observed in other M_6O_{19} anions.[21] The low precision of the present structure determination does not permit detailed comparisons.

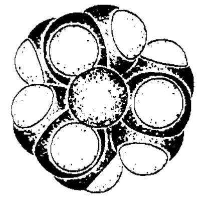
A space-filling model of the $[(C_5H_5)_3U(NbW_5O_{19})_2]^{5-}$ anion (see a), employing van der Waals radii for carbon, hydrogen, and oxygen atoms,[22] shows only one nonbonded contact between the C_5H_5 ligands and oxygens in the NbW_5O_{19} ligands that are not coordinated to uranium ($H_{5v}\cdots O_{B1r}$ = 2.30 Å): all other H···O distances exceed the 2.6 Å sum of hydrogen and oxygen van der Waals radii and all C···O distances exceed the 3.1 Å sum of carbon and oxygen van der Waals radii. Within the uranium coordination sphere, however, steric crowding is severe: each of the two axial oxygens is in very close contact with three C_5H_5 carbons ($O_{Fr}\cdots C_{4t}$ = 2.79 Å; $O_{Fr}\cdots C_{3u}$ = 2.83 Å; $O_{Fr}\cdots C_{5v}$ = 2.76 Å; $O_{Fs}\cdots C_{2t}$ = 2.84 Å; $O_{Fs}\cdots C_{5u}$ = 2.85 Å; $O_{Fs}\cdots C_{3v}$ = 2.77 Å). This steric crowding is evident in the space-filling models of the $(C_5H_5)_3UO_2$ subunit shown in b and c. The C_5H_5 ligands are locked into a conformation that minimizes H···H contacts, and the oxygen atoms fit snugly into "nests" formed by the C_5H_5 ligands.



a



b



c

Unlike the $\{[(CH_3)_5C_5]Rh(Nb_2W_4O_{19})\}^{2-}$[6] and $[(OC)_3Mn(Nb_2W_4O_{19})]^{3-}$[7] anions, which form as mixtures of permutational isomers, the $[(C_5H_5)_3U(NbW_5O_{19})_2]^{5-}$ anion is formed as a single isomer in which U^{IV} binds only to ONb^V terminal oxygens in $NbW_5O_{19}{}^{3-}$ anions, not as a mixture of isomers in which U^{IV} binds to both OW^{VI} and ONb^V terminal oxygens. In the cases of the $Nb_2W_4O_{19}{}^{4-}$ derivatives just mentioned, organometal binding to doubly bridging ONb_2, ONbW, and OW_2 oxygens is unselective and mixtures of isomeric adducts result. The contrasting selectivity of organometal binding to terminal oxygens has been invoked to two other contexts: the molecular structure proposed for $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$, derived from a disordered crystal structure, assumes binding of Rh^I only to ONb terminal oxygens, not OW terminal oxygens;[23] the mechanism of formation of $\{[(CH_3)_5C_5]Rh$-

---

[18] Fischer, R. D.; Klähne, E.; Kopf, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1393.

[19] Bombieri, G.; Benetollo, F.; Bagnall, K. W.; Plews, M. J.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1983**, 45.

[20] Bombieri, G.; Benetollo, F.; Klahne, E.; Fischer, R. D. *J. Chem. Soc., Dalton Trans.* **1983**, 1115.

[21] Reference 3, pp 20–21, and references cited therein.

[22] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

[23] Besecker, C. J.; Klemperer, W. G.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 6158.

Table I. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $[(C_5H_5)_3U(NbW_5O_{19})_2][(n\text{-}C_4H_9)_4N]_5$ (1)[a]

