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Simplified Preparations and Electrochemical Behavior of Two Chromium-Substituted Heteropolytungstate Anions

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Simplified preparative procedures are described for the generation of α-$[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-}$ and α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ anions which can be readily oxidized, chemically or electrochemically, to α-$[PW_{11}O_{39}Cr^{V}O]^{4-}$ and α_2-$[P_2W_{17}O_{61}Cr^{V}O]^{7-}$. The oxidized complexes are stable in aqueous solutions. They react with benzyl or ethyl alcohol, but the rates of the oxidations are too slow to make the Cr(V) derivatives attractive as electrocatalysts. The voltammetry of the Cr^{V}/Cr^{III} couples is only quasi-reversible, but approximate formal potentials with their pH dependencies are reported. Diffusion coefficients evaluated for the polyanions show the larger anion to diffuse more slowly and neither anion to be highly hydrated.

Transition metal-substituted heteropolymetalates[1] exhibit chemical and electrochemical properties which make them attractive for catalytic and electrocatalytic applications.[2–5] These attractive features include stability under highly oxidizing conditions, availability of a variety of transition metal cations which can be incorporated into the heteropolymetalate structure,[6] reversible reduction and oxidation of incorporated transition metals, sometimes with multiple-electron transfers involved, and the ability to modify the formal potentials of the redox processes by altering the identity of the heteroion placed at the center of the heteropolymetalate structure. In previous publications from this laboratory electrochemical and catalytic investigations of iron-substituted heteropolytungstates were described.[2] The present report contains the results of an extension of these studies to two chromium(III)-substituted heteropolytungstates.

The preparation of $[SiW_{11}O_{39}Cr^{III}(OH_2)]^{5-}$ and its chemical oxidation to the corresponding Cr(V) derivative was first described in a brief report,[3b] and Cr(III)-substituted derivatives of other heteropolymetalates have been prepared.[7,8] After this report was submitted, a description of the preparation and oxo-transfer reactivity of α-$[PW_{11}O_{39}Cr^{V}O]^{4-}$ appeared.[4c] However, no detailed electrochemical studies of any of these complexes have appeared. Simple, facile preparations for α-$[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-}$, α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$, and their Cr(V) counterparts are given in this report along with electrochemical characterization of these complexes.

Experimental Section

Materials. The lacunary polytungstate α-$K_7[PW_{11}O_{39}]\cdot nH_2O$ was prepared as described in ref 9 for the corresponding silicotungstate. The value of n was measured as 15 from weight loss in a vacuum oven at 170 °C. The lacunary α_2-$K_{10}[P_2W_{17}O_{61}]\cdot 15H_2O$ was prepared according to the procedure in ref 5a. The chromium-substituted derivatives were prepared as follows:

α-$K_4[PW_{11}O_{39}Cr^{III}(OH_2)]$ (1). To 30 mL of a solution containing 0.80 g of $Cr(NO_3)_3\cdot 9H_2O$ was added 6.40 g of α-$K_7[PW_{11}O_{39}]\cdot 15H_2O$. The mixture was stirred and heated gently in a mineral oil bath to dissolve the lacunary salt. The temperature was then increased to the boiling point, and the solution was refluxed for 1 h. The color of the solution changed from blue-violet to dark green. The solution volume was decreased to 5–6 mL by rotary evaporation at 50 °C, and 1.0 g of KCl was added to the concentrated solution. The resulting precipitate was collected, recrystallized from a minimum volume of warm water (it was very soluble), and air-dried. UV–vis: λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 642 (23). Its water content was determined by weight loss in a vacuum oven at 170 °C. Anal. Calcd for α-$K_4[PW_{11}O_{39}Cr^{III}(OH_2)]\cdot 11H_2O$: K, 5.04; H_2O, 6.97; Cr, 1.68. Found: K, 4.86; H_2O, 7.08; Cr, 1.69.

α_2-$K_7[P_2W_{17}O_{61}Cr^{III}(OH_2)]$ (2). To 10 mL of a solution containing 0.40 g of $Cr(NO_3)_3\cdot 9H_2O$ and maintained at 40–60 °C was added gradually 4.84 g of solid α_2-$K_{10}[P_2W_{17}O_{61}]\cdot 15H_2O$. After most of the solid had dissolved, the solution was heated to boiling in a mineral oil bath and refluxed for 1 h. The blue-violet color of the solution changed to dark brown during the heating. The solution was cooled to room temperature and filtered to remove a small amount of green precipitate. To the filtrate was added 1.5 g of KCl, and the resulting dark precipitate was collected and purified as described for **1**. UV–vis: λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 628 (48). Anal. Calcd for α_2-$K_7[P_2W_{17}O_{61}Cr^{III}(OH_2)]\cdot 19H_2O$: K, 5.65; H_2O, 7.42; Cr, 1.07. Found: K, 5.59; H_2O, 7.24; Cr, 1.10.

α-$[(C_2H_5)_4N]_4[PW_{11}O_{39}Cr^{III}(OH_2)]$. A 0.062-g sample of **1** dissolved in 5 mL of 0.5 M $NaHSO_4$ (pH = 1) was added to 0.0184 g of $(C_2H_5)_4NClO_4$ dissolved in 2 mL of H_2O. The resulting precipitate was filtered, washed with water, and dried at 50 °C under vacuum. Anal. Calcd for α-$[(C_2H_5)_4N]_4[PW_{11}O_{39}Cr^{III}(OH_2)]$: C, 11.75; H, 2.45; N, 1.71; Cr, 1.59. Found: C, 11.55; H, 2.43; N, 1.58; Cr, 1.60.

