coupled rotations of the six water molecules about the M–O bonds. Each water molecule is rotated 45°, but depending on the overall direction of the six coupled rotations, one arrives at either the all-horizontal or the all-vertical conformation. In the $[Mo(H_2O)_6]^{3+}$ ion the angle of rotation is 22 (3)° and the conformation is intermediate between the T_h and the all-horizontal D_{3d} conformations (cf. Figure 2).

Generally, the symmetry lowering from T_h to D_{3d} splits the triply degenerate t_{2g} orbital level into a nondegenerate $a_{1g}(D_{3d})$ level and a doubly degenerate $e_g(D_{3d})$ level. The absolute magnitude of this splitting amounts to $3e_{\pi\perp}$ in an angular overlap model[13] description, where $e_{\pi\perp}$ is the parameter associated with the water π orbital, which is perpendicular to the molecular plane, and where $e_{\pi\parallel}$ is assumed to vanish. As also found[5] by other methods the energetic ordering of the orbital levels is opposite in the two conformations: In the all-horizontal conformation the $e_g(D_{3d})$ level is the lower; in the all-vertical conformation the $a_{1g}(D_{3d})$ level is the lower. In the AOM description the splitting of the t_{2g} orbital level follow the barycenter principle, i.e. the $a_{1g}(D_{3d})$ level has the relative energy $\pm 2e_{\pi\perp}$ and the $e_g(D_{3d})$ level the relative energy $\mp e_{\pi\perp}$. On the basis of the ligand field stabilization energies associated with the D_{3d} field component one would expect[5] d^1 transition-metal hexaaqua ions to take the all-vertical conformation, d^2 ions to take the all-horizontal conformation, and d^3 ions to be equally stable in any of the three conformations and in fact in any conformation. The fact that cesium titanium[14] (d^1), cesium vanadium[3] (d^2), and cesium chromium[3] (d^3) alums, as well as the alums of closed-shell trivalent metal ions, have trivalent metal ions in conformations that are very similar to that of $[Mo(H_2O)_6]^{3+}$ (Figure 2) indicates, however, that the electronic structure has little influence on the conformation found in the alums. Rather it is the hydrogen-bonding pattern of the crystal that determines the conformation of these planarly ligated hexaaqua ions (Figure 3).

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Supplementary Material Available: Table SI, listing thermal parameters (1 page); a table of structure factors (6 pages). Ordering information is given on any current masthead page.

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Vanadium-51 NMR Spectroscopy of Tungstovanadate Polyanions. Chemical Shift and Line-Width Patterns for the Identification of Stereoisomers[1]

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Vanadium-51 NMR spectra are reported for several tungstovanadate polyoxoanions, including $V_xW_{6-x}O_{19}^{(2+x)-}$ (x = 1–3), α-$SiV_xW_{12-x}O_{40}^{(4+x)-}$ (x = 1–3), β_1-, β_2-, and β_3-$SiVW_{11}O_{39}^{5-}$, α-$PV_2W_{10}O_{40}^{5-}$ (mixture of isomers), $VV_2W_{10}O_{40}^{5-}$ (mixture of isomers), and $VV_3W_9O_{40}^{6-}$ (mixture of isomers). Two-bond coupling of ^{51}V to ^{183}W was resolved in spectra of $VW_5O_{19}^{3-}$ and α-$BVW_{11}O_{40}^{6-}$. The pH dependence of the chemical shift permits evaluation of pK_a's for $HV_2W_4O_{19}^{3-}$ and for α- and β-$HSiV_3W_9O_{40}^{6-}$. There is a linear correlation between δ and the square root of the line width for structurally related anions such as $RVW_{11}O_{40}^{n-}$ (R = H_2, B, Si, P). As more adjacent VO_6 octahedra are incorporated into a polyanion structure, both line width and chemical shift increase. The effect on line width is greater if the VO_6 octahedra share corners, and the effect on δ is greater if the VO_6 groups share edges. This pattern enables the identification of resonance lines for the 1,2- and 1,4-isomers of $PV_2W_{10}O_{40}^{5-}$ and $VV_2W_{10}O_{40}^{5-}$ in spectra of samples containing all possible stereoisomers and of the line for the 1,4,9-isomer of $VV_3W_9O_{40}^{6-}$ in a mixture of at least 13 isomers.

Characterization and structural identification of solute species by NMR spectroscopy is dramatically advancing the field of heteropoly- and isopolyanion chemistry. In particular, chemical shifts of ^{17}O NMR lines,[2] relative line intensities,[3] and connectivity patterns revealed by $^{183}W\cdots{}^{183}W$ coupling[4] are powerful structure indicators. However, both ^{17}O and ^{183}W are difficult nuclei to observe on account of low natural abundance or low inherent sensitivity, and satisfactory NMR spectra require the use of concentrated solutions and long accumulation times. In contrast, ^{51}V is an abundant, NMR-sensitive nucleus[5] and spectra are easily and rapidly recorded by normal FT techniques on millimolar solutions. Indeed, several earlier ^{51}V NMR studies of polyvanadates were made by using CW techniques.[6] At present there is no satisfactory correlation between structure and ^{51}V spectral parameters for polyanion solutions. We have therefore investigated several series of tungstovanadate heteropolyanions, including mixtures of stereoisomers, to seek structure–spectra correlation patterns and to explore the value of ^{51}V NMR spectra in this field.

