

Although the solid-state results (Figure 1) indicate a η^3 interaction of the two RhP_2 fragments with the *cis*- C_4H_6 moiety, both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts of **3** are more consistent with typical η^4 *cis*-1,3-butadiene complexes¹⁶ than with η^3 allyl derivatives; in Table I, a comparison of the chemical shifts of **3** vs. the corresponding shifts in the *anti*-1-methylallyl isomer **4** clearly shows dramatic differences in the ^1H NMR (i.e., H_a in **3** vs. H_a in **4**) and the $^{13}\text{C}\{^1\text{H}\}$ NMR (i.e., C_2 in **3** vs. C_2 in **4**).

Further studies will be aimed at the rational syntheses of other complexes that contain this novel structural unit; in addition, we are continuing to probe the mechanism by which **3** is generated in an effort to understand the pronounced influence of the chelate ring size¹⁷ on the course of the reaction of 1,3-butadiene with binuclear rhodium hydrides.

Acknowledgment. Financial support was provided by NSERC and the Alfred P. Sloan Foundation. We also thank Professor James Trotter for the use of the diffractometer and computer programs for structure solution. Johnson-Matthey is also acknowledged for the generous loan of RhCl_3 .

Supplementary Material Available: Tables of final positional and isotropic thermal parameters, calculated hydrogen coordinates and isotropic thermal parameters, final anisotropic thermal parameters, bond lengths, and bond angles (5 pages). Ordering information is given on any current masthead page.

(16) See Table III in: Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics* **1982**, *1*, 388 (for ^1H NMR). Retcofsky, H. L.; Frankel, E. N.; Gutowsky, H. S. *J. Am. Chem. Soc.* **1966**, *88*, 2710 (for ^{13}C NMR).

(17) Otsuka, S. *J. Organomet. Chem.* **1980**, *200*, 191.

Synthesis, Structure, and Reactivity of the $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{U}]_2(\mu\text{-}\kappa^2\text{-O-TiW}_5\text{O}_{19})_2\}^{4-}$ Anion

V. W. Day,*^{1a} C. W. Earley,^{1b} W. G. Klemperer,*^{1b} and D. J. Maltbie^{1b}

Crystallitics Co., Lincoln, Nebraska 68501
Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588
Department of Chemistry, University of Illinois
Urbana, Illinois 61801

Received June 27, 1985

If polyoxoanion-supported organometallic complexes are to become involved in organometallic reaction chemistry, the balance between metal-carbon and metal-oxygen bond strengths at the organometallic center must be such that metal-oxygen bonds can withstand conditions under which metal-carbon bonds are broken and reformed. Polyoxoanion-supported organoactinides offer such a possibility,² but compounds of this type like $[(\eta^5\text{-C}_5\text{H}_5)_3\text{U}(\kappa^1\text{-O-NbW}_5\text{O}_{19})_2]^{5-}$ (**1**)² and $[(\eta^5\text{-C}_5\text{H}_5)_3\text{U}(\kappa^1\text{-O-NbW}_5\text{O}_{19})]^{2-}$ (**2**)³ have been disappointing from this point of view on account of the ease with which the organometallic unit dissociates from its polyoxoanion ligand.² Since this lability arises in part from the unidentate polyoxoanion binding mode in **1** and **2**, we sought to prepare analogous compounds containing tridentate polyoxoanion ligands. To this end, we prepared $\text{CITiW}_5\text{O}_{18}^{3-}$ (**3**), a potential tridentate ligand,⁴ from TiCl_4 plus WO_4^{2-} and reacted