atom type[b]	fractional coordinates				atom type[b]	fractional coordinates			
	10^4x	10^4y	10^4z	$10B$,[c] Å^2		10^4x	10^4y	10^4z	$10B$,[c] Å^2
				Anion					
W_{1r}	2905 (2)	3740 (1)	−2533 (1)	39 (1)	O_{B2s}	3750 (20)	956 (10)	1353 (15)	41 (6)
W_{2r}	1146 (2)	2535 (1)	−3305 (1)	42 (1)	O_{B3s}	2515 (19)	1463 (10)	1940 (14)	37 (6)
W_{3r}	−600 (2)	2954 (1)	−2594 (1)	38 (1)	O_{B4s}	4049 (19)	2509 (10)	2176 (14)	37 (6)
W_{4r}	1154 (2)	4154 (1)	−1818 (1)	35 (1)	O_{D1s}	5628 (17)	1041 (9)	1987 (12)	23 (5)
W_{5r}	757 (2)	3811 (1)	−3421 (1)	40 (1)	O_{D2s}	2968 (21)	537 (11)	2287 (15)	48 (7)
Nb_r	1540 (3)	2881 (2)	−1712 (2)	34 (1)	O_{D3s}	3298 (18)	2084 (9)	3120 (13)	29 (5)
O_{Ar}	1172 (22)	3359 (11)	−2538 (16)	49 (7)	O_{D4s}	5901 (18)	2570 (9)	2776 (14)	32 (6)
O_{B1r}	2923 (21)	3314 (11)	−1848 (15)	45 (7)	O_{E1s}	6337 (19)	1662 (10)	3160 (14)	35 (6)
O_{B2r}	1484 (20)	2342 (10)	−2508 (15)	42 (6)	O_{E2s}	4765 (22)	640 (11)	2941 (16)	53 (8)
O_{B3r}	44 (18)	2677 (9)	−1916 (13)	32 (6)	O_{E3s}	3700 (18)	1153 (10)	3494 (14)	32 (6)
O_{B4r}	1413 (21)	3641 (11)	−1348 (15)	44 (7)	O_{E4s}	5149 (18)	2151 (9)	3712 (13)	31 (6)
O_{D1r}	2475 (23)	3012 (12)	−3132 (17)	62 (8)	O_{Fs}	3252 (20)	1940 (10)	802 (15)	41 (6)
O_{D2r}	−301 (20)	2368 (10)	−3198 (15)	43 (7)	O_{G1s}	7302 (20)	2074 (10)	2180 (14)	40 (6)
O_{D3r}	−218 (20)	3691 (10)	−2018 (14)	40 (6)	O_{G2s}	4074 (20)	−97 (10)	1676 (15)	41 (6)
O_{D4r}	2507 (20)	4320 (10)	−1948 (15)	41 (6)	O_{G3s}	1631 (20)	1046 (10)	2951 (15)	42 (6)
O_{E1r}	2222 (21)	4037 (11)	−3229 (16)	49 (7)	O_{G4s}	4789 (24)	3207 (12)	3424 (18)	65 (8)
O_{E2r}	830 (22)	3067 (11)	−3789 (16)	50 (7)	O_{Hs}	5583 (22)	1248 (11)	4225 (16)	50 (7)
O_{E3r}	−576 (23)	3388 (12)	−3302 (17)	59 (8)	U	2558 (1)	2238 (1)	−127 (1)	31 (1)
O_{E4r}	806 (18)	4338 (9)	−2661 (14)	31 (6)	C_{1t}	1814 (24)	2729 (16)	856 (16)	75 (15)
O_{Fr}	1871 (20)	2540 (10)	−1059 (15)	42 (6)	C_{2t}	1284 (24)	2138 (16)	753 (16)	74 (15)
O_{G1r}	4131 (22)	4040 (11)	−2539 (16)	52 (7)	C_{3t}	580 (24)	2001 (16)	167 (16)	99 (19)
O_{G2r}	1114 (23)	1936 (12)	−3840 (17)	62 (8)	C_{4t}	677 (24)	2506 (16)	−92 (16)	74 (15)
O_{G3r}	−1836 (23)	2660 (12)	−2611 (17)	61 (8)	C_{5t}	1439 (24)	2956 (16)	334 (16)	60 (13)
O_{G4r}	1147 (22)	4748 (12)	−1299 (17)	58 (8)	C_{1u}	1689 (25)	1056 (12)	−502 (16)	49 (11)
O_{Hr}	424 (22)	4130 (12)	−4043 (17)	57 (8)	C_{2u}	1469 (25)	1284 (12)	−1056 (16)	60 (13)
W_{1s}	6084 (1)	1856 (1)	2314 (1)	34 (1)	C_{3u}	2387 (25)	1475 (12)	−1279 (16)	76 (15)
W_{2s}	4248 (2)	623 (1)	2013 (1)	34 (1)	C_{4u}	3174 (25)	1365 (12)	−863 (16)	83 (16)
W_{3s}	2793 (1)	1289 (1)	2771 (1)	34 (1)	C_{5u}	2742 (25)	1106 (12)	−382 (16)	67 (13)
W_{4s}	4620 (2)	2524 (1)	3053 (1)	33 (1)	C_{1v}	4373 (29)	2734 (15)	−543 (20)	85 (16)
W_{5s}	5117 (2)	1359 (1)	3519 (1)	34 (1)	C_{2v}	4719 (29)	2618 (15)	63 (20)	131 (23)
Nb_s	3753 (3)	1781 (2)	1557 (2)	36 (2)	C_{3v}	4407 (29)	2969 (15)	534 (20)	107 (20)
O_{As}	4398 (21)	1551 (11)	2541 (15)	39 (6)	C_{4v}	3868 (29)	3302 (15)	220 (20)	86 (16)
