+ OH^- for which $K_b = 2 \times 10^{-10}$. The presence of the highly mobile hydroxide ion will of course increase the conductivity. A plot of Λ_M *vs.* the square root of the concentration for the aqueous solutions also rises more steeply with dilution than is expected for a 1:1 strong electrolyte. Dissociation of the cyanotrihydroborate ligands in both water and methanol, therefore, appears to involve similar processes.

Conductivity measurements were also carried out in nitromethane. The compound decomposes in CH_3NO_2; in a fairly short time the color of the solution changes from deep royal blue to a light blue-green. The conductivity of a 1.0×10^{-3} *M* solution in nitromethane is initially quite low ($\Lambda_M \approx 14$ ohm^{-1} cm^2 mol^{-1}) but it increases fairly rapidly with time. After 21.5 hr $\Lambda_M = 29.2$ ohm^{-1} cm^2 mol^{-1}.

Magnetic Susceptibilty. The gram magnetic susceptibility was measured as a function of temperature over the range 80-300°K by the Faraday method.[49] The calibrant used was $HgCo(SCN)_4$. The temperature calibration of the cryostat was checked by calculating the magnet constant[49] β at a series of temperatures. The values of β measured on our equipment for three different field strengths over the temperature range 80-350°K were constant to within 1-2%. The molar magnetic susceptibility was corrected for diamagnetic substituents using Pascal's constants[50] and also for temperature-independent paramagnetism.[51] The diamagnetic correction term is -176×10^{-6}. Since the visible spectrum of $(Me_5dien)Cu(NCBH_3)_2$ in methanol solution consists of one single broad peak with λ_{max} 6450 Å, the correction term for temperature-independent paramagnetism is $\chi_{TIP} = 1.04/\Delta = (1.04)(6.45 \times 10^{-5}) = 67 \times 10^{-6}$.[51]

The effective magnetic moment, in Bohr magnetons, was obtained from the corrected molar magnetic susceptibility using the relation $\mu_{eff} = 2.83(\chi_M^{cor}T)^{1/2}$ where T is the absolute temperature. The value of the effective magnetic moment of $(Me_5dien)Cu(NCBH_3)_2$ was 1.79 ± 0.02 BM throughout the temperature range 80-300°K. This is just slightly above the "spin-only" value of 1.73 BM and is typical of a monomeric molecular copper(II) compound.

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Registry No. $(Me_5dien)Cu(NCBH_3)_2$, 50276-24-9.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-822.

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Synthesis and Properties of Cationic Molybdenum(IV) Oxohaloisocyanide Complexes

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The reactivity of binary molybdenum chlorides toward isocyanide ligands in the presence of oxygen-containing solvents has been investigated under an atmosphere of dry nitrogen. If ether is used as the solvent, the known seven-coordinate $[Mo(CNR)_7]X_2$ compounds are formed. When methanol is used as the solvent, new oxo species of the type $[(RNC)_4MoOCl]Y$ can be prepared. These latter complexes are characterized by infrared, pmr, and optical spectroscopy and by solution conductivity studies in nitromethane. The trans isomer predominates. The synthesis of the oxobromo analog, $[(CH_3NC)_4MoOBr]^+$, from molybdenum hexacarbonyl is described.

Introduction

The present study grew out of a program to prepare and characterize eight-coordinate MX_4Y_4 complexes containing only monodentate ligands.[1] In particular, we were interested in carrying out reaction 1 with various R groups and

$$\mathrm{MoX_4 + 4RNC \rightarrow Mo(CNR)_4X_4} \qquad (1)$$

halides and structurally characterizing the products. The chemistry represented by eq 1 has not yet been observed, however, because of the tendency for anhydrous metal halides to abstract oxygen from solvent molecules[2] or to be reduced by isocyanide ligands.[3] As described in this report, several new examples of the relatively rare molybdenum(IV)-oxo species,[4,5] as well as the known heptacoordinate molybdenum(II) isocyanide cation,[6] were isolated.