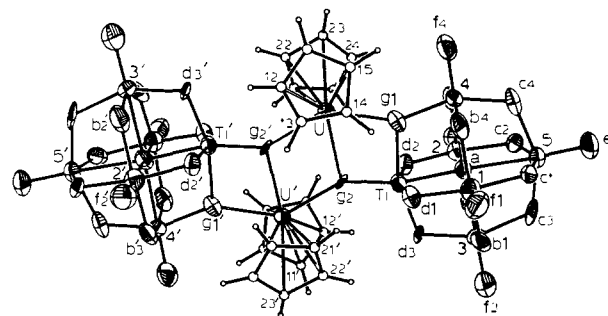


Figure 1. Perspective drawing of the solid-state structure for the $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{U}]_2(\mu\text{-}\kappa^2\text{-O-TiW}_5\text{O}_{19})_2\}^{4-}$ anion (**4**), as observed in the form of acetonitrile-solvated crystals of its $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ salt. Metal and oxygen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Carbon atoms are represented by large open circles and hydrogen atoms by small open circles. Uranium and titanium atoms are labeled with their atomic symbols while tungsten atoms are labeled with numbers. Oxygen atoms are labeled with letters and numbers. Atoms labeled with a prime are related to those labeled without a prime by the crystallographic inversion center at $(1/2, 0, 0)$ in the unit cell.

it with $(\text{C}_5\text{H}_5)_3\text{UCl}$ in an attempt to form $[(\eta^5\text{-C}_5\text{H}_5)_3\text{U}(\kappa^3\text{-O-CITiW}_5\text{O}_{18})]^{2-}$. Instead of the expected adduct, however, we isolated a more complex product in 30% yield having the empirical formula $[(\text{C}_5\text{H}_5)_2\text{U}(\text{TiW}_5\text{O}_{19})]^{2-}$. In contrast to **1** and **2**, this anion is quite stable and is not readily attacked by electrophilic and weakly nucleophilic reagents such as H_2O , $\text{CH}_3\text{CH}_2\text{OH}$, $(\text{C}_5\text{H}_5)_2\text{CHNO}_2$, and CH_3CN .⁵

X-ray structural analysis⁶ of crystalline $(\text{C}_5\text{H}_5)_2\text{U}(\text{TiW}_5\text{O}_{19})[(\text{C}_4\text{H}_9)_4\text{N}]_2$, obtained from CH_3CN solution, revealed the presence of discrete $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ cations, acetonitrile molecules of crystallization, and $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{U}]_2(\mu\text{-}\kappa^2\text{-O-TiW}_5\text{O}_{19})_2\}^{4-}$ anions, **4**, shown in Figure 1, in which two $\text{TiW}_5\text{O}_{19}^{4-}$ polyoxoanions are bridged by two "bent sandwich" $(\text{C}_5\text{H}_5)_2\text{U}^{2+}$ units. Although the preferred coordination number is usually 10-12 when two or more C_5H_5^- ligands η^5 -bond to a single actinide ion,⁸ the U(IV) centers in **4** are both formally nine-coordinate by being η^5 -bonded to two C_5H_5^- groups and σ -bonded to three polyoxoanion oxygen atoms. Similar coordination geometries have been observed in several organoactinide systems, but these complexes usually employ the sterically bulky $(\text{CH}_3)_5\text{C}_5^-$ ligand.⁸ The manner in which the $(\text{C}_5\text{H}_5)_2\text{U}^{2+}$ units are linked in **4** bears a close resemblance to the linkage of the same units by $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH})(\text{CH}_2)^{2-}$ ligands in $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{U}]_2[\mu\text{-}\eta^2\text{-}(\text{C}_6\text{H}_5)_2\text{P}(\text{CH})(\text{CH}_2)]_2\}^{2-}$,⁹ where the three oxygen atoms of **4** have been replaced by sterically bulkier carbon atoms, and the linkage of $(\text{C}_5\text{H}_5)_2\text{Ti}$ units by $(\text{C}_6\text{H}_5)_2\text{C}_2\text{O}$ ligands in $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}]_2[\mu\text{-}\eta^2\text{-}(\text{C}_6\text{H}_5)_2\text{C}_2\text{O}]_2\}^{2-}$,¹⁰ where the large U(IV) center of **4** has been replaced by the smaller Ti(IV) center. Presumably, the stability of the observed U(IV) coordination geometry in **4** can be attributed in part to the steric bulk of the $\text{TiW}_5\text{O}_{19}^{4-}$ ligands that effectively block off a substantial portion