O_{B1s}	5239 (18)	1971 (9)	1586 (13)	26 (5)	C_{5v}	3847 (29)	3157 (15)	−446 (20)	76 (15)
				Cation 1					
N	2209 (25)	−820 (13)	3370 (18)	36 (7)	C_{1g}	1658 (46)	−1245 (24)	4996 (35)	88 (17)
C_{1a}	1892 (39)	−1128 (20)	3928 (29)	72 (14)	C_{2g}	1882 (61)	−1527 (32)	1421 (46)	157 (29)
C_{2a}	2156 (41)	−1263 (22)	2767 (31)	76 (15)	C_{3g}	−273 (56)	−425 (30)	2933 (42)	148 (26)
C_{3a}	1526 (44)	−416 (23)	3289 (32)	86 (17)	C_{4g}	5182 (42)	−260 (22)	4042 (31)	81 (15)
C_{4a}	3310 (34)	−391 (17)	3632 (25)	50 (11)	C_{1d}	1782 (49)	−903 (26)	5615 (38)	102 (20)
C_{1b}	1956 (38)	−788 (20)	4551 (28)	68 (14)	C_{2d}	2695 (69)	−1693 (37)	1577 (54)	188 (36)
C_{2b}	2332 (49)	−1019 (26)	2158 (37)	104 (20)	C_{3d}[d]	−1236 (74)	−593 (38)	3302 (55)	65 (26)
C_{3b}	362 (47)	−791 (25)	2914 (35)	103 (19)	C'_{3d}[d]	−359 (84)	−356 (43)	3739 (62)	88 (32)
C_{4b}	4068 (34)	−724 (18)	3892 (25)	54 (12)	C_{4d}	5888 (40)	−624 (21)	4314 (29)	71 (14)
				Cation 2					
N	−2282 (26)	3901 (13)	2220 (19)	45 (8)	C_{1g}	−2810 (33)	2680 (17)	698 (25)	50 (11)
C_{1a}	−2571 (31)	3308 (16)	1804 (23)	41 (10)	C_{2g}	576 (48)	4445 (25)	2006 (35)	106 (19)
C_{2a}	−1243 (30)	4291 (15)	2138 (22)	37 (9)	C_{3g}	−2013 (60)	4082 (32)	4007 (45)	143 (27)
C_{3a}	−2205 (31)	3758 (16)	2873 (23)	36 (9)	C_{4g}	−4802 (42)	4432 (22)	2040 (31)	84 (16)
C_{4a}	−3012 (36)	4289 (18)	2059 (26)	60 (13)	C_{1d}	−1741 (42)	2529 (21)	766 (30)	80 (15)
C_{1b}	−2660 (32)	3301 (16)	1090 (24)	43 (10)	C_{2d}	1049 (60)	4217 (31)	1766 (45)	151 (27)
C_{2b}	−394 (40)	3973 (21)	2132 (30)	70 (15)	C_{3d}	−1709 (62)	4579 (32)	4547 (46)	158 (30)
C_{3b}	−1903 (43)	4365 (23)	3462 (33)	80 (16)	C_{4d}	−5856 (43)	4181 (22)	2155 (32)	84 (16)
C_{4b}	−4042 (38)	4005 (20)	2200 (28)	67 (13)					
				Cation 3					
N	−3281 (30)	−3077 (15)	4952 (21)	60 (10)	C_{1g}	−4349 (41)	−4616 (22)	3901 (30)	74 (14)
C_{1a}	−3556 (37)	−3535 (20)	4332 (27)	55 (12)	C_{2g}	−5793 (56)	−2507 (27)	4596 (39)	123 (23)
C_{2a}	−4319 (34)	−2928 (18)	5044 (26)	55 (12)	C_{3g}	−1892 (48)	−4020 (25)	5862 (36)	110 (20)
C_{3a}	−2857 (41)	−3305 (21)	5573 (30)	82 (15)	C_{4g}	−1168 (66)	−1462 (35)	5467 (47)	169 (30)
C_{4a}	−2424 (35)	−2557 (19)	4865 (26)	52 (12)	C_{1d}	−5029 (47)	−5156 (24)	3970 (34)	101 (18)
C_{1b}	−4310 (40)	−4099 (20)	4417 (29)	73 (14)	C_{2d}	−6312 (37)	−2347 (19)	4070 (27)	63 (13)
C_{2b}	−4848 (47)	−2679 (23)	4497 (32)	82 (16)	C_{3d}	−866 (58)	−4141 (30)	5915 (43)	139 (26)
C_{3b}	−1932 (44)	−3468 (23)	5585 (32)	91 (17)	C_{4d}	−1882 (55)	−1105 (29)	5180 (41)	129 (24)
C_{4b}	−2193 (44)	−2030 (23)	5429 (32)	83 (16)					
				Cation 4					
N	−1482 (28)	764 (14)	1557 (21)	46 (9)	C_{4a}	−2134 (34)	675 (17)	2061 (25)	45 (11)
C_{1a}	−694 (32)	387 (16)	1672 (23)	42 (10)	C_{1b}	80 (34)	497 (17)	1125 (25)	49 (11)
C_{2a}	−901 (31)	1424 (16)	1643 (23)	39 (10)	C_{2b}	−60 (42)	1710 (22)	2265 (31)	77 (15)
C_{3a}	−2090 (35)	569 (17)	861 (26)	46 (11)	C_{3b}	−2970 (38)	855 (19)	761 (28)	57 (12)