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Experimental Section

All compounds were prepared under an atmosphere of nitrogen using anhydrous solvents that were degassed by bubbling dry nitrogen through them for at least 10 min. Isocyanides were obtained by dehydration of the appropriate N-substituted formamides.[7,8] Other starting materials were commercially available. Microchemical analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Chlorooxotetrakis(methyl isocyanide)molybdenum(IV) Triodide, $[MoOCl(CNCH_3)_4](I_3)$. A solution containing 0.571 g (2.25 mmol) of iodine dissolved in 40 ml of methanol was added to 0.357 g (1.5 mmol) of molybdenum tetrachloride. After a vigorous solvolytic reaction subsided, the mixture was stirred for ~15 min and filtered. Addition of 0.492 g (12 mmol, excess) of methyl isocyanide to the filtrate yielded dark red crystals that were filtered, washed with 20 ml of ice-cold methanol and then with ethyl ether, and dried *in vacuo*. The yield was 0.56 g (54% based on molybdenum). *Anal.* Calcd for $C_8H_{12}N_4MoOClI_3$: C, 13.9; H, 1.75; N, 8.09; Mo, 13.9; Cl, 5.12; I, 55.0. Found: C, 13.3; H, 1.52; N, 7.89; Mo, 13.9; Cl, 5.30; I, 55.0. Pmr: singlet, δ 3.83, in CD_3CN.

Chlorooxotetrakis(methyl isocyanide)molybdenum(IV) Hexafluorophosphate, $[MoOCl(CNCH_3)_4](PF_6)$. (A) A solution of 0.12 g (0.75 mmol) of bromine in 30 ml of methanol was added to 0.357 g (1.5 mmol) of molybdenum tetrachloride. After the vigorous reaction subsided, the solution was filtered and 0.492 g (12 mmol, excess) of methyl isocyanide in 10 ml of methanol was slowly added to the green filtrate. The color changed to dark yellow and finally to light purple. After the addition of 0.504 g of sodium hexafluorophosphate dissolved in 10 ml of methanol, purple microcrystals appeared within about 1 hr. The product was filtered and washed with ~20 ml of methanol and then with ethyl ether. The yield, after drying *in vacuo*, was 0.46 g (66% based on Mo). *Anal.* Calcd for $C_8H_{12}N_4MoOClPF_6$: C, 21.0; H, 2.65; N, 12.3; Mo, 21.0; Cl, 7.77; P, 6.78. Found: C, 20.4; H, 2.66; N, 11.9; Cl, 7.38.

(B) Molybdenum(V) pentachloride (0.546 g, 2 mmol) was dissolved in 20 ml of methanol to produce a green solution. Addition of 0.676 g (16 mmol) of methyl isocyanide resulted in a red solution from which purple crystals of product separated upon the addition of 0.672 g of $NaPF_6$ dissolved in 10 ml of methanol. The yield, after washing with methanol and ethyl ether and then drying, was ~0.6 g (66% based on Mo). *Anal.* Found: C, 21.4; H, 2.63; N, 12.0; Mo, 20.6; P, 6.68.

Bromooxotetrakis(methyl isocyanide)molybdenum(IV) Diiodobromide, $[MoOBr(CNCH_3)_4](BrI_2)$. A mixture of 0.528 g (2 mmol) of molybdenum hexacarbonyl, 30 ml of methanol, and 0.660 g (4.1 mmol) of bromine was refluxed for about 1 hr. The resulting brown solution was cooled to room temperature and 0.5 g of methyl isocyanide was added slowly with stirring. The violet solution was then treated with 0.508 g (2 mmol) of iodine dissolved in 10 ml of methanol. Almost immediately a light purple crystalline material appeared. After 30 min the product was collected by filtration, washed with methanol and ethyl ether, and then dried *in vacuo* at room temperature. A yield of ~30% (0.41 g) based on molybdenum was obtained. *Anal.* Calcd for $C_4H_{12}N_4MoOBr_2I_2$: C, 13.9; H, 1.75; N, 8.12; Mo, 13.9; Br, 23.2; I, 36.8. Found: C, 13.9; H, 1.97; N, 8.13; Mo, 13.7; Br, 23.0; I, 36.9. Pmr: singlet, δ 3.87, in CD_3CN.