Experimental Section

Preparation of Compounds. Hexametalate Salts. Tetra-*n*-butylammonium pentatungstovanadate was prepared according to Flynn's

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method.[7] Anal. Calcd (found) for $[(C_4H_9)_4N]_3VW_5O_{19}$: C, 28.80 (28.81); H, 5.44 (5.10); N, 2.10 (2.08); V, 2.55 (2.75); W, 45.93 (46.20). A sample enriched in ^{183}W was prepared similarly, by starting with 199 mg of WO_3 (82.5% ^{183}W, Union Carbide Corp), and was identified by its IR spectrum. Water-soluble **tetramethylammonium pentatungstovanadate** and **potassium tetratungstodivanadate** were also prepared by literature methods[6] and identified by their IR spectra. **Sodium tritungstotrivanadate** was prepared by a modification of the method reported by Takezhanova et al.[8] A 300-mL quantity of 1 M Na_2WO_4 was added to 300 mL of 1 M $NaVO_3$, and the aqueous solution was then heated to 70–80 °C. This was followed by the dropwise addition of dilute HCl to pH 7–8, whereupon the color changed from yellow to red-orange. The solution was maintained at 70–80 °C and pH 7–8 for 3–8 h. After 1–2 days at room temperature, the solution deposited efflorescent orange crystals with some yellow powder. The product was filtered and washed with a small amount of cold water. The preparation in which the reaction solution had been heated for 8 h appeared to yield a smaller amount of the yellow powder. Recrystallization of 5 g of the orange crystals in 3 mL of hot water gave a final yield of ~20%. Anal. Calcd for $Na_5V_3W_3O_{19}\cdot 12H_2O$: V, 11.41; W, 41.17; Na, 8.58. Found (recrystallized product from the 8-h preparation): V, 11.42; W, 40.45; Na, 8.56; W/V, 0.98/1; Na/V, 5.07/3. Found (product of 8-h preparation before recrystallization): V, 11.18; W, 40.87; Na, 8.14; W/V, 1.0/1; Na/W, 4.77/1.

Keggin Anion Derivatives. α-Cesium 11-Tungsto-1-vanado(IV)silicate. The α-$SiV^{IV}W_{11}O_{40}^{6-}$ anion was prepared by adding a stoichiometric amount (2.0 g) of the potassium salt of α-$SiW_{11}O_{39}^{8-}$ [9] to 30 mL of an acetate-buffered solution (pH 4.7) containing 0.133 g of $VOSO_4$. The color changed to purple. The solution was stirred for a few minutes, and then the cesium salt of the product was precipitated by the addition of a saturated aqueous solution of ~0.7 g of CsCl. The product was filtered, washed with distilled water, and air-dried. The electronic spectrum in 0.5 M NaOAc (pH 4.7) was in excellent agreement with that in the literature,[10] as was the cyclic voltammogram.[10] For NMR measurements, a solution of α-$SiV^{IV}W_{11}O_{40}^{6-}$ was oxidized with bromine to yield a yellow solution of $SiV^{V}W_{11}O_{40}^{5-}$. The stability of the oxidized anion was verified by cyclic voltammetry.

β-Sodium 9-Tungstosilicate. This salt was prepared according to the method of Ortēga.[11] A polarogram of a 5×10^{-4} M solution in 0.5 M Tris and 0.5 M LiCl at pH 8 agreed with that reported in the literature.[12]

β_1-11-Tungsto-1-vanado(IV)silicate. A stoichiometric amount of solid β_1-$Na_8SiW_{11}O_{39}$[9] was added to an acetate-buffered solution (pH 4.7) of ~0.01 M $VOSO_4$ to produce the β_1-$SiV^{IV}W_{11}O_{40}^{6-}$ anion. The electronic spectrum of the blue-green solution was in excellent agreement with that reported in the literature.[10] For NMR measurements, a solution of the anion was oxidized with bromine to produce a yellow solution of β_1-$SiV^{V}W_{11}O_{40}^{5-}$.

β_2-Cesium 11-Tungsto-1-vanado(IV)silicate. The cesium salt of $SiV^{IV}W_{11}O_{40}^{6-}$ was prepared by the addition of a stoichiometric amount (1.00 g) of solid β_2-$K_8SiW_{11}O_{39}$[9] to an acetate-buffered solution (pH 4.7) containing 65 mg of $VOSO_4$, whereupon the color changed to purple. The cesium salt was precipitated by the addition of an aqueous solution of CsCl. The purple salt was filtered off, washed with distilled water, and air-dried. The electronic spectrum of an acetate-buffered solution (pH 4.7) was in excellent agreement with that reported in the literature.[10] For NMR measurements, a solution of the anion was oxidized with bromine to produce a yellow solution of β_2-$SiV^{V}W_{11}O_{40}^{5-}$.