Table I (*Continued*)

atom type[b]	fractional coordinates 10⁴x	10⁴y	10⁴z	10B,[c] Å²	atom type[b]	fractional coordinates 10⁴x	10⁴y	10⁴z	10B,[c] Å²
Cation 4									
C_{4b}	−2941 (35)	34 (18)	1935 (26)	54 (12)	C_{1d}	1521 (37)	−17 (19)	811 (27)	63 (13)
C_{1g}	830 (35)	27 (18)	1340 (26)	58 (12)	C_{2d}	1122 (55)	2678 (28)	2640 (40)	115 (22)
C_{2g}	159 (43)	2392 (21)	2182 (30)	71 (14)	C_{3d}	−4477 (41)	898 (21)	−103 (29)	74 (15)
C_{3g}	−3446 (41)	685 (21)	86 (31)	76 (15)	C_{4d}	−4102 (37)	−679 (19)	2421 (27)	64 (13)
C_{4g}	−3328 (37)	−54 (19)	2522 (28)	58 (12)					
Cation 5									
N	3134 (31)	−3763 (15)	1546 (22)	55 (10)	C_{1g}	2931 (51)	−4294 (26)	3149 (40)	111 (20)
C_{1a}	3220 (49)	−4152 (26)	2114 (36)	109 (20)	C_{2g}	5177 (44)	−2236 (22)	2383 (32)	88 (17)
C_{2a}	3643 (44)	−3076 (24)	1807 (33)	91 (17)	C_{3g}	676 (51)	−3704 (28)	487 (38)	109 (20)
C_{3a}	1991 (51)	−3844 (25)	1186 (36)	107 (19)	C_{4g}	3752 (73)	−4817 (41)	252 (60)	176 (33)
C_{4a}	3942 (42)	−3921 (21)	1085 (31)	77 (15)	C_{1d}	2309 (51)	−4224 (25)	3667 (37)	107 (20)
C_{1b}	2657 (37)	−3959 (20)	2617 (28)	67 (13)	C_{2d}	5939 (41)	−2072 (21)	2877 (30)	81 (15)
C_{2b}	4685 (42)	−2963 (22)	2170 (31)	84 (16)	C_{3d}	16 (64)	−4274 (35)	153 (46)	164 (30)
C_{3b}	1939 (41)	−3503 (20)	720 (28)	69 (14)	C_{4d}[d]	3187 (67)	−5327 (34)	−456 (50)	59 (22)
C_{4b}	3347 (56)	−4552 (30)	760 (44)	131 (25)	C'_{4d}[d]	3623 (88)	−4722 (45)	−494 (65)	94 (34)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figures 2 and 3. The naming scheme for atoms of **1** follows. Tungsten atoms within each NbW_5O_{19} unit are distinguished by numerical subscripts; W_1-W_4 are the "equatorial" metals and W_5 is the unique "axial" metal. Oxygen atoms are labeled with a subscripted A, B, D, E, F, G, or H depending on its structural type: A is the six-coordinate oxygen; B, D, and E are doubly bridging oxygens; F, G, and H are terminally bonded oxygens. Whenever necessary, oxygen atoms within a given structural type are distinguished from one another by a (second) numerical subscript: for B-, E-, and G-type oxygens this is the same as the numerical subscript of the "equatorial" W atom to which it is bonded. The following scheme is used for D-type oxygen atoms: O_{D1} bridges W_1 and W_2; O_{D2} bridges W_2 and W_3; O_{D3} bridges W_3 and W_4; O_{D4} bridges W_4 and W_1. Uranium and niobium atoms are represented by their atomic symbols. The two independent (NbW_5O_{19}) units are distinguished from each other by a (final) subscripted r or s and the three independent cyclopentadienyl ligands by a (final) subscripted t, u, or v. The carbon and hydrogen atoms within a given cyclopentadienyl ligand are distinguished from one another by numerical subscripts. [c] Equivalent isotropic thermal parameters. For the metal atoms, this is one-third of the trace of the orthogonalized B_{ij} tensor; for all remaining atoms, this is the refined value of the isotropic thermal parameter. [d] Terminal methyl carbon atoms C_{3d} of cation 1 and C_{4d} of cation 5 each appear to be statistically disordered between two sites; all 4 sites were included in the structure factor calculations as carbon atoms with occupancies of 0.50.