Chlorooxotetrakis(ethyl isocyanide)molybdenum(IV) Triiodide, $[MoOCl(CNC_2H_5)_4](I_3)$. This compound was prepared from 0.66 g (12 mmol) of ethyl isocyanide in a manner identical with the synthesis of the methyl analog. The yield of dark reddish brown microcrystalline material was 0.52 g (46% based on molybdenum). *Anal.* Calcd for $C_{12}H_{20}N_4MoOClI_3$: C, 19.3; H, 2.69; Cl, 4.74; I, 50.9. Found: C, 19.8; H, 2.74; Cl, 3.90; I, 50.7. Despite the poor chlorine analysis, the compound is believed to be pure and properly characterized. Pmr: triplet ($J = 7.3$ Hz) at δ 1.53 and quartet ($J = 7.3$ Hz) at δ 4.17, in CD_3CN.

Chlorooxotetrakis(*tert*-butyl isocyanide)molybdenum(IV) Triiodide, $[MoOCl(CNC_4H_9)_4](I_3)$. The procedure described for the methyl derivative was used, employing 0.996 g (12 mmol) of *tert*-butyl isocyanide. Because of the greater solubility of the product, crystallization was completed at 0° and only 5 ml of cold methanol was used to wash the product. The yield of dark orange mica-like crystals was 0.51 g (40% based on Mo). *Anal.* Calcd for $C_{20}H_{36}N_4MoOClI_3$: C, 27.9; H, 4.22; N, 6.51; Mo, 11.2; Cl, 4.12; I, 44.2. Found: C, 28.3 (28.3); H, 4.38 (4.06); N, 6.40 (7.22); Mo, 11.1; Cl, 3.65; I, 42.5 (44.8) (the numbers in parentheses were obtained on a second sample of product). Pmr: singlet, δ 1.73, in $CDCl_3$.

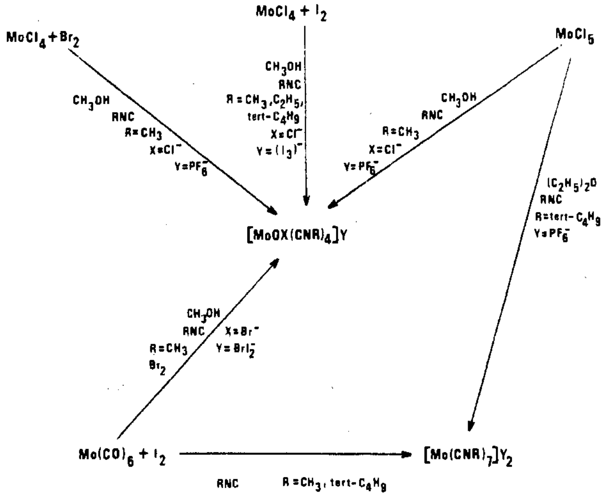

Figure 1. Synthetic routes to molybdenum isocyanide complexes.

Heptakis(*tert*-butyl isocyanide)molybdenum(II) Hexafluorophosphate, $[Mo(CNC_4H_9)_7](PF_6)_2$. About 0.8 g of *tert*-butyl isocyanide was added to a mixture of 0.546 g (2 mmol) of molybdenum pentachloride and 50 ml of diethyl ether. A yellow precipitate immediately formed. The mixture was stirred overnight and filtered. The product was dried and redissolved in 30 ml of methanol. A solution of 0.672 g (4 mmol) of $NaPF_6$ in 10 ml of methanol was added and the mixture was kept at 0° overnight. The resultant yellow mica-like crystalline product was filtered, washed with 5 ml of ice-cold methanol and 20 ml of ether, and dried *in vacuo*. The yield was 0.29 g (~15% based on Mo). *Anal.* Calcd for $C_{35}H_{63}N_7MoP_2F_{12}$: C, 43.4; H, 6.56; N, 10.1; P, 6.40. Found: C, 43.5; H, 6.43; N, 10.0; P, 6.98.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer calibrated with polystyrene film. Solid samples were examined as Nujol mulls or KBr pellets and solutions were made using Spectrograde acetonitrile. Solution electronic spectra were run at concentrations of approximately 10^{-2} to 10^{-3} *M* in acetone on a Cary Model 17 spectrometer using 1-cm matched quartz cells. Conductivities were determined at a constant temperature of 25° with an Industrial Instruments Inc. Model RC 16B2 conductance bridge. The nitromethane solvent was dried and distilled under nitrogen. Measurements were made shortly after dissolution to eliminate error caused by decomposition. Magnetic susceptibility studies were carried out by the Gouy method at room temperature. Proton nmr spectra were recorded on a Varian A-60A spectrometer at ambient probe temperature. Chemical shifts (δ) are in ppm downfield from tetramethylsilane.