α_2-$[(C_2H_5)_4N]_{6.3}H_{0.7}[P_2W_{17}O_{61}Cr^{V}O]$. Electrochemical Oxidation. A 0.0485-g sample of **2** dissolved in 10 mL of 0.5 M $NaHSO_4$ adjusted to pH 1 was electrooxidized at +1.35 V at a platinum gauze electrode in a two-compartment electrochemical cell until 2–2.5 equiv of anodic charge had passed, which typically required 2–3 h. UV–vis: λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 564 (57). A 0.032-g quantity of $(C_2H_5)_4NClO_4$ dissolved in a few

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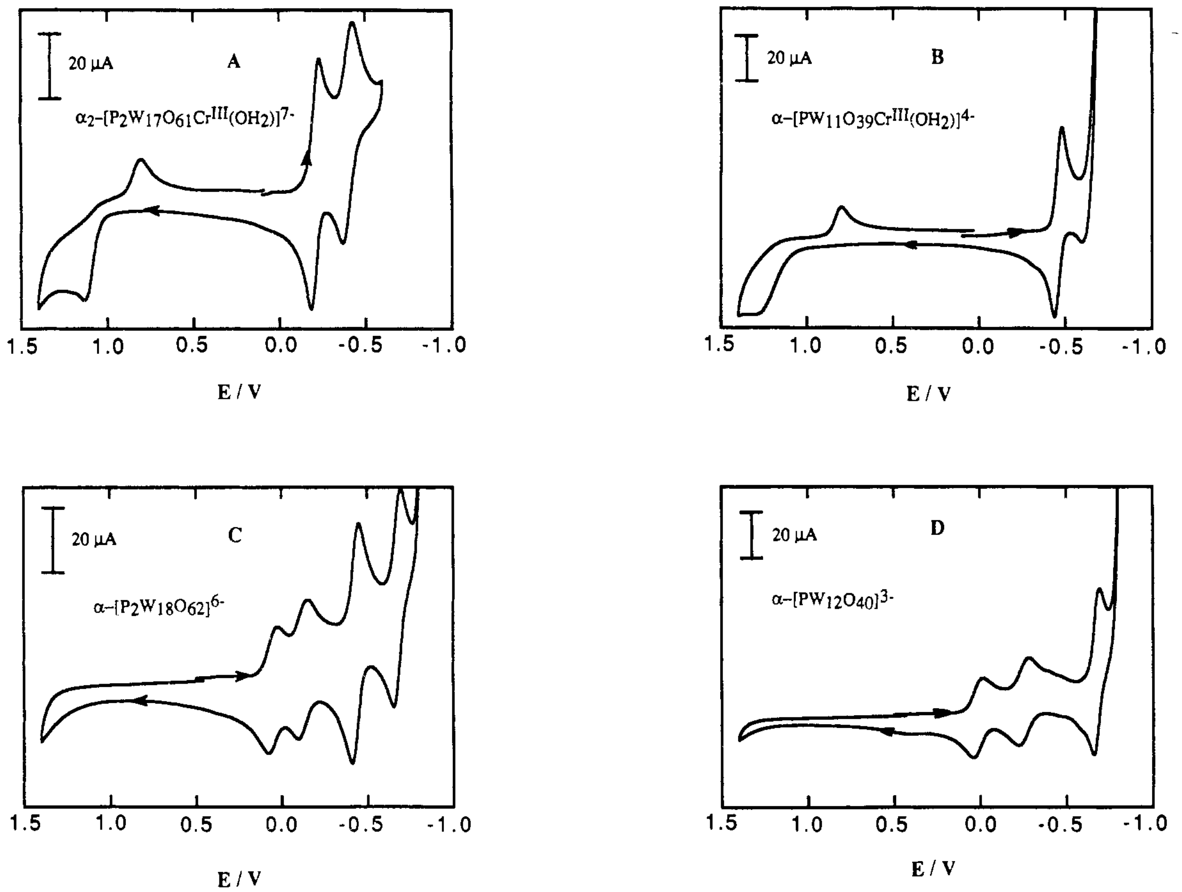

Figure 1. Cyclic voltammograms at a pyrolytic graphite electrode for 1 mM solutions of two heteropolytungstates and their Cr(III)-substituted derivatives. Supporting electrolyte: 0.5 M $NaHSO_4$ adjusted to pH 1.0. Scan rate = 10 mV s^{-1}. The initial potential was 0.1 V for A and B and 0.5 V for C and D, and the initial scan direction was toward more negative potentials.

milliliters of H_2O was added to the electrolyzed solution. The yellow precipitate which formed was collected, washed with water, and dried under vacuum.

Chemical Oxidation. A 0.097 g sample of **2** was dissolved in 5 mL of 0.5 M $NaHSO_4$ adjusted to pH = 1, and 0.0022 g of $KMnO_4$ was added. The mixture was heated to boiling for a few minutes, which produced a precipitate of MnO_2. After the solution was cooled to room temperature, the MnO_2 was removed by filtration, and 0.065 g of $(C_2H_5)_4NClO_4$ dissolved in 5 mL of H_2O was added to the filtrate. The precipitate which resulted was collected, washed with water, and dried under vacuum. Anal. Calcd for α_2-$[(C_2H_5)_4N]_{6.3}H_{0.7}[P_2W_{17}O_{61}Cr^{V}O]$: C, 11.98; H, 2.50; N, 1.75; Cr, 1.02. Found: C, 12.14; H, 2.48; N, 1.70; Cr, 0.94.

Titration of a sample of the solid with standard base demonstrated the presence of 0.67 mol of H^+ per formula mass of 5050 Da, consistent with the indicated composition of the salt. Similar nonstoichiometric mixed tetraalkylammonium–proton salts of transition metal-substituted Dawson anions have been described by Finke and co-workers.[5a]

α-$[(C_2H_5)_4N]_4[PW_{11}O_{39}Cr^{V}O]$. When complex **1** was subjected to the same two procedures, a stoichiometric oxidized product resulted. UV–vis: λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 556 (24). Anal. Calcd for $[(C_2H_5)N_4]_4[PW_{11}O_{39}Cr^{V}O]$: C, 11.76; H, 2.45; N, 1.72; Cr, 1.59. Found: C, 11.95; H, 2.54; N, 1.80; Cr, 1.58.