$(Nb_2W_4O_{19})\}^{2-}$ as a two diastereomer mixture from $\{[(CH_3)_5C_5]RhCl_2\}_2$ and $Nb_2W_4O_{19}{}^{4-}$ is assumed to involve an intermediate $\{[(CH_3)_5C_5]RhCl_2(Nb_2W_4O_{19})\}^{4-}$ anion[7] in which Rh^{III} binds only to ONb oxygens, not OW oxygens.

Solution Structures. The ^{17}O NMR spectra of **1**–**4** in CH_3CN solution are all consistent with the anion structure for **1** determined in the solid state (see Table VII and Figure 4). Resonances for terminal and doubly bridging oxygens not bonded to the actinide center are displaced downfield relative to the resonances for the free ligands, behavior expected for diamagnetic early transition-metal polyoxoanions.[6,7,23-26] For the dimagnetic thorium complexes, resonances for the doubly bridging OThNb and OThTa oxygens are observed at higher field than the ONb and OTa resonances, respectively, for the free ligands. This is also the expected behavior.[6,7,23-26] For the paramagnetic uranium complexes, no OUNb or OUTa resonances are observed. The failure to observe these resonances might arise from paramagnetic broadening, ^{17}O quadrupolar broadening, and/or spin–spin coupling to ^{93}Nb or ^{181}Ta.[9,27]

Oxygen-17 NMR spectra of **3** and **4** both display shoulders in the OW region having the same chemical shift values as the resonances for OW oxygens in the free $MW_5O_{19}{}^{3-}$ ligands. These shoulders could arise from (a) partial resolution of resonances assigned to the two types of OW oxygens in **3** and **4** labeled F and G in Figure 4a, (b) a reversible equilibrium established upon dissolution of **3** or **4** in CH_3CN (see eq 3), and/or (c) irreversible

$$[(C_5H_5)_3Ac(MW_5O_{19})_2]^{5-} + CH_3CN =$$
$$[(C_5H_5)_3Ac(MW_5O_{19})(NCCH_3)]^{2-} + MW_5O_{19}{}^{3-} \quad (3)$$

sample decomposition occurring during the ca. 5-h time elapsing between sample preparation and completion of ^{17}O NMR spectral measurements. When ^{93}Nb NMR spectra of compound **3** in CH_3CN are measured within 1 h of sample preparation, distinct resonances are observed for $[(C_5H_5)_3Th(NbW_5O_{19})_2]^{5-}$ at δ −943 (see Experimental Section) and free $NbW_5O_{19}{}^{3-}$ at δ −888 (see ref 9), thus ruling out possibility a. A choice cannot be made, however, between possibilities b and c because quantitative, time-dependent data are not available. Niobium-93 spectra of **3** in CH_3CN at 25 °C show a relatively sharp (ca. 700-Hz line width) $NbW_5O_{19}{}^{3-}$ resonance superposed upon a very broad (ca. 8200-Hz line width) $[(C_5H_5)_3Th(NbW_5O_{19})_2]^{5-}$ resonance, making integrated intensity measurements virtually meaningless. Proton NMR spectroscopy provided no useful information since only one C_5H_5 resonance is observed from CH_3CN solutions of **3** or **4** after ca. 5 h.