Results

Synthesis and Chemical Properties of $[MoOX(CNR)_4]^+$ Cations. Cations of the type $[MoOX(CNR)_4]^+$ were prepared as summarized in Figure 1. The use of diethyl ether as a solvent in one instance produced the $[Mo(CNR)_7]^{2+}$ dication as the major product of the reaction of an alkyl isocyanide with molybdenum pentachloride. The cationic species can easily be isolated as salts of large anions such as PF_6^-, I_3^-, or $B(C_6H_5)_4^-$. In a crystalline state, the complexes were found to be fairly stable in air. They are readily soluble in acetone and nitromethane and partially soluble in methanol and acetonitrile. Although solutions of the seven-coordinate dications[6,9] are fairly stable, the oxo compounds, when dissolved in acetone or methanol, undergo decomposition. In addition, they are highly reactive toward amines and thiols. These reactions, which are usually accompanied by color changes, are under further study.

Physical Properties. The $[MoOCl(CNCH_3)_4](PF_6)$ salt was found to be diamagnetic at room temperature. The

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Table I. Summary of Infrared Spectral Bands in the C≡N and Mo=O Stretching Frequency Regions[a,b] and Conductivity Data[c]

Compd	ν(C≡N), cm^{-1}		ν(Mo=O), cm^{-1}		Λ_m, ohm^{-1} cm^2 mol^{-1}
	Nujol mull	Soln[d]	Nujol mull	Soln[d]	
$[MoOCl(CNCH_3)_4](PF_6)$	2241 sh, 2230 s	*e*	952 m, 942 m	*e*	*e*
$[MoOCl(CNCH_3)_4](I_3)$	2229 s	2230 s	952 m, 941 s, 933 s	946 br	*e*
$[MoOBr(CNCH_3)_4](BrI_2)$	2228 s, 2213 sh	2231 s	954 m, 943 s, 936 sh	950 br	76.3
$[MoOCl(CNC_2H_5)_4](I_3)$	2218 s, 2180 sh	2223 s	946 sh, 937 m	950 s	87.4
$[MoOCl(CN\text{-}t\text{-}C_4H_9)_4](I_3)$	2196 s	*e*	942 s	*e*	81.9

[a] Frequencies are estimated to be accurate to ±2 cm^{-1}. [b] Abbreviations: s, strong; m, medium; sh, shoulder; br, broad. [c] In 10^{-3} *M* nitromethane solutions at 25°. [d] In acetonitrile. [e] Not measured.

measured room-temperature molar susceptibility was -182×10^{-6} cgsu/mol. The value calculated from Pascal's constants is -190×10^{-6} cgsu/mol, excluding a contribution from the molybdenum atom. Infrared spectral bands in the C≡N and Mo=O stretching frequency regions are summarized in Table I. Proton nmr results are reported in the Experimental Section. The ionic nature of the $[MoOX(CNR)_4]Y$ complexes is exemplified by their conductivities in nitromethane solution. The data summarized in Table I are in accord with the literature values for 1:1 electrolytes in this solvent.[10] Because of the instability of the nitromethane solutions, however, the precision of the measurements was limited and concentration dependence studies were found to be unreliable. The uv-visible spectrum of 10^{-2}-10^{-3} *M* solutions of $[MoOCl(CNCH_3)_4](PF_6)$ in acetone showed a broad absorption band with a maximum at 547 nm (18,280 cm^{-1}), ϵ_{max} 124. The spectra of the other salts were not studied in any detail owing to interference from the polyhalide ion absorptions.