Apparatus and Procedure. Electrochemical measurements were conducted with conventional commercially available instrumentation using two-compartment cells with edge-plane pyrolytic graphite working electrodes, platinum wire counter electrodes, and a Ag/AgCl reference electrode. The 0.34-cm^2 graphite electrode was polished with 0.3-μm alumina, followed by sonication for 3 min in purified water before each run. Controlled-potential electrolyses were carried out with a platinum gauze working electrode with the reference electrode separated from the main cell compartment by a double junction. Buffer solutions were prepared from 0.5 M HSO_4^- (pH 1–3), 0.5 M CH_3COO^- (pH 4–6), 0.25 M HPO_4^{2-} (pH 7–8), and 0.1 M borate (pH 9). All potentials are quoted with respect to a Ag/AgCl (3 M NaCl) reference electrode which had a potential 26 mV less positive than a saturated calomel electrode.

A Hewlett-Packard (Model 8450A) spectrophotometer was used to record visible spectra. The kinetics of the homogeneous oxidation of benzyl alcohol were followed at 420 nm. Iodometric titrations followed conventional methods. Chromium was determined as CrO_4^{2-} from spectrophotometric measurements at 370 nm after oxidative decomposition of the polyanion by heating in 3 M NaOH for 30 min, followed by oxidation with H_2O_2. Potassium analyses were obtained by atomic absorption spectroscopy using a Perkin-Elmer (Model 3100) instrument. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer with samples prepared in KBr pellets. ^{31}P NMR spectra were obtained on a Bruker AM500 NMR spectrometer. EPR spectra were recorded on a Varian E-line Century Series X-band spectrometer at ambient temperature with solid samples.

Results and Discussion

Voltammetry of α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ and α-$[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-}$. Cyclic voltammograms recorded with pyrolytic graphite electrodes in solutions of α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ or α-$[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-}$ are shown in Figure 1. At pH 1 a pair of sharp, reversible peaks is obtained between 0 and −800 mV (Figure 1A,B). The second reduction peak for the α-$[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-}$ anion is superimposed on the cathodic background current. These responses are similar to the final reduction peaks exhibited by the parent anions, α_2-$[P_2W_{18}O_{62}]^{6-}$ and α-$[PW_{12}O_{40}]^{3-}$ (Figure 1C,D). They correspond to two-electron reductions and reoxidations of the tungsten–oxo cage.[10] The fact that the magnitudes of the pair of cathodic peaks are no larger for the Cr(III) derivatives than for the parent anions shows that the Cr(III) center incorporated in the heteropolyanion is not reducible to Cr(II) within the potential range examined in Figure 1. Even when a hanging mercury drop electrode was employed to allow more negative potentials to be explored before the evolution of hydrogen, no evidence for the reduction of the Cr(III) center was encountered.

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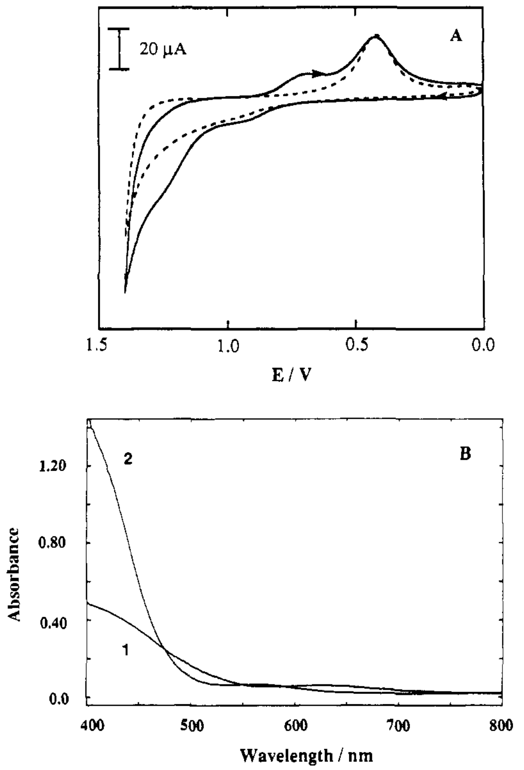

Figure 2. (A) Cyclic voltammograms: (—) for 1.0 mM α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ recorded at a 0.46-cm^2 platinum disk electrode (other conditions as in Figure 1A); (- - -) for the platinum electrode recorded in pure supporting electrolyte (0.5 M $NaHSO_4$). (B) Absorption spectra: (curve 1) spectrum of a 1.0 mM solution of α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ before electrolysis; (curve 2) spectrum after electrolysis of the solution for 2.5 h at a platinum gauze electrode maintained at 1.35 V.

The Cr(III) center in the α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ and α-$[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-}$ anions is responsible for the voltammetric peaks between 700 and 1200 mV in Figure 1A,B. These peaks are not present in voltammograms for the parent, unsubstituted, anions (Figure 1C,D). The separation between the anodic and cathodic peaks varied between 300 and 500 mV (depending on the pH) while the corresponding separation for the peaks between 0 and −800 mV was much smaller, typically 60–100 mV. The quasi-reversibility of the chromium-based peaks prevented the use of their peak currents to estimate the number of electrons involved in the half-reactions by comparison with the magnitude of the first reversible, two-electron, cathodic peak current in the same voltammograms. Instead, controlled-potential electrolyses were carried out to determine the number of electrons involved in the oxidation of the Cr(III) center.

Controlled-Potential Electrolyses. The electrooxidation of α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2]^{7-}$ proceeded at a large platinum gauze electrode maintained at potentials between 1.25 and 1.6 V. The cyclic voltammogram in Figure 2A, recorded at a small platinum disk electrode, shows that the oxidation of the heteropolyanion occurs at potentials where the platinum surface is also oxidized (the cathodic peak at 0.4 V arises from the reduction of platinum oxide, which is formed at potentials positive of 1.0 V). The inhibiting effect of the oxide on the surface of the platinum gauze electrode caused the controlled-potential oxidation to proceed rather slowly at well below the diffusion-convection-controlled rate. The progress of the electrolysis was monitored by removing aliquots of the electrolysis solution to record UV–vis absorption spectra. Spectra of the original solution and that obtained after electrooxidation at 1.35 V are shown in Figure 2B. The change in absorbance at 420 nm provided a measure of the extent of oxidation of the complex. The anodic charge consumed in the electrolysis at 1.35 V at the point where no further spectral changes occurred corresponded to between two and three electrons per molecule of complex, but this value included significant contributions from anodic background reactions for which no correction was attempted.