(5) According to ^1H NMR spectroscopy, solutions of the title anion in CH_3CN as a $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ salt show <10% decomposition after 2-h exposure to 10 equiv of water or $\text{CH}_3\text{CH}_2\text{OH}$ in air. The anion similarly fails to react significantly with 10 equiv of $(\text{CH}_3)_2\text{CHNO}_2$ in CH_3CN under N_2 after 5 days at ambient temperature.

(6) Single crystals of $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{U}]_2(\mu\text{-}\kappa^2\text{-O-TiW}_5\text{O}_{19})_2\}[(\text{C}_4\text{H}_9)_4\text{N}]_4 \cdot 4\text{CH}_3\text{CN}$ are at $20 \pm 1^\circ\text{C}$ triclinic, space group $P\bar{1}C_1$ (No. 2), with $a = 12.903(3)$ Å, $b = 15.604(5)$ Å, $c = 19.199(5)$ Å, $\alpha = 115.04(2)^\circ$, $\beta = 88.96(2)^\circ$, $\gamma = 108.33(2)^\circ$, and $Z = 1$ dimeric unit [$d_{\text{calcd}} = 2.224$ g cm^{-3} ; $\mu_{\text{a}}(\text{Mo K}\alpha) = 11.38$ mm $^{-1}$]. A structural model which utilized anisotropic thermal parameters for all anionic U, W, Ti, and O atoms as well as all cationic and solvent N and C atoms and isotropic thermal parameters for all cyclopentadienyl C and H atoms has been refined to convergence⁷ [$R(\text{unweighted, based on } F) = 0.058$ for 6477 independent absorption-corrected reflections having $2\theta_{\text{Mo K}\alpha} < 48.3^\circ$ and $I > 3\sigma(I)$] using counting statistics weighted cascade block diagonal least-squares techniques. Two carbons in the cations were not located.⁷

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

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

(9) Cramer, R. E.; Maynard, R. B.; Gilje, J. W. *Inorg. Chem.* **1981**, *20*, 2466.

(10) Fachinetti, G.; Biran C.; Floriani, C.; Villa, A. C.; Guastini, C. *Inorg. Chem.* **1978**, *17*, 2995.

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

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

(3) Klemperer, W. G.; Maltbie, D. J., manuscript in preparation.

(4) Cf. $\text{C}_5\text{H}_5\text{TiMo}_5\text{O}_{18}^{3-}$ as a $\kappa^3\text{O}$ ligand in $[(\kappa^3\text{O-C}_5\text{H}_5\text{TiMo}_5\text{O}_{18})\text{Mn}(\text{CO})_2]^{2-}$ and $[(\kappa^3\text{O-C}_5\text{H}_5\text{TiMo}_5\text{O}_{18})\text{MoO}_2\text{Cl}]^{2-}$: Day, V. W.; Fredrich, M. F.; Thompson, M. R.; Klemperer, W. G.; Liu, R.-S.; Shum, W. *J. Am. Chem. Soc.* **1981**, *103*, 3597.