Discussion

Syntheses. Complexes of the type $[MoOX(CNR)_4]Y$ represent a fairly stable class of molybdenum(IV) compounds. They can be considered as isocyanide analogs of the known cyanide complexes $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$ and $K_4[MoO_2(CN)_4]\cdot 6H_2O$.[4] The existence of oxomolybdenum(IV) species is rare compared to the more abundant molybdenum(V)- and molybdenum(VI)-oxo complexes.[5] Apparently the tendencies of oxygen to stabilize the higher oxidation states and of isocyanide to stabilize the lower are balanced in these d^2 molybdenum(IV) compounds. If ethyl ether is used as a reaction medium, seven-coordinate d^4 Mo(II) complexes are formed. The $[Mo(CNR)_7]^{2+}$ cations have already been prepared in our laboratory by a different route,[6] and the present results further attest to their stability.

The fact that the oxomolybdenum(IV) isocyanide complexes are formed when methanol is used as the solvent but not in diethyl ether suggests that the oxygen is supplied in a solvolysis reaction such as (2).[2] The possibility is not

$$MoCl_5 + CH_3OH \rightarrow [MoCl_5(OCH_3)]^- + H^+ \qquad (2a)$$

$$[MoCl_5(OCH_3)]^- \rightarrow [MoOCl_4]^- + \text{other products} \qquad (2b)$$

excluded that, despite careful drying the oxygen comes from trace amounts of water. In those cases where molybdenum(IV) chloride is used as the starting material (Figure 1), the addition of excess elemental halogen is required, perhaps to oxidize the molybdenum to the 5+ state. After solvolysis (eq 2), the addition of isocyanide reduces the metal and substitutes for halide, as suggested by reaction 3, and the prod-

$$2[MoOCl_4]^- + 9RNC \rightarrow 2[MoOCl(CNR)_4]^+ + RN{=}CCl_2 + 4Cl^- \qquad (3)$$

uct is precipitated with a large anion. The oxidized isocyanide product was neither isolated nor identified.

Since the $[MoOCl(CNCH_3)_4]^+$ cation precipitates with PF_6^- from a reaction medium containing I_3^-, chloride is assumed to be in the coordination sphere of the molybdenum atom in the triiodide salt. The assignment of the coordination isomer[11] of "$MoO(CNCH_3)_4Br_2I_2$" as $[MoOBr(CNCH_3)_4]^+$ is more ambiguous, both IBr_2^- and BrI_2^- anions being known.[12] Since the synthesis of this complex involves oxidation of $Mo(CO)_6$ by bromine in methanol, the product probably is attained through intermediate formation of $[MoOBr_4]^-$. Subsequent addition of iodine presumably provides the bulky BrI_2^- anion which precipitates the oxobromotetrakis(methyl isocyanide)molybdenum(IV) cation.

Structure. Although oxygen was not directly analyzed, its presence in the compounds was required to fit the analytical data. It was also detected by the well-known[13] Mo=O stretching frequency ~950 cm^{-1} (Table I). The splitting of this band into more than one component in the solid infrared spectra can be accounted for by (i) the presence of more than one oxygen atom, (ii) the existence of geometrical isomers, or (iii) intermolecular interactions in the solid state giving rise to nonequivalent site symmetries. The last possibility is strongly favored by the fact that the splitting disappears in the solution spectra and by the presence of a single sharp band in the spectrum of the *tert*-butyl derivative. The existence of (cis and trans) isomers, at least in solution, is inconsistent with the proton nmr results (Experimental Section). Assuming no fluxional character, the sharp alkyl group resonances are consistent only with C_{4v} symmetry and a trans disposition of the oxygen and halogen ligands.

As for related complexes such as $Mo(CN)_4(CNR)_4$[1,14] and $[Mo(CNR)_7]^{2+}$,[6] little useful structural information can be obtained from the C≡N stretching frequencies (Table I). It may be noted, however, that the ν_{CN} values for the oxo complexes are comparable with those of the eight-coordinate species.[1,14] It thus appears that for Mo(IV) complexes in general the shift to higher energy of ν_{CN} caused by σ-bond formation is larger than any low-frequency shift due to π back-bonding.[15]