β_3-11-Tungsto-1-vanado(IV)silicate. A stoichiometric amount of solid β_3-$K_8SiW_{11}O_{39}$[9] was added to an acetate-buffered solution (pH 4.7) of ~0.01 M $VOSO_4$, to produce the β_3-$SiV^{IV}W_{11}O_{40}^{6-}$ anion. The electronic spectrum of the blue-green solution was in excellent agreement with that reported in the literature.[10] For NMR measurements, a solution of the anion was oxidized with bromine to produce a yellow solution of β_3-$SiV^{V}W_{11}O_{40}^{5-}$.

α-10-Tungsto-2-vanado(V)silicate. An aqueous solution of the potassium salt of α-$SiV^{IV}V^{V}W_{10}O_{40}^{7-}$ [13] was oxidized with bromine to produce an orange-red solution. Cyclic voltammograms (containing two one-electron V^{V}/V^{IV} reduction waves) of the oxidized anion, in acetate buffer (pH 5), as compared to that of the reduced anion,[13] confirmed the stability of the oxidized polyanion.

Samples of potassium 9-tungsto-3-vanado(V)silicates (α and β isomers) were kindly prepared and supplied by Professor A. Tézé at the Université Pierre et Marie Curie, Paris, France.

α-11-Tungsto-1-vanado(V)phosphate. The potassium salt of $PV^{IV}W_{11}O_{40}^{5-}$ [14] was dissolved in a buffered solution, pH ~2.5–3.2, and immediately oxidized with bromine to produce a yellow solution of $PV^{V}W_{11}O_{40}^{4-}$. Cyclic voltammograms of the oxidized anion, as compared to that of the reduced anion, confirmed the stability of the oxidized anion.

α-Tetra-*n*-butylammonium 11-Tungsto-1-vanado(V)phosphate. A solution of tetra-*n*-butylammonium bromide was added to a solution of $PV^{V}W_{11}O_{40}^{4-}$, and the precipitated salt was filtered off, washed with water, air-dried, and recrystallized from 1:1 methanol–acetonitrile. **Potassium 10-tungsto-2-vanado(IV,V)phosphate** (an equimolar mixture of the (IV,IV) and (IV,V) salts) was prepared and purified according to Pope et al.[15] Anal. Calcd for $K_{6.5}PV_2W_{10}O_{40}\cdot 16H_2O$: V, 3.23; W, 58.30; K, 8.06. Found: V, 3.35; W, 58.28; K. 8.04. For NMR measurements, solutions of the potassium salt of the reduced anion were oxidized with bromine.

Potassium 11-Tungsto-1-vanado(IV)borate. Two different procedures were carried out to prepare the potassium salt of $BV^{IV}W_{11}O_{40}^{7-}$. In the first, 1 g of solid $K_9BW_{11}O_{39}$ was added to 6 mL of an acetate-buffered solution (pH 5) of 99 mg of $VOSO_4$, whereupon the color changed to purple. After filtration, the addition of 0.45 g of potassium chloride to the filtrate yielded a purple powder, which was washed with distilled water and air-dried. In acetate buffer (pH 6) the cyclic voltammogram showed a clean V^{V}/V^{IV} reduction wave in agreement with that reported in the literature.[16] For NMR measurements, a solution of the anion was oxidized with bromine to yield a yellow solution. The stability of the oxidized anion was confirmed with cyclic voltammetry. In the second procedure, the potassium salt of $BV^{IV}W_{11}O_{40}^{7-}$ was prepared according to the method of Altenau et al.[16] The pH of a solution of 75 g (0.22 mol) of $Na_2WO_4\cdot 2H_2O$ in 200 mL of water was adjusted to pH 6.3 with acetic acid, and 1.24 g (40 mmol) of boric acid, H_3BO_3, was added. The solution was heated to 80–90 °C, and an aqueous solution of 3.98 g (1 mmol) of $VOSO_4$ was added, whereupon the color changed to purple. Thirteen grams of potassium chloride was added to the hot solution, and the product crystallized upon cooling. The product was recrystallized in acetate buffer (pH 5) to yield cubic crystals. In acetate buffer (pH 6) the cyclic voltammogram showed two V^{IV}/V^{V} reduction waves, one at the potential observed for $BVW_{11}O_{40}^{7-}$ prepared by the first method and the other at a potential ~0.1 V more positive. For NMR measurements, a solution of the anion was oxidized with bromine, whereupon the color changed to yellow. Cyclic voltammetry confirmed the stability of the oxidized polyanion. **Potassium 9-tungsto-4-vanadate**, $K_6V_4W_9O_{40}\cdot 24H_2O$, and **potassium 10-tungsto-3-vanadate**, $K_5V_3W_{10}O_{40}\cdot 20H_2O$, were prepared as described earlier and compared with authentic samples.[17]

Analysis. Carbon, hydrogen, nitrogen, vanadium, tungsten, sodium, potassium, cesium, and silicon analysis were made by Galbraith Laboratories, Knoxville, TN.