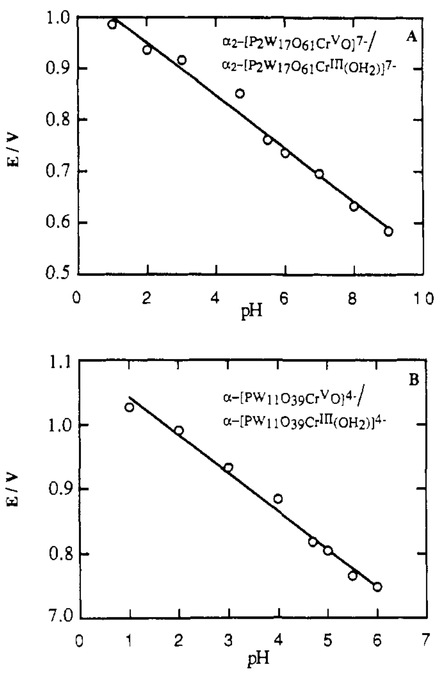

Figure 3. pH dependence of the approximate formal potentials for the Cr^V/Cr^{III} couples of the two chromium-substituted heteropolytungstates. The formal potentials were taken as the average of the anodic and cathodic peak potentials in cyclic voltammograms such as those in Figure 1A,B despite the large separation between the anodic and cathodic peaks.

The α-$[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-}$ anion behaved similarly during controlled-potential electrolyses at 1.5 V, which also consumed more than two electrons per anion by the time full oxidation was achieved.

The oxidation of the two Cr(III)-substituted heteropolyanions could also be accomplished chemically using MnO_4^- as described in the Experimental Section. The oxidized complexes obtained by chemical or electrochemical oxidations gave the same spectra, and tetraethylammonium salts obtained by either route gave the same carbon–hydrogen–nitrogen elemental analyses. Solutions of the oxidized complex were very stable at pH 1. No changes were noted in the visible spectrum of the solutions prepared and examined over several weeks.

Solutions of the two fully oxidized anions were analyzed iodometrically to determine the oxidation state of Cr. The results showed that each oxidized complex contained 2 oxidizing equiv, as expected if the oxidation produced Cr(V). The fully oxidized solutions were also analyzed by controlled-potential electrolytic reductions at 0.4 V. These electrolyses proceeded much more rapidly than did the electrooxidations, and background currents were much smaller. Two electrons per molecule of oxidized complex were consumed during the reductions, and the reduced solutions exhibited spectra identical to those of the original Cr(III) complexes.

The electrochemical results are all consistent with the oxidation's proceeding according to half-reactions 1a and 1b.

$$\alpha_2\text{-}[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-} - 2e = \alpha_2\text{-}[P_2W_{17}O_{61}Cr^{V}O]^{7-} + 2H^+ \quad (1a)$$

$$\alpha\text{-}[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-} - 2e = \alpha\text{-}[PW_{11}O_{39}CrO]^{4-} + 2H^+ \quad (1b)$$

Very approximate values of the formal potentials for the redox couples involved in half-reactions 1a and 1b were estimated from the average of the anodic and cathodic peak potentials in cyclic voltammograms such as those in Figure 1A,B. The pH depend-

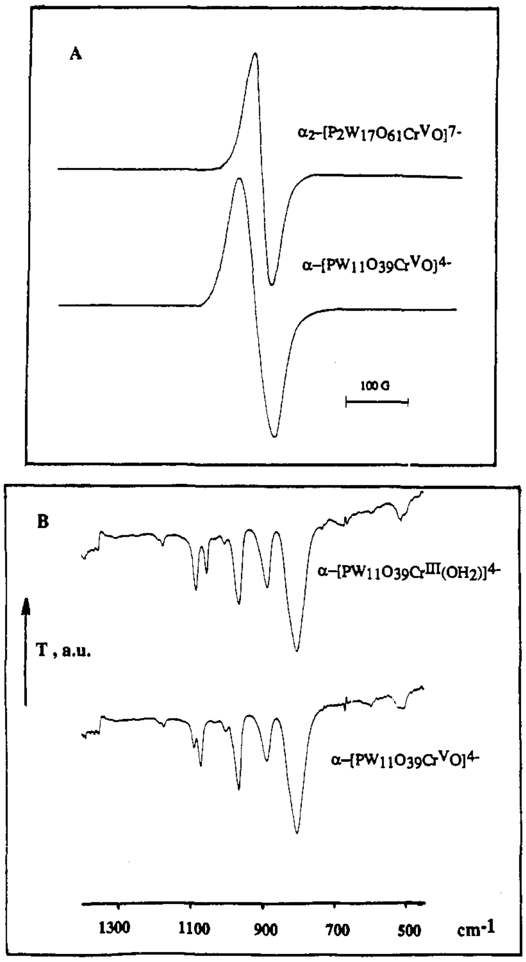

Figure 4. (A) X-band ESR spectra recorded at room temperature with powder samples of tetraethylammonium salts of α_2-$[P_2W_{17}O_{61}Cr^VO]^{7-}$ and α-$[PW_{11}O_{39}Cr^VO]$. (B) Infrared spectra of α-$[(C_2H_5)_4N]_4[PW_{11}O_{39}Cr^{III}(OH_2)]$ and α-$[(C_2H_5)_4N]_4[PW_{11}O_{39}Cr^VO]$ in KBr pellets. The ordinate gives transmission in arbitrary units.

ences of the resulting formal potentials are shown in Figure 3. The approximately linear dependence with a slope close to 60 mV per unit change in pH is consistent with the two-electron, two-proton processes depicted in half-reactions 1a and 1b. The depiction of the ligand on the Cr(V) center of the oxidized complex as a terminal oxo groups follows the lead of previous workers.[3b,4c] It is consistent with the electrochemical results as well as the elemental analyses of the isolated salts of the oxidized complex. Khenken and Hill[4c] recently summarized the array of evidence that supports the depiction of heteropolyanion complexes as containing a terminal oxo group on the Cr(V) center.