The conductivity data (Table I) indicate fully ionized $[MoOX(CNR)_4]^+$ cations and Y^- anions in solution. The measured diamagnetism of the $[MoOCl(CNCH_3)_4](PF_6)$ salt is consistent with a spin-paired d^2 electronic configuration, as found for the $[MoO_2(CN)_4]^{4-}$ and $[MoO(OH)(CN)_4]^{3-}$ anions.[4a] By analogy to our earlier analysis of these oxocyanide complexes,[4a] we assign the 18,280-cm^{-1} electronic transition observed for $[MoOCl(CNCH_3)_4]^+$ to the $^1B_2(d_{xy})$

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$\rightarrow {}^1E(d_{xz}, d_{yz})$ transition. Since this band occurs at higher energy than in $[MoO(OH)(CN)_4]^{3-}$ ($16{,}900\ cm^{-1}$)[4a] and because the $\nu(Mo{=}O)$ frequency of $\sim 950\ cm^{-1}$ (Table I) is higher than for the oxohydroxotetracyanomolybdate(IV) complex ($921\ cm^{-1}$),[4a] the degree of oxygen to metal π bonding appears to be slightly greater in the present compounds.

Studies of the chemical reactivity of the $[MoOX(CNR)_4]^+$ cations are in progress.

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Registry No. $[MoOCl(CNCH_3)_4](PF_6)$, 50432-35-4; $[MoOCl(CNCH_3)_4](I_3)$, 50432-36-5; $[MoOBr(CNCH_3)_4](BrI_2)$, 50432-37-6; $[MoOCl(CNC_2H_5)_4(I_3)$, 50432-38-7; $[MoOCl(CN\text{-}t\text{-}C_4H_9)_4](I_3)$, 50546-24-2; $[Mo(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$, 41982-05-2; $MoCl_4$, 13320-71-3; $MoCl_5$, 10241-05-1; $Mo(CO)_6$, 13939-06-5.

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Tungstovanadate Heteropoly Complexes. V. The Ion $H_2W_{11}V^VO_{40}{}^{7-}$ and the Oxidation and Reduction of Tungstovanadates

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The yellow heteropoly anion $H_2W_{11}V^VO_{40}{}^{7-}$, isolated as potassium and tetramethylammonium salts, is obtained by chlorine oxidation of $H_2W_{11}V^{IV}O_{40}{}^{8-}$. The complex decomposes to metatungstate and cationic vanadium(V) at pH 0–2 and to $V_2W_4O_{19}{}^{4-}$ among other products at pH 5. Proton nmr demonstrates the presence of nonlabile (internal) protons in $H_2W_{11}VO_{40}{}^{7-}$ as in metatungstate. Reversible electron transfer for $H_2W_{11}VO_{40}{}^{7-} + e^- \rightarrow H_2W_{11}VO_{40}{}^{8-}$ ($E = +0.26$, pH 4) and for $VW_5O_{19}{}^{3-} + e^- \rightarrow VW_5O_{19}{}^{4}$ ($E = +0.20$ V, pH 2–4) is established by voltammetry at a wax-impregnated graphite electrode. Chemical reduction of tungstovanadates(V) and their interconversions are reported.

Introduction

In previous investigations[1] we have isolated and characterized eight tungstovanadates(IV) and -(V). This paper describes the preparation and characterization of 11-tungstovanadate(V) and cyclic voltammetry of complexes containing a single vanadium atom and summarizes the interconversion reactions of tungstovanadates(V).

Experimental Section

Reagents not obtained commercially were prepared as described.[1] Chlorine was conveniently handled as a solution in carbon tetrachloride, prepared by slowly passing the gas from a cylinder into the solvent under continuous agitation. Solutions up to 1 *M* in Cl_2 are easily prepared; they must be stored in a tightly stoppered container. The concentration was estimated by reaction of aliquots with excess aqueous KI followed by titration with sodium thiosulfate.

Chemical analyses and spectroscopic and electrochemical measurements were carried out as described previously.[1,2] A Bruker MFX-90 instrument was used for the ^1H and ^{51}V nmr measurements.