Electrochemical Measurements. Voltammetry. Samples for cyclic voltammetry studies were usually prepared in aqueous solution having a concentration range of $(1–10) \times 10^{-4}$ M with 0.5 M NaOAc/0.5 M LiCl, 1 M KOAc, or 1 M NaOAc as supporting electrolyte. For tetra-*n*-butylammonium (TBA) salts of polyanions, propylene carbonate was the solvent and 0.2 M $(TBA)ClO_4$ was the supporting electrolyte. A combination of McKee-Pederson modules consisting of two millivolt sources (Model MP-1008B), a voltammetry controller (MP-1042), an integrator (MP-1012), an electrometer/operational amplifier (MP-1031), a chopper-stabilized operational amplifier (MP-1031), an impedance selector (MP-1009A), and an operational amplifier (MP-1006C), housed in a Mckee-Pederson cabinet, attached to a Hewlett-Packard Moseley X-Y recorder (Model 7035B) were used. A polarographic cell containing a Ag/AgCl reference electrode, a saturated KCl bridge, a glassy-carbon working electrode (Princeton Applied Research Model 9333), and a platinum wire as the counter electrode was used.

Controlled-Potential Electrolyses. A Brinkman Wenking potentiostat (Model 70TST) was used for oxidations and reductions of polyanions in solution. A digital Koslow Scientific Co. coulometer (Model 541) was attached in series to the potentiostat in order to determine the number of microequivalents per mole involved in the electrochemical process. All

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electrolyses were carried out in aqueous solution. The electrolysis cell contained a Ag/AgCl reference electrode and graphite cloth (Union Carbide Corp., X2010) serving as the working electrode. A KCl salt bridge connected the solution compartment to a solution of 0.1 M H_2SO_4, in which a few drops of hydrazine hydrate was added and a platinum wire, serving as the counter electrode, was placed.

Polarography. Samples having a concentration of 5×10^{-4} M were prepared in 0.5 M NaOAc (pH 4.7) or 0.5 M tris(hydroxymethyl)aminomethane (pH 8.5), with 0.5 M LiCl as supporting electrolyte. Polarograms were obtained with a Heath Model EUA-19-2 polarography module and Model EUA-19-4 power supply and a Heath model EUA-20A servo recorder along with a polarographic cell containing a Ag/AgCl reference electrode, a dropping mercury electrode, and a platinum wire as the counter electrode.

NMR Spectroscopy. All NMR spectra were obtained in the pulse mode with a wide-band multinuclear probe and an internal deuterium lock. The deuteriated solvents providing the internal lock signal were usually D_2O (50–99.7%, Aldrich or Merck Sharp and Dohme), acetonitrile-d_3 (99%, Merck Sharp and Dohme), and methylene chloride-d_2 (99%, Merck Sharp and Dohme). Spinning 10-mm NMR tubes (Thompson-Packard, Inc.) were used to obtain the spectra. Most spectra were obtained at the normal probe temperature (room temperature) of the spectrometer (~30 °C on the Bruker WH/HFX90 instrument). The majority of the experiments were carried out on a Bruker WH/HFX90 NMR spectrometer (Georgetown University) equipped with a Nicolet BNC-12 computer and a Programmed Test Sources, Inc., Model 160 frequency synthesizer. Some NMR spectra were obtained at higher fields by using spectrometers equipped with superconducting magnets. These spectrometers are as follows: a home-built NMR spectrometer equipped with a Bruker 270-MHz magnet and a Nicolet 1180 computer;[18] a Bruker WM300 NMR spectrometer;[19] a Bruker WM400 NMR spectrometer;[20] a Nicolet NT500 NMR spectrometer equipped with an Oxford magnet.[21] Methods used to measure chemical shifts involved substitution of the sample and reference NMR tubes while the reference frequency was stored in the computer memory and later recalled to calculate chemical shifts. Usually, an external reference (the neat reference liquid added to a capillary inserted into an NMR tube containing the lock solvent) was used. In this case, the lock for the reference tube was provided by the same solvent used to make the sample solution, but in pure form (i.e., the lock solvent was not diluted by the addition of other compounds). Occasionally, a secondary reference (an appropriate compound with a known chemical shift) was also used.