Properties of the Cr^V Complexes. Powdered samples of the tetraethylammonium salts of α-$[PW_{11}O_{39}Cr^VO]^{4-}$ and α_2-$[P_2W_{17}O_{61}Cr^VO]^{7-}$ both exhibited strong, simple ESR spectra at room temperature (Figure 4A). Both spectra corresponded to an isotropic *g* value of 1.956, which is similar to the value reported for α-$[SiW_{11}O_{39}Cr^VO]^{5-}$ dissolved in toluene.[3b]

Infrared spectra of samples of α-$[(C_2H_5)_4N]_4$-$[PW_{11}O_{39}Cr^{III}(OH_2)]$ and α-$[(C_2H_5)_4N]_4[PW_{11}O_{39}Cr^VO]$ are shown in Figure 4B. The primary difference produced by oxidation of the Cr^{III} center is the change in relative intensity of the two bands near 1100 cm^{-1} which arise from P–O stretching vibrations. These bonds are known to be sensitive to structural changes within the anion.[11] Replacement of a tungsten center with a different metal causes the corresponding band at 1080 cm^{-1} in the parent anion, α-$[PW_{12}O_{40}]^{3-}$, to be split by 20–40 cm^{-1}, depending on the strength of the interaction between the replacement ion and the polytungstate structure.[11,12] Oxidation of Cr(III) to Cr(V) produces a decrease in separation and a change in intensity of the bands near 1100 cm^{-1} in Figure 4B. This behavior is consistent with a stronger interaction of Cr(V) with the oxo ligands of the polytungstate cage. The other bands in Figure 4B, which exhibit no sensitivity to the oxidation state of the Cr center, arise from terminal and bridging W–O groups, which are less perturbed by the presence and the oxidation state of the Cr center.

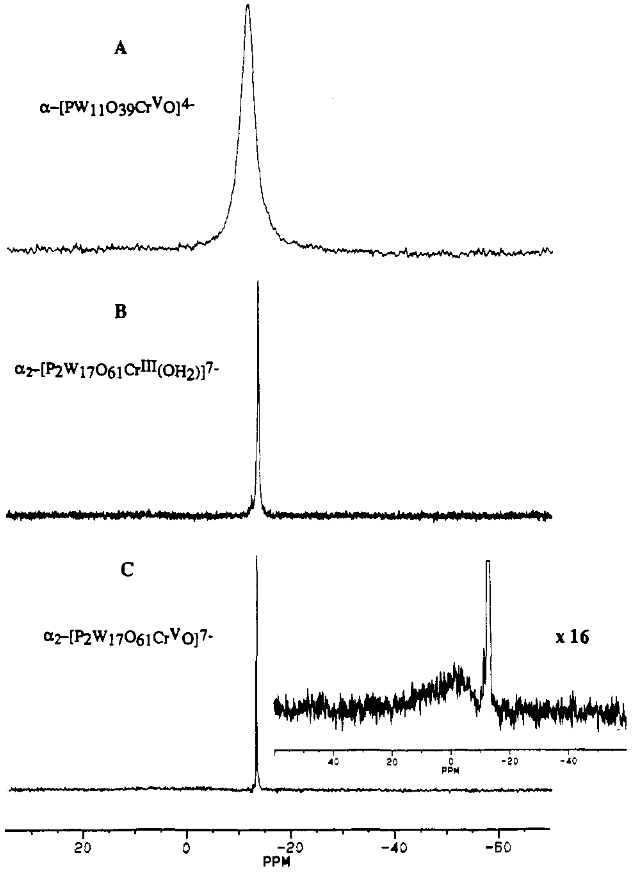

Figure 5. ^{31}P NMR spectra of chromium-substituted heteropolytungstates: The samples consisted of 5 mM aqueous solutions of the anions in 0.5 M $NaHSO_4$ adjusted to pH 1. The insert in part C shows the same spectrum recorded with a sensitivity 16 times higher.

^{31}P NMR spectra recorded for the two anions are shown in Figure 5. For α-$[PW_{11}O_{39}Cr^VO]^{4-}$ the single line (Figure 5A) is broadened considerably by the Cr(V) center. No resonance was observed for the corresponding Cr(III) complex presumably because of its greater paramagnetism. For α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ only a single, somewhat broadened line could be observed (Figure 5B), which presumably arises from the ^{31}P atom further from the Cr(III) center. However, for the corresponding oxidized complex there is a sharp line at −13.2 ppm and a very weak, broad line near −2 ppm (Figure 5C). The weak, broad line (insert in Figure 5C) presumably arises from the ^{31}P closer to the Cr center while the sharper resonance arises from the more remote ^{31}P atom.

Rotating-Disk Voltammetry and Diffusion Coefficients. Current–potential curves recorded at a rotating pyrolytic graphite disk electrode for the reduction of the α_2-$[P_2W_{17}O_{61}Cr^VO]^{7-}$ anion in a solution, prepared by electrooxidation of α_2-$[P_2W_{17}O_{61}Cr^{III}OH_2]^{7-}$ at 1.25 V, are shown in Figure 6A. The waves are well-formed, and the equality of the plateau currents for the first wave, corresponding to the reduction of the Cr(V) center, and that for the second wave, corresponding to the two-electron reduction of the tungsten–oxo cage, confirms that both processes involve the same number of electrons, namely two.