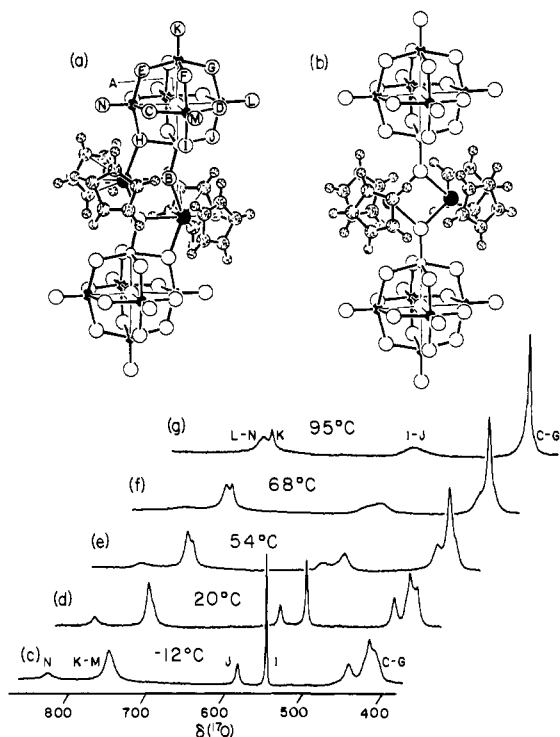
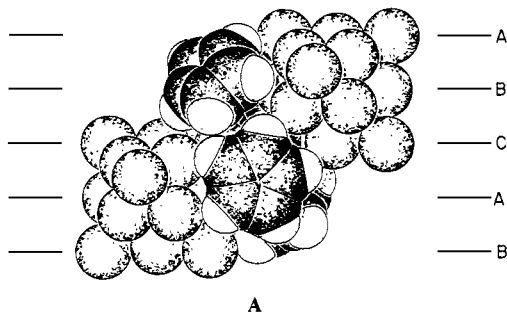


Figure 2. SCHAKAL drawings of (a) anion **4** as observed in the solid-state X-ray crystallographically and (b) anion **4** in the coordinatively unsaturated configuration proposed as an intermediate during rearrangement (see text). Oxygen atoms are represented by large open circles, uranium atoms by large filled circles, carbon atoms by large shaded circles, titanium atoms by small open circles, tungsten atoms by small filled circles, and hydrogen atoms by small shaded circles. One member of each symmetry-equivalent set of oxygen atoms is labeled in (a). Variable-temperature 33.9-MHz ^{17}O NMR spectra of anion **4** as a $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ salt in CH_3CN are shown in (c)–(g). Only the 375–875 ppm region is included; i.e., the O_A resonance is not shown.

of the U(IV) coordination sphere. The space-filling model of anion **4** shown in A illustrates the nonbonding interactions contributing



to this stability. The four C_5H_5 rings are packed tightly around a cubic-close-packed array of 38 oxygens, protecting the uranium centers from the anion's environment. Bonding interactions also play a key role in stabilizing the U(IV) coordination sphere in **4**. Specifically, the stability of anion **4** relative to $[(\eta^5\text{-C}_5\text{H}_5)_3\text{U}(\kappa^1\text{O-NbW}_5\text{O}_{19})_2]^{5-}$ (**1**) and $[(\eta^5\text{-C}_5\text{H}_5)_3\text{U}(\kappa^1\text{O-NbW}_5\text{O}_{19})]^{2-}$ (**2**) can be explained in terms of the chelate effect in **4** and the greater basicity of an OTi^{IV} terminal oxygen in $\text{TiW}_5\text{O}_{19}^{4-}$ relative to an ONb^{V} terminal oxygen in $\text{NbW}_5\text{O}_{19}^{3-}$.

The title anion, although relatively inert toward electrophiles and weak nucleophiles,⁵ is rapidly degraded by strong nucleophiles such as OH^- and $(\text{C}_2\text{H}_5)_2\text{NH}$. Since $\text{TiW}_5\text{O}_{19}^{4-}$ is stable toward these reagents under the same conditions, the site of attack is most likely the uranium center. The avenue of approach to uranium in **4** (see A) is too restricted, however, and nucleophilic attack must therefore be accompanied by structural rearrangement. A plausible mode of rearrangement can be derived from variable-temperature ^{17}O NMR spectra shown in Figure 2c–g. At low