Preparation of 11-Tungstovanadate(V). (a) Potassium Salt. Potassium 11-tungstovanadate(IV) (6.5 g, 2.0 mmol) was dissolved by heating in 50–60 ml of 0.02 *M* potassium acetate–0.04 *M* acetic acid. The solution was cooled quickly to 25–40° and treated immediately with a moderate excess of Cl_2–CCl_4 solution and shaken. This resulted in a rapid color change to lemon yellow. The solution was separated from the carbon tetrachloride. A solution prepared by dissolving 5 g (50 mmol) of potassium acetate in 5 ml of water and adding 6 ml (100 mmol) of glacial acetic acid and 40 ml of 95% ethanol was added slowly to the tungstovanadate(V) solution with stirring. The potassium salt precipitated as a yellow powder; after a few minutes it was isolated by filtration (washing with ethanol-water followed by 95% ethanol). A yield of 6.1 g (90–95%) of bright lemon-yellow powder was obtained (tiny rods or laths under the microscope). *Anal.* Calcd for $K_7H_2W_{11}V^VO_{40}\cdot 14H_2O$: V, 1.57; W, 62.40; K, 8.44; H_2O, 8.34. Found: V, 1.54 (1); W, 62.40; K, 8.61 (2); H_2O, 8.05 (8); matter sum 99.86. In another preparation, the product was recrystallized as follows. The solid was dissolved in 10 ml of 0.1 *M* potassium acetate–0.5 *M* acetic acid. Saturated aqueous KCl solution (10 ml) was added, whereupon some solid precipitated. Sufficient water was added to redissolve the precipitate, and the solution was allowed to stand. When it had evaporated to 10–15 ml, much product had separated as deep yellow tabular to prismatic crystals. The crystals were isolated by washing successively with aqueous 2 *M* potassium acetate–2 *M* acetic acid buffer to remove KCl, buffer–ethanol mixture, and 95% ethanol. The air-dried crystals appeared to be slightly efflorescent and were stored in a tightly closed container. *Anal.* Found: V, 1.53; W, 62.20; K, 8.54 (3); H_2O, 8.53 by difference.

(b) Tetramethylammonium Salt. A solution of potassium 11-tungstovanadate(IV) in 100 ml of 0.01 *M* potassium acetate–0.01 *M* acetic acid was chlorinated as described above. A solution of tetramethylammonium chloride (6.6 g, 60 mmol) in 10 ml of water was added slowly with stirring to precipitate the product. The mixture was cooled in ice with stirring (about 20 min); then the product was isolated by filtration and washed with aqueous 1 *M* tetramethylammonium chloride. For recrystallization the solid was redissolved in the minimum amount (about 400 ml) of 0.01 *M* potassium acetate–0.05 *M* acetic acid. A solution of 22 g (200 mmol) of tetramethylammonium chloride in 10 ml of water was added to precipitate the product. After the mixture was stirred for 20 min, the solid was isolated by filtration (washed successively with aqueous 1 *M* tetramethylammonium chloride, ethanol–water, and ethanol). The air-dried product consisted of 6.0 g (about 85%) of bright lemon-yellow powder (tiny six-sided laths under the microscope). *Anal.* Calcd for $((CH_3)_4N)_6H(H_2W_{11}V^VO_{40})\cdot 4H_2O$: V, 1.58; W, 62.55; C, 8.92; H, 2.59. Found: V, 1.54 (1); W, 62.56; C, 8.83; H, 2.25.

(c) Attempt to Obtain an Ammonium Salt. Substitution of ammonium 11-tungstovanadate(IV) and ammonium acetate for the potassium salts in the above procedure did not result in quantitative oxidation to the vanadate(V) complex because of reactions of ammonium ion with the chlorine. The reaction mixtures had an odor like that of hypochlorous acid, in contrast to the other preparations.

Results and Discussion

11-Tungstovanadate(V). The method of preparation of this anion indicates that it has a Keggin structure based on that of metatungstate, $H_2W_{12}O_{40}{}^{6-}$. The following evidence also supports this conclusion. (1) The tetramethylammonium salt formed solid solutions with the corresponding meta-

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[1] (a) C. M. Flynn, Jr., and M. T. Pope, *Inorg. Chem.*, 10, 2524 (1971); (b) *ibid.*, 10, 2745 (1971); (c) *ibid.*, 11, 1950 (1972); (d) C. M. Flynn, Jr., H. So, and M. T. Pope, *ibid.*, 12, 1626 (1973).

[2] D. P. Smith and M. T. Pope, *Inorg. Chem.*, 12, 331 (1973).