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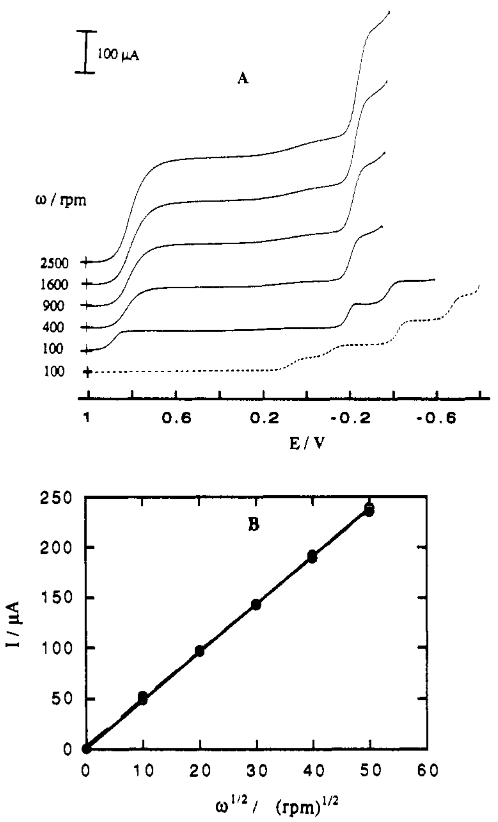

Figure 6. (A) Reduction of 1.0 mM α_2-$[P_2W_{17}O_{61}Cr^{V}O]^{7-}$ at a rotating graphite disk electrode. The oxidized complex was obtained by controlled-potential electrooxidation of the Cr(III) complex at 1.25 V. Supporting electrolyte: 0.5 M $NaHSO_4$ adjusted to pH 1. Potential was scanned at 10 mV s^{-1}. Electrode rotation rates, ω, are as shown. The dashed curve was obtained with a 1 mM solution of α_2-$[P_2W_{18}O_{62}]^{5-}$. (B) Levich plots of the plateau currents for the first (○) and second (●) reduction waves in (A).

Table 1. Diffusion Coefficients of Cr- and Fe-Substituted Heteropolytungstate Anions

anion[b]	10^6D, $cm^2\ s^{-1}$ [a]			
	$Cr^{III/V}$	$Cr^{V/III}$	$Fe^{III/II}$	$W^{VI/V}$
α_2-$[P_2W_{17}O_{61}Cr^{V}O]^{7-}$		2.9		2.9
α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$	2.6			3.0
α_2-$[P_2W_{17}O_{61}Fe^{III}(OH_2)]^{7-}$			2.8	2.7
α_2-$[P_2W_{18}O_{62}]^{6-}$				3.0
α-$[PW_{11}O_{39}Cr^{V}O]^{4-}$		3.9		4.4
α-$[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-}$				4.0
α-$[PW_{11}O_{39}Fe^{III}(OH_2)]^{4-}$			3.8	3.4

[a] Temperature 22 ± 2 °C; supporting electrolyte 0.5 M $NaHSO_4$ adjusted to pH 1. [b] Anion concentration 1.0 mM.

The dashed current–potential curve in Figure 6A was obtained with a solution of the unsubstituted polyanion, α_2-$[P_2W_{18}O_{62}]^{6-}$, at the same concentration. This anion exhibits two, one-electron reductions followed by two, two-electron reduction waves.[10] Comparison of the plateau currents for the two-electron reductions of the unsubstituted anion with those obtained with the Cr-substituted anion shows that the Cr(III) center is not coreduced during the reduction of the tungsten–oxo cage.

Levich plots of plateau currents vs (rotation rate)$^{1/2}$ for the Cr(V)/Cr(III) wave and the first cage reduction wave (Figure 6B) are linear with equal slopes, as expected for a diffusion-convection-controlled process. Diffusion coefficients calculated from the slopes are listed in Table 1.

Current–potential curves at the rotating disk electrode for the oxidation of α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ (Figure 7A) are not as well-formed as those in Figure 6A, and the potentials where the anodic waves appear are close to the potentials where solvent oxidation commences. Nevertheless, Levich plots prepared from curves such as those in Figure 7A were reasonably linear (Figure 7B) and yielded a diffusion coefficient in reasonable agreement with those obtained from the reduction of the oxidized complex and from the reduction of the tungsten–oxo cage (Table 1).

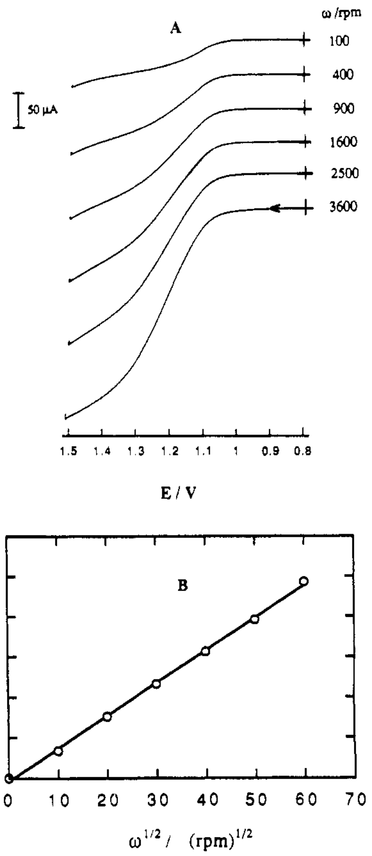

Figure 7. (A) Oxidation of 1.0 mM α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ at a rotating graphite disk electrode. (B) Levich plot of the plateau currents in (A). Other conditions were as in Figure 6.

Similar rotating-disk measurements were also made with solutions of α-$[PW_{11}O_{39}Cr^{V}O]^{4-}$ and α-$[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-}$. The oxidation wave for the latter complex was so poorly developed that no reliable estimates of anodic plateau currents could be made. However, the first reduction wave of the tungsten–oxo cage provided clear plateau currents and linear Levich plots from which the diffusion coefficient given in Table 1 was obtained. The reduction of the Cr(V) center in α-$[PW_{11}O_{39}Cr^{V}O]^{4-}$ produced well-formed current–potential curves similar to those in Figure 6A. The diffusion coefficient calculated from the corresponding linear Levich plot (Table 1) agreed with the value obtained for the Cr(III) complex. The somewhat larger diffusion coefficient obtained from the reduction of the oxo cage is an anomaly for which no explanation suggests itself.