temperatures, ^{17}O NMR resonances can be assigned to oxygens in **4** by using well-established chemical shift scales,¹¹ assuming that resonances from oxygens bonded to uranium are too broad to be observed, as is the case with **1**² and **2**.³ Spectra measured at elevated temperatures are relatively simple and correspond to the resonances expected for a C_{4v} $\text{TiW}_5\text{O}_{19}^{4-}$ ligand. Such effective ligand symmetry can be obtained for $\text{TiW}_5\text{O}_{19}^{4-}$ in **4** by cleaving both¹² U– O_{g1} bonds (U– O_{g1} in Figure 1a), and symmetrizing the entire structure to the D_{2h} configuration shown in Figure 2b. Assuming rapid rotation about the Ti– O_{U2} bond in this coordinatively unsaturated intermediate configuration, the $\text{TiW}_5\text{O}_{19}^{4-}$ ligand achieves effective C_{4v} symmetry on the NMR time scale.

Acknowledgment. We acknowledge the National Science Foundation for support of this research and are grateful to Dr. Egbert Keller for providing a copy of his SCHAKAL program.

Registry No. **2**, 99127-88-5; **3**, 99127-89-6; **4**, 99112-31-9; $4\text{CH}_3\text{CN}$, 99127-87-4; TiCl_4 , 7550-45-0; WO_4^{2-} , 14311-52-5; $(\text{C}_5\text{H}_5)_3\text{VCl}$, 1284-81-7.

Supplementary Material Available: Crystal structure analysis report, Table I (fractional atomic coordinates and isotropic thermal parameters for non-hydrogen atoms), Table II (anisotropic thermal parameters), Table III (fractional coordinates for hydrogen atoms), Table IV (bond lengths for the anion), Table V (bond angles for the anion), Table VI (bond lengths and angles for the cations), Table VII (bond lengths and angles for CH_3CN molecules of crystallization), Figure 3 (perspective drawings of cations), Figure 4 (perspective drawings of CH_3CN molecules of crystallization), and structure factor tables for the crystal structure analysis of $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{U}]_2(\mu\text{-}\kappa^2\text{O-TiW}_5\text{O}_{19})_2\}[(n\text{-C}_4\text{H}_9)_4\text{N}]_4 \cdot 4\text{CH}_3\text{CN}$ (53 pages). Ordering information is given on any current masthead page.

(11) (a) Filowitz, M.; Ho, R. K. C.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93. (b) Che, T. M.; Day, V. W.; Francesconi, L. C.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *Inorg. Chem.*, in press.

(12) Although cleavage of a single U– O_{WTi} bond is a reasonable alternative, we consider it less likely than a concerted process since it leads to short $\text{C}_5\text{H}_5 \cdots \text{OTiW}$ contacts. Specifically, the $\text{TiW}_5\text{O}_{19}^{4-}$ reorientation accompanying U– O_{g1} cleavage (see Figure 1a) implies close $\text{C}_5\text{H}_5 \cdots \text{O}_{g3}$ contacts at the other uranium center.

Molecular Building Blocks for the Synthesis of Ceramic Materials: $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$

V. W. Day,*^{1a} W. G. Klemperer,*^{1b} V. V. Mainz,^{1b} and D. M. Millar^{1b}

Crystalytics Co., Lincoln, Nebraska 68501
Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588
Department of Chemistry and Materials Research
Laboratory, University of Illinois
Urbana, Illinois 61801

Received June 24, 1985

Ceramic materials have traditionally been prepared from structurally simple starting materials. As a result, their structural features are relatively difficult to control or modify in a systematic fashion. Many polymeric organic and organometallic materials, on the other hand, can be designed and synthesized in a more controlled fashion by proceeding in a stepwise manner, i.e., by first preparing tailor-made molecular building blocks and then polymerizing these monomers in a subsequent reaction step. Any attempt to extend this building-block approach to the synthesis of ceramic materials must begin with the preparation of suitable

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