Solution Dynamics. When equimolar quantities of the thorium complexes **3** and **4** are dissolved in CH_3NO_2 at 25 °C, ^1H NMR spectra measured 30–360 min after sample preparation show three C_5H_5 resonances: one at δ 6.384, arising from $[(C_5H_5)_3Th(NbW_5O_{19})_2]^{5-}$; a second at δ 6.310 having equal intensity, arising from $[(C_5H_5)_3Th(TaW_5O_{19})_2]^{5-}$; and a third at δ 6.349 having twice the intensity of each of the other resonances.[28] The third

---

(24) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 3544.

(25) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1978**, *100*, 4891.

(26) Day, V. W.; Fredrich, M. F.; Thompson, M. R.; Klemperer, W. G.; Lui, R.-S.; Shum, W. *J. Am. Chem. Soc.* **1981**, *103*, 3597.

(27) Note that ^{93}Nb–^{17}O spin–spin coupling broadens the OThNb oxygens' ^{17}O NMR line width in **3**. Partial decoupling can be achieved by lowering the sample temperature: the 203-Hz line width observed at 25 °C narrows to 170 Hz at −15 °C (see Table VII and the Experimental Section).

(28) Analogous experiments using **1** and **2** yield similar results, but these are more ambiguous in a quantitative sense due the the broadness of the ^1H NMR resonances observed.

Table IV. Average Bond Lengths and Angles in the $(C_5H_5)_3U(NbW_5O_{19})_2^{5-}$ Anion of Crystalline $[(C_5H_5)_3U(NbW_5O_{19})_2][(n\text{-}C_4H_9)_4N]_5$ (1)[a]

parameter[b]	value	parameter[b]	value
	Lengths, Å		
U-C	2.76 (3, 4, 10, 15)	W_e-O_E[d]	1.93 (3, 3, 8, 8)
U-C_g[c]	2.49 (–, 1, 2, 3)	W_5-O_E	1.90 (3, 2, 5, 8)
U-O_F	2.36 (3, 1, 1, 2)	W_e-O_G[d]	1.68 (3, 2, 4, 8)
Nb-O_F	1.78 (3, 1, 1, 2)	W_5-O_H	1.66 (4, 3, 3, 2)
Nb-O_A	2.33 (4, 3, 3, 2)	$W_5\cdots W_e$[d]	3.301 (3, 8, 17, 8)
W_e-O_A[d]	2.33 (3, 4 6, 8)		
W_5-O_A	2.36 (3, 3, 3, 2)	$W_e\cdots W_e$[d]	3.289 (3, 5, 9, 8)
Nb-O_B	1.97 (3, 2 4, 8)	$Nb\cdots W_e$[d]	3.294 (5, 6, 12, 8)
W_e-O_B[d]	1.86 (3, 3, 9, 8)	$Nb\cdots U$	4.123 (5, 7, 7, 2)
W_e-O_D[d]	1.91 (3, 4, 13, 16)		
	Angles, deg		
$C_gUC'_g$[c]	120 (–, 2, 3, 3)	O_FUC_g[c]	90 (–, 2, 2, 6)
$O_{Fr}UO_{Fs}$	179.7 (5)	NbO_FU	172 (2, 2, 2, 2)

[a] The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value. [b] Atoms are labeled in agreement with Tables I and II and Figure 2. See footnote b of Table I. [c] C_g refers to the center-of-gravity for a given cyclopentadienyl ligand. [d] The "equatorial" tungsten atoms (W_1, W_2, W_3, and W_4) of each (NbW_5O_{19}) unit are collectively referred to as W_e atoms in this table.

resonance is assigned to the $[(C_5H_5)_3Th(NbW_5O_{19})(TaW_5O_{19})]^{5-}$ ion on the basis of its ^1H chemical shift value of δ 6.349, which closely approximates the δ 6.347 average of the other two resonances, and its intensity, which corresponds to that expected if equilibrium 4 is controlled by statistical factors alone.