For the purposes of comparison, diffusion coefficients were also evaluated by rotating-disk voltammetry for the related Fe(III)-substituted heteropolyanions and one unsubstituted anion. The results are also included in Table 1.

The values of the diffusion coefficients collected in Table 1 are reasonably self-consistent and indicate that the smaller anions, which are also less highly charged, and therefore likely to be less solvated, diffuse more rapidly, as expected. The Stokes–Einstein hydrodynamic radii[13] calculated from the average values of the diffusion coefficients for α-$[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-}$ and α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ are 5.4 and 8.9 Å, respectively. The crystallographic radius for the smaller anion is 5.6 Å,[14] and the elliptically shaped larger anion has an average "radius" of about

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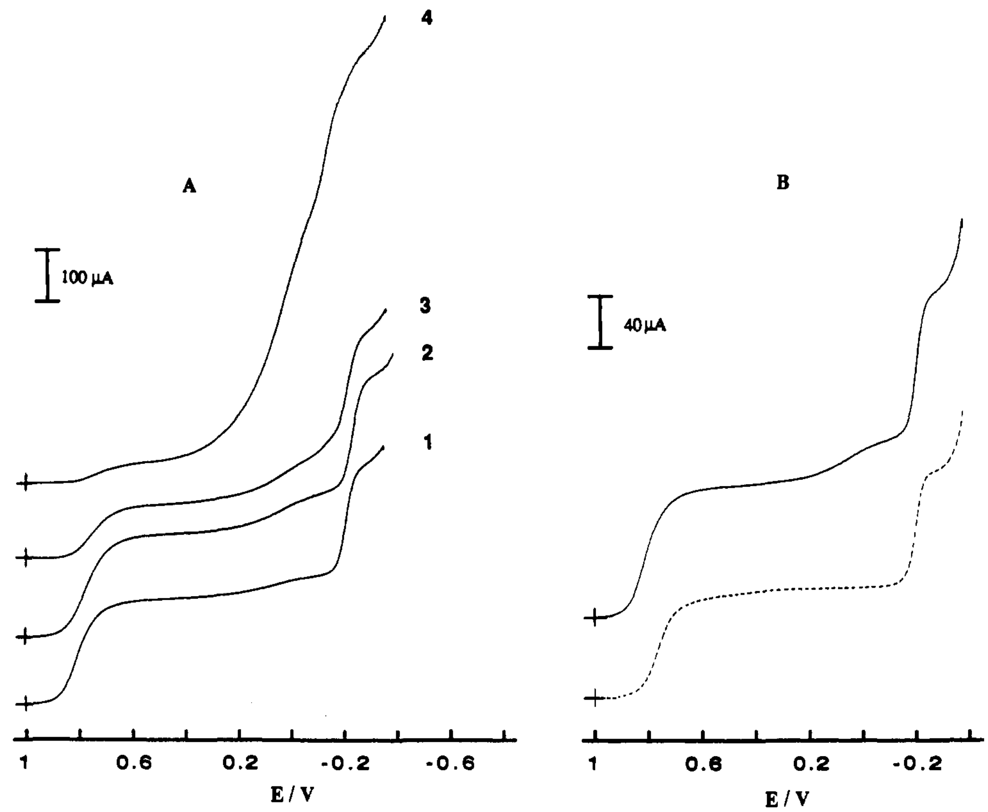

Figure 8. (A) Current–potential curves at a rotating graphite disk electrode recorded with 1 mM solutions of α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ which had been exhaustively electrooxidized at (1) 1.25, (2) 1.35, (3) 1.5, and (4) 1.6 V. Electrode rotation rate was 1600 rpm; other conditions were as in Figure 6. (B) Current–potential responses: (—) from a 0.31 mM solution of α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ which had had been electrooxidized at 1.35 V; (- - -) after isolation of $[(C_2H_5)_4N]_{6.3}H_{0.7}[P_2W_{17}O_{61}Cr^{V}O]$ from the oxidized solution and dissolution of the salt in the supporting electrolyte. Electrode rotation rate was 3600 rpm; other conditions were as in Figure 6.

8 Å.[15] Thus, the crystallographic dimensions of the anions do not differ significantly from their hydrodynamic dimensions, a result which indicates that these large anions are not extensively hydrated despite their relatively high negative charge.[16]

Oxidation above Cr(V). Careful inspection of the current–potential curves in Figure 6 at the higher rotation rates reveals that a small, less well-formed wave is present at potentials between 0.2 and -0.2 V. To explore the origin of this wave in more detail, a series of controlled-potential electrooxidations of α_2-$[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-}$ was carried out at increasingly positive potentials between 1.25 and 1.6 V. Rotating-disk voltammograms recorded with the resulting oxidized solutions are shown in Figure 8A. As the potential used to perform the electrooxidation was made more positive, the magnitude of the reduction wave which resulted at 0.2 V increased. With an oxidation potential of 1.6 V (curve 4 in Figure 8A), the reduction wave became much larger and the wave corresponding to the reduction of Cr(V) to Cr(III) was greatly diminished. The wave for the reduction of the tungsten–oxo cage was also affected by the more extensive oxidation. A response essentially similar to that of curve 4 in Figure 8A also resulted if the solution used to record the voltammogram in curve 1 was subjected to additional electrooxidation at 1.6 V. These results show that the Cr(V) complex can be further oxidized at more positive potentials. Iodometric redox titrations of solutions electrooxidized at 1.6 V showed that almost 3 oxidizing equiv per chromium present in the resulting oxidized species. However, it does not appear that a stable Cr(VI) derivative of the original polyanion was generated. The ^{31}P NMR spectrum of the oxidized solution contained a major peak at -12.7 ppm, corresponding to the chromium-free, parent anion, $[P_2W_{18}O_{62}]^{6-}$,[1a] as well as several new peaks indicating the presence of additional species. The same spectrum was obtained by mixing equivalent quantities of the lacunary anion, α_2-$[P_2W_{17}O_{61}]^{10-}$, with $Cr_2O_7^{2-}$ in 0.1 M acid where the lacunary anion is known to decompose to form $[P_2W_{18}O_{62}]^{6-}$ and other products.[1a] The voltammetry of the strongly oxidized solution lacked the peak corresponding to the reduction of α_2-$[P_2W_{17}O_{61}Cr^{V}O]^{7-}$ and matched the voltammetry obtained with the mixture prepared from α_2-$[P_2W_{17}O_{61}]^{10-}$ and $Cr_2O_7^{2-}$. Thus, it seems likely that the aggressive oxidation of the Cr(III) center in the polyanion to Cr(VI) leads to ejection of the Cr(VI) center from the polyoxo cage accompanied by decomposition of the resulting lacunary complex. For this reason, the behavior of the aggressively oxidized complex was not pursued.

The pure α_2-$[P_2W_{17}O_{61}Cr^{V}O]^{7-}$ complex can be separated from mixtures with the more extensively oxidized complex by precipitation of α_2-$[(C_2H_5)_4N]_{6.3}H_{0.7}[P_2W_{17}O_{61}Cr^{V}O]$. For example, the dashed curve in Figure 8B is the current–potential curve for a solution prepared by dissolution of the α_2-$[(C_2H_5)_4N]_{6.3}H_{0.7}[P_2W_{17}O_{61}Cr^{V}O]$ salt isolated from a solution of the Cr(III) complex which had been exhaustively oxidized at 1.35 V. The current–potential response of the oxidized solution before precipitation of the Cr(V) salt is shown by the solid curve in Figure 8B. The more extensively oxidized complex apparently does not coprecipitate when $(C_2H_5)_4N^+$ cations are used to precipitate the Cr(V) salt.

Oxidative Reactivity of the Cr(V) Complexes. One of our objectives in preparing the chromium-substituted heteropolytungstates was to investigate their reactivity as two-electron-oxidizing agents for various substrates, including organic molecules such as alcohols. Despite the relatively positive formal potentials of the Cr(V)/Cr(III) couple in the heteropolyanions, the reactions of α_2-$[P_2W_{17}O_{61}Cr^{V}O]^{7-}$ and α-$[PW_{11}O_{39}Cr^{V}O]^{4-}$ with alcohols are not facile. The useful chemical stability, which allows the Cr(V) complexes to be readily prepared and isolated, becomes a detriment in attempts to exploit them as oxidants for relatively unreactive substrates. The rate of the oxidation of benzyl alcohol by the Cr(V) complexes was monitored spectro-

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(16) Baker, L. C. W. In *Advances in the Chemistry of Coordination Compounds*; Kirschner, S., Ed.; Macmillan: New York, 1961; p 604.

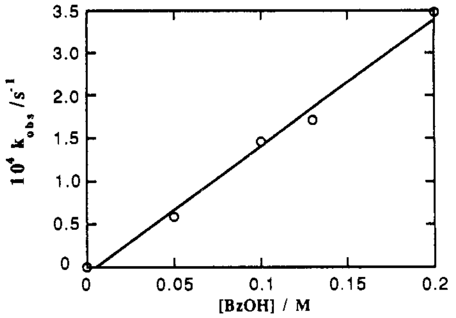

Figure 9. Pseudo-first-order rate constants for the oxidation of benzyl alcohol by α_2-$[P_2W_{17}O_{61}Cr^VO]^{7-}$ as a function of the concentration of benzyl alcohol. Reaction rates were measured spectrophotometrically at 22 ± 2 °C. Supporting electrolyte: 0.5 M $NaHSO_4$ adjusted to pH 1. Initial concentration of the polytungstate anion was 1.0 mM.

photometrically at 420 nm under pseudo-first-order conditions. The appropriate logarithmic kinetic plots were linear, and the values of k_{obs} obtained from the slopes of the plots were linearly dependent on the concentration of benzyl alcohol, as shown in Figure 9 for the α_2-$[P_2W_{17}O_{61}Cr^VO]^{7-}$ anion. Proton NMR measurements demonstrated that the oxidation product was benzaldehyde, and the spectrum of the solution showed that the heteropolyanions were reduced to their Cr(III) state. The second-order rate constants for the reactions of both α-$[PW_{11}O_{39}Cr^VO]^{4-}$ and α_2-$[P_2W^{17}O_{61}Cr^VO]^{7-}$ with benzyl alcohol are ca. 1.5×10^{-3} M^{-1} s^{-1}, which is much too small for the chromium-substituted heteropolyanions to be useful as electrocatalysts for the oxidation of benzyl alcohol. The oxidized heteropolyanions also react with ethyl alcohol and benzaldehyde but at even smaller rates. The oxidations of I^-, $Fe(CN)_6^{4-}$, Fe^{2+}, and ascorbate proceeded considerably more rapidly, but the kinetics were not evaluated quantitatively.

The relatively low reactivity of the Cr(V) complexes toward the oxidation of alcohols may reflect the inability of the terminal oxo group on the Cr(V) center to serve as a good hydride acceptor. The relevant reasoning for the analogous case of alcohol oxidation by polypyridyl complexes of oxo–Ru(IV) complexes has been presented by Thompson and Meyer.[17]

Conclusions

The synthetic procedure developed in this study provides a facile pathway for the preparation of Cr(III)-substituted heteropolyanions. The Cr(III) center introduced into the polyanion can be readily oxidized either electrochemically or chemically to obtain complexes of Cr(V) which are quite stable. The oxidized complexes are about as strongly oxidizing as $CrO_4^{2-}/Cr_2O_7^{2-}$, but the rates of reactions of the oxidized heteropolyanions with organic alcohols are too slow to make the complexes attractive as oxidation catalysts. Attempts to reduce the Cr(III) center incorporated in the heteropolyanions to Cr(II) resulted only in the reduction of the tungsten–oxo cage, and all attempts to oxidize the Cr(V) complex to a stable Cr(VI) derivative proved fruitless.

Acknowledgment. This work was supported by a grant from the ONR/DARPA.

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