Vanadium-51 Spectra. At 23.67 MHz, the spectra were obtained on the Bruker WH/HFX90 NMR spectrometer. The spectra were accumulated with a 90° (5.1-μs) pulse. Vanadium oxytrichloride, $VOCl_3$, provided the external reference. Chemical shifts were usually measured at 23.670 600 MHz, with use of a sweep width (SW) of 20 000 Hz, 4K real data points, and a repetition rate (acqt) of 0.2 s. At 70.98 MHz, the spectra were recorded by Dr. J. Wooten on the home-built spectrometer equipped with a 270-MHz magnet using a 25-μs pulse. At 78.906 MHz, the spectra were recorded on the WM300 spectrometer using a 30-μs pulse. At 105.26 MHz, the spectra were obtained on the Bruker WM400 spectrometer using a 90° pulse (30 μs) and the chemical shifts were referenced externally to $VOCl_3$. At 131.57 MHz, the spectra were obtained on the Nicolet NT500 spectrometer using a 9-μs pulse and a secondary reference was provided by α-$SiVW_{11}O_{40}{}^{5-}$ in 0.25 M NaOAc (50% D_2O; pH 4.7) at −548.3 ppm.

Phosphorus-31 Spectra. The external reference was provided by 85% H_3PO_4. At 36.44 MHz, the spectra were obtained on the Bruker WH/HFX90 spectrometer using a 30° (5.0-μs) pulse. At 202.44 MHz, the spectra were recorded on the Nicolet NT500 NMR spectrometer using a 7-μs pulse.

Boron-11 Spectra. Chemical shifts were measured with respect to 0.1 M H_3BO_3 (98% D_2O). The spectra were obtained at 28.88 MHz on the Bruker WH/HFX90 spectrometer using a 13.5-μs pulse.

Electronic and vibrational spectra were recorded on a Cary 14 spectrophotometer and on Perkin-Elmer grating infrared spectrophotometers, Models 225 and 457, using KBr disks.

Results and Discussion

Lindqvist-Structure Hexametalate Anions. Vanadium-51 NMR data for these anions are summarized in Table I. A previously noted large solvent shift of ca. 16 ppm for $VW_5O_{19}{}^{3-}$ in water and CD_3CN is confirmed. In the latter solvent the line width of the ^{51}V resonance is narrow enough to permit direct observation of ^{51}V–O–^{183}W spin coupling (see Figure 1). A value of $^2J = 10.8$ Hz was estimated by simulation (assuming that only coupling to the cis-related tungsten atoms was observed). Also shown in Figure 1 is the spectrum of the same anion enriched with 82.5% ^{183}W. The envelope of this spectrum was satisfactorily simulated by the summation of the appropriate multiplets (46% pentet, 39% quartet, 13% triplet) with the same J value.

Table I. ^{51}V NMR Data[a] for the Hexametalate Anions

compd	$[V]_T$, M	medium	$-\delta$[b]	$\Delta\nu_{1/2}$, Hz
$(Bu_4N)_3VMo_5O_{19}$[c]	0.02	CD_3CN	487.0	18 ± 2[d]
$(Bu_4N)_3VW_5O_{19}$[c]	0.05	CD_3CN	507.1	5 ± 1[e,f]
$[(CH_3)_4N]_3VW_5O_{19}$	0.01	pH 2.5	522.9	13 ± 5
$K_4V_2W_4O_{19}$	0.01	pH 4.7	508.3	24 ± 5
$Na_5V_3W_3O_{19}$	0.02	pH 8.5	496.7	43 ± 5
	0.02	pH 7.5	500 ± 1	74 ± 5

[a] Spectra accumulated at 23.670 600 MHz; SW = 20 000 Hz (4K real points); acqt = 0.2 s; NS = 1300–5200; $T \approx 30$ °C unless otherwise noted. [b] ±0.4 ppm; δ vs. $VOCl_3$ by external substitution referencing with 98% D_2O as reference lock. [c] Bu = n-C_4H_9. [d] Line width measured with SW = 1000 Hz (4K real points) at 23.666 000 MHz; acqt = 4 s. [e] Line width (after deconvolution, see Figure 1, J = 11 Hz) measured with SW = 2000 Hz (4K real points) at 23.666 780 MHz; acqt = 2 s. [f] 3.2 (0.3) Hz at 80 °C.

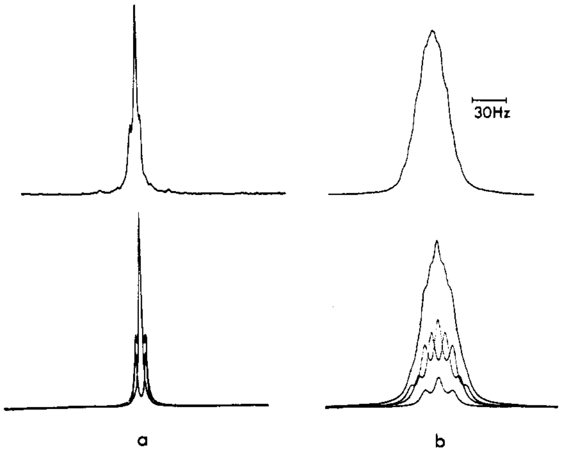

Figure 1. (a) 23.67-MHz ^{51}V NMR spectrum of $(Bu_4N)_3VW_5O_{19}$ in CD_3CN at 80 °C (upper) and the simulated spectrum (lower). (b) 78.9-MHz ^{51}V NMR spectrum of $(Bu_4N)_3VW_5O_{19}$, enriched with 82.5% ^{183}W, in CD_3CN at 80 °C (upper) and the simulated spectrum (lower).

Domaille has verified that ^{51}V line widths are, as expected, controlled by quadrupolar relaxation.[4d] We therefore can interpret variations in line width according to the conventional equation

$$\frac{1}{T_2} = \frac{1}{T_1} = \frac{3}{40}\,\frac{2I+3}{I^2(2I-1)}\left(1+\frac{\eta^2}{3}\right)\left(\frac{e^2Qq}{h/2\pi}\right)^2\tau_c \qquad (1)$$

in which I and eQ are respectively the spin and quadrupole moment of ^{51}V, eq is the electric field gradient (EFG), and η is the asymmetry parameter. The correlation time τ_c can for polyanions be satisfactorily estimated from the Stokes–Einstein equation

$$\tau_c = \frac{4\pi r^3\eta_s}{3kT} \qquad (2)$$

where r is the anion radius and η_s is solvent viscosity. The narrow line width for $VW_5O_{19}{}^{3-}$ in CD_3CN implies that, in spite of the terminal V=O bond, the field gradient at the vanadium nucleus is very small. Akitt and McDonald[22] have demonstrated that there are numerous noncubic arrangements of ligands that can generate zero field gradients at a given nucleus, and so the small EFG for vanadium in $VW_5O_{19}{}^{3-}$ is not necessarily bizarre.[23] The line width

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(18) National Institutes of Health, Bethesda, MD (Dr. J. Wooten).
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(22) Akitt, J. W.; McDonald, W. S. *J. Magn. Reson.* **1984**, *58*, 401.
(23) If the (admittedly unrealitic) assumption is made that only nearest-neighbor W^{6+} ions contribute, then the EFG at the vanadium nucleus is zero in $[VW_5O_{19}]^{3-}$.

Table II. ^{51}V NMR Data[a] for $K_4V_2W_4O_{19}$[b] vs. pH

pH[c]	$-\delta$[d]	$\Delta\nu_{1/2}$, Hz[e]	pH[c]	$-\delta$[d]	$\Delta\nu_{1/2}$, Hz[e]
7.6	508.5	23	3.0	512.6	33
6.1	508.5	24	2.6	515.9	34
4.7	508.3	24	2.4	518.8	38
4.0	509.1	26	2.0	521.1[f]	42
3.3	511.0	28	1.4	524.4[f]	

[a] Spectra accumulated at 23.670600 MHz; SW = 20000 Hz (4K real points); acqt = 0.2 s; NS = 224–3040; T = 30 °C. [b] In 0.25 M NaOAc buffer (50% D_2O); $[V]_T$ = 0.01 M. [c] pH adjusted with HCl and NaOH. [d] ±0.4 ppm; δ vs. $VOCl_3$ by external substitution referencing using 98% D_2O as reference lock. [e] ±5 Hz. [f] V_2W_4 begins to decompose into VW_5 at this pH. The VW_5 resonance appears at −523.2 ppm and grows, with respect to the V_2W_4 resonance, over time.

for the same anion in aqueous buffer (pH 2.5), at the same temperature, is 13 Hz. The difference, a factor of 2.6, can almost be entirely accounted for by the difference in solvent viscosities (0.349 and 0.890 cP, respectively, at 25 °C) because all other factors in the above equations remain unchanged. Since it might be expected that the field gradient at V in $VMo_5O_{19}^{3-}$ would be identical with that in $VW_5O_{19}^{3-}$, a sample of the molybdate[2a] was examined. The line width was found to be about 3 times that of the tungstate. We tentatively attribute the increased line width to an intermediate rate of relaxation of the more abundant (25% vs. 14.3%) magnetic molybdenum isotopes to which the V nucleus would be coupled.

The ^{51}V spectrum of $V_2W_4O_{19}^{4-}$ consists of a single line, the width and chemical shift of which vary below pH ca. 4.7. As the pH is lowered, the line shifts upfield and broadens (see Table II). We attribute these changes to protonation of the polyanion. Chauveau[24] has reported a pK_a of 2.7 for $HV_2W_4O_{19}^{3-}$ from spectroscopic data, and a plot of δ vs. pH is in satisfactory agreement with this above pH 2.4. In more acidic solutions $VW_5O_{19}^{3-}$ (δ −523.2) dominates the spectrum. The chemical shift for $HV_2W_4O_{19}^{3-}$ is estimated to be −522 ppm. Although the ^{51}V NMR data do not directly address the problem of structure, ^{17}O and ^{183}W NMR have shown that the vanadium atoms occupy cis octahedra in the hexametalate structure.[4d,25] The relatively large effect of protonation upon the vanadium chemical shift (13.5 ppm) is consistent with protonation at the unique V–O–V oxygen atom as originally suggested by Kazanskii[26] and subsequently by ^{17}O NMR.[25]

The early literature[26] contains descriptions of a variety of vanadium–tungsten heteropoly complexes including salts with V:W mole ratios of 1:2 and 1:1. The synthetic procedures involved boiling solutions of paratungstate with vanadate(V) or tungstic acid with vanadium(V) oxide, and salts having the formulations $2M_2O{\cdot}V_2O_5{\cdot}4WO_3{\cdot}nH_2O$ and $5M_2O{\cdot}3V_2O_5{\cdot}6WO_3{\cdot}5H_2O$ (M = univalent cation) were described.

The existence of the former series of salts, later reformulated as containing $V_2W_4O_{19}^{4-}$, was confirmed in solution by Chauveau[24] (who also identified $VW_5O_{19}^{3-}$), and the salts were later isolated by Flynn and Pope.[7] Although chemical analysis reported in the early literature gave V:W ratios of 1:1 (Anal. Calcd for $5Na_2O{\cdot}3V_2O_5{\cdot}6WO_3{\cdot}34H_2O$: Na_2O, 10.83; V_2O_5, 19.12; WO_3, 48.64; H_2O, 21.14. Found: Na_2O, 10.90, 10.86; V_2O_5, 19.20, 19.19; WO_3, 48.68, 48.63; H_2O, 21.40[27]), Chauveau[24] and Flynn[7,17] did not detect a tungstovanadate with V:W = 1:1. However in 1974, Il'yasova et al.[8] reported the synthesis of sodium and lithium salts of $V_3W_3O_{19}^{5-}$ that were crystallized from aqueous solutions of high pH (ca. pH 8). We have repeated the Il'yasova preparation, as described in the Experimental section. Initial ^{51}V NMR measurements on the analyzed products of these preparations indicated a mixture of $V_2W_4O_{19}^{4-}$ (−508.5 ppm) and "metavanadates" $V_4O_{12}^{4-}$ and $V_5O_{15}^{5-}$ (−574 and −583 ppm[28]) together with traces of a species with δ ca. −500. If the spectrum was recorded within a few minutes of solution preparation, the −500 ppm resonance was the major feature. Spectra recorded at different time intervals are shown in Figure 2. Note that the integrated intensities of the $V_2W_4O_{19}^{4-}$ and metavanadate peaks are equal and remain equal during the course of the evolution of the spectrum. This is consistent only with decomposition of a polyanion in which the mole ratio of V:W is 1:1, e.g.

Figure 2. 23.67-MHz ^{51}V NMR spectra of $Na_3V_3W_3O_{19}$ recorded at different times from the preparation of the solution (pH 7.5, 30 °C).

$$2H^+ + 4V_3W_3O_{19}^{5-} \rightarrow 3V_2W_4O_{19}^{4-} + 6VO_3^- + H_2O \quad (3)$$

The similarity of the IR spectrum of the solid material to that of $V_2W_4O_{19}^{4-}$ salts supports the assignment of a hexametalate structure to the species responsible for the −500 ppm line at pH 7.5. Inspection of Figure 2 reveals a small line at −515 ppm that disappears as the solution ages. At pH 8.5 the −500 ppm line appears at −496.5 ppm and the line at −515 ppm is not seen. When the solution is aged at pH 8.5, the major vanadium-containing species produced are metavanadates since $V_2W_4O_{19}^{4-}$ is unstable at this pH. We have not identified the species responsible for the resonance at −515 ppm. Two isomers ("facial" and "meridional" arrangements of VO_6 octahedra) are possible for $V_3W_3O_{19}^{5-}$. Since only one resonance was observed, we presume that the facial isomer is the major and probably only species formed, although it is conceivable (but not very likely since it is not observed at pH 8.5) that the −515 ppm line represents one of the nonequivalent vanadium atoms in the meridional isomer. Recently Maksimovskaya et al.[29] have reported ^{51}V (δ −494) and ^{17}O NMR spectra for solutions containing $V_3W_3O_{19}^{5-}$ and conclude that it is the facial isomer.

Keggin-Structure Anions: Tungstosilicates. Selected ^{51}V NMR data for tungstovanadosilicate anions are given in Table III. Of the four monosubstituted anions α-, β_1-, β_2-, and β_3-$SiW_{11}VO_{40}^{5-}$, three have chemical shifts within 1 ppm of −549 ppm, yet the lines are narrow enough that mixtures can be resolved. There are, however, small changes in δ caused by a change in solvent medium,

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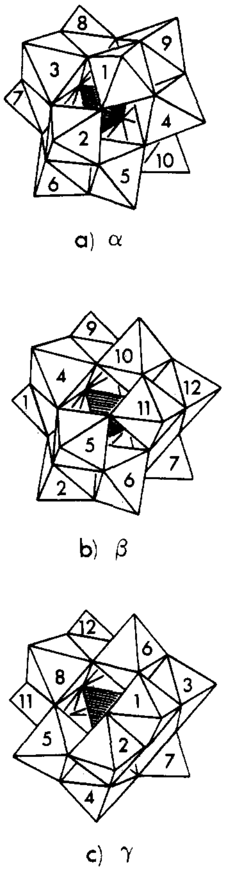
Table III. ^{51}V NMR Data[a] for $SiV_xW_{12-x}O_{40}^{(4+x)-}$[b] ($x$ = 1–3)

isomer	salt	x	pH	$-\delta$[c]	$\Delta\nu_{1/2}$, Hz
α	Cs^+	1	4.7	548.3	40 ± 5
			2.5	548.3	45 ± 5
β_1	Cs^+	1	4.7	556.4	40 ± 5
β_2	Cs^+	1	4.7	549.5 ± 0.3	75 ± 5
β_3	Cs^+	1	4.7	550.3	34 ± 3
α	K^+	2	4.7	544.8	160 ± 10
			2.0	544.2	160 ± 20
α	K^+	3	7.3	536	300 ± 40
			4.7	556.5	360 ± 40
			2.5	567	400 ± 40
			2.0[d]	570[e]	410 ± 40[e]
β	K^+	3	7.2	541	320 ± 40
			4.7	564	420 ± 40
			2.5	574	430 ± 50
			2.3[d]	574.9[f]	430 ± 50[f]

[a] Spectra accumulated at 23.670600 MHz; SW = 20000 Hz (4K real points); acqt = 0.2 s; NS = 4000–50000; T = 30 °C unless noted otherwise. [b] 50% D_2O for NaAc buffer solutions, 98% D_2O for all other solutions. [c] ±0.2 ppm; δ vs. $VOCl_3$ at 30 °C by external substitution referencing using 98% D_2O as reference lock. [d] pH adjusted with DCl. [e] 565.6 ppm and 130 (10) Hz at 80 °C. [f] 568.6 ppm and 120 (10) Hz at 80 °C.



a) α

b) β

c) γ

Figure 3. IUPAC numbering of metal atom positions in α, β, and γ isomers of the Keggin anion.

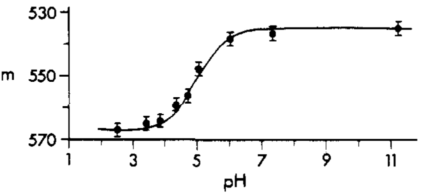


Figure 4. Plot of $\delta(^{51}V)$ vs. pH for α-1,2,3-$SiV_3W_9O_{40}^{7-}$. The line was calculated for pK_a = 4.97.

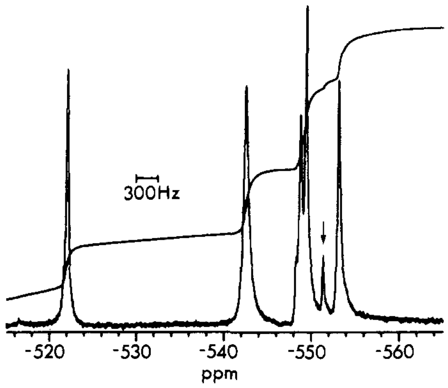


Figure 5. 131.4-MHz ^{51}V NMR spectrum of α-$K_5PV_2W_{10}O_{40}$ (pH 2.5, 80 °C). The arrow indicates the impurity of $PVW_{11}O_{40}^{4-}$.

e.g. 0.25 M sodium acetate vs. 1 M lithium acetate, but no significant effect of changing pH was seen. The site symmetry of a single vanadium atom in the Keggin structure is lower than that in the hexametalate structure (C_{4v}), and this is part of the reason for the larger line widths observed in Table III. Another contribution to the increased line widths is the longer rotational correlation time for the larger Keggin anion. The β_2 isomer contains the vanadium atom in a site adjacent to the rotated W_3 group of the β Keggin structure.[30] Such a site would be expected to have a lower local symmetry than the others, and this is reflected in the greater line width for this isomer. We have previously noted the large difference in line widths for α_1- and α_2-$P_2W_{17}VO_{62}^{7-}$, which were also attributed to effects of local symmetry.[31]

Anions containing two vanadium atoms can exist in several isomeric forms (see Figure 3 for numbering schemes[32]). The species α-$SiW_{10}V_2O_{40}^{6-}$ contains adjacent corner-shared VO_6 octahedra in the α Keggin structure (we shall denote this as α-1,2(Si)) as suggested by earlier electrochemical and ESR studies and