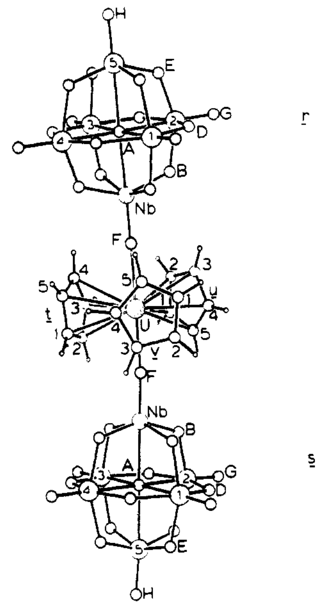


Figure 2. Perspective ORTEP drawing of the $[(C_5H_5)_3U(NbW_5O_{19})_2]^{5-}$ anion in crystalline 1. For purposes of clarity, metal atoms are represented by large open circles, oxygen and carbon atoms are represented by medium-sized circles, and hydrogen atoms are represented by small open circles. The two independent NbW_5O_{19} units are labeled r and s in the drawing. One oxygen atom of each C_{4v}-averaged structural type (A–H) is labeled in each unit. The tungsten atoms within each unit are labeled 1–5. The niobium and uranium atoms are labeled with their elemental symbols. The three independent cyclopentadienyl ligands are labeled t, u, and v in the drawing; their carbon atoms are labeled 1–5. Hydrogen atoms are not labeled.

$$[(C_5H_5)_3Th(NbW_5O_{19})_2]^{5-} + [(C_5H_5)_3Th(TaW_5O_{19})_2]^{5-} = 2[(C_5H_5)_3Th(NbW_5O_{19})(TaW_5O_{19})]^{5-} \quad (4)$$

The lability of the actinide–oxygen bond can also be probed by ^{17}O labeling experiments. When ^{17}O-enriched $TaW_5O_{19}^{3-}$ is mixed with unenriched 4 in a 2:1 mole ratio in CH_3CN, ^{17}O NMR spectra measured 2–3 h after sample preparation show resonances for both $TaW_5O_{19}^{3-}$ and $[(C_5H_5)_3Th(TaW_5O_{19})_2]^{5-}$, with resonances arising from free

Table VII. 33.9 MHz ^{17}O NMR Spectral Data for Compounds 1–4 and $(MW_5O_{19})[(n\text{-}C_4H_9)_4N]_3$, M = Nb and Ta at Ambient Temperatures in CH_3CN[a]

	chemical shifts,[b] line widths,[c] assignments[d]					
anion	OM	OW	OMAc	OMW	OW_2	OMW_5
$[(C_5H_5)_3U(NbW_5O_{19})_2]^{5-}$		743 (136)	e	463 (128)	397 (124)	−61 (58)
$[(C_5H_5)_3U(TaW_5O_{19})_2]^{5-}$		749 (165)	e	445 (117)	404 (167)	−47 (32)
$[(C_5H_5)_3Th(NbW_5O_{19})_2]^{2-}$		744 (181)	660 (203)	464 (116)	398 (164)	−70 (29)
$[(C_5H_5)_3Th(TaW_5O_{19})_2]^{5-}$		744 (171)	572 (41)	423 (104)	398 (161)	−76 (21)
$(NbW_5O_{19})^{3-}$	799 (88)	732, 730[f] (62)[g]		456 (23)	394, 392 (99)[g]	−67 (16)
$(TaW_5O_{19})^{3-}$	666 (122)	733 (78)		419 (45)	393 (82)	−75 (16)

[a] For compounds 1–4 spectral parameters are given in the Experimental Section. Data for $(NbW_5O_{19})[(n\text{-}C_4H_9)_4N]_3$ are taken from ref 9. The spectral data for $(TaW_5O_{19})[(n\text{-}C_4H_9)_4N]_3$ at 28 °C were measured from the ^{17}O-enriched sample described in ref 9, using precisely the same spectral parameters given there for the spectrum measured at 80 °C. [b] Positive chemical shifts in ppm downfield from fresh tap water at 25 °C. [c] In parentheses below chemical shift value, fwhm. [d] Each oxygen environment is identified by the number and type of metal atoms the oxygen is bonded to: M = Nb or Ta; Ac = U or Th. [e] Not observed. [f] Shoulder. [g] Combined line width of resonances listed measured at the half-height of the most intense resonance.

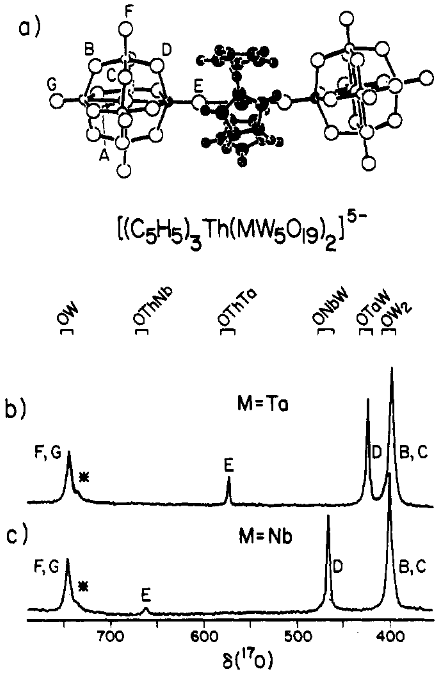


Figure 4. A SCHAKAL drawing of the anion of structure of 1 in the solid state is shown in a. One number of each set of symmetry-equivalent oxygen atoms in the NbW_5O_{19} ligand is labeled assuming local C_{4v} symmetry. The 33.9-MHz ^{17}O NMR spectra of the $[(C_5H_5)_3Th(TaW_5O_{19})_2]^{5-}$ and $[(C_5H_5)_3Th(NbW_5O_{19})_2]^{5-}$, as $[(n\text{-}C_4H_9)_4N]^+$ salts in CH_3CN at 25 °C, are shown in b and c, respectively. In each spectrum, only the δ 350–800 region is shown. Resonances are assigned by using the labeling scheme given in a. See Table VII for numerical data and the Experimental Section for spectral parameters. The asterisks in b and c label shoulders in the OW region that arise from free $MW_5O_{19}^{3-}$ ligands (see text).

and bound $TaW_5O_{19}^{3-}$ having approximately equal intensities. This result shows that polyoxoanion ligand exchange according to eq 5 is a facile process, a result that

$$2(TaW_5O_{19}{}^*)^{3-} + [(C_5H_5)_3Th(TaW_5O_{19})_2]^{5-} = (TaW_5O_{19}{}^*)^{3-} + (TaW_5O_{19})^{3-} + [(C_5H_5)_3Th(TaW_5O_{19})(TaW_5O_{19}{}^*)]^{5-} = 2(TaW_5O_{19})^{3-} + [(C_5H_5)_3Th(TaW_5O_{19}{}^*)_2]^{5-} \quad (5)$$

is not surprising in light of the ease with which eq 4 proceeds. More important, however, this result shows that eq 5, and by inference eq 4, proceeds with cleavage of Th–O bonds, not Ta–O bonds, since the equilibrium solution displays OThTa and OTa ^{17}O NMR resonances having approximately equal intensities.

The lability of thorium(IV)–polyoxoanion bonds in 3 and 4 stands in marked contrast with the kinetic stability of rhodium(III)–polyoxoanion bonds in $\{[(CH_3)_5C_5]Rh(\kappa^3O\text{-}Nb_2W_4O_{19})\}^{2-}$.[6] Four different factors might contribute to this lability. First, the thorium coordination spheres in 3 and 4 are very crowded (see above) and the implied ligand–ligand repulsion is undoubtedly significant. Second, the $MW_5O_{19}^{3-}$ ligands in 3 and 4 bind to thorium using terminal, not bridging, oxygens. There is reason to believe that bridging oxygens in niobotungstates are more basic than terminal oxygens and that binding to bridging oxygens is therefore preferred in the absence of steric effects.[29] Third, the $MW_5O_{19}^{3-}$ ligands in 3 and 4 are monodentate, not tridentate as in the rhodium complex: metal–ligand dissociation involves breaking only one metal–oxygen bond, not three metal–oxygen bonds. Finally, the $NbW_5O_{19}^{3-}$ ion is almost certainly less basic than the $Nb_2W_4O_{19}^{4-}$ ion since it carries less negative charge.

Acknowledgment. W.G.K. acknowledges the National Science Foundation for support of this research. NMR experiments were conducted at the University of Illinois Regional NMR Facility (Grant CHE 79-16100). We are grateful to Dr. Egbert Keller for providing a copy of his SCHAKAL program.

Supplementary Material Available: Crystal structure analysis report, Table II (anisotropic thermal parameters for metal atoms in 1), Table III (idealized atomic coordinates for cyclopentadienyl hydrogen atoms in 1), Table V (detailed bond lengths and angles in the anion of 1), Table VI (bond lengths and angles in cations of 1), Figure 3 (ORTEP drawings for cations of 1), and structure factor tables for the X-ray structural study of 1 (53 pages). Ordering information is given on any current masthead page.

---

(29) Klemperer, W. G.; Schwartz, C., manuscript in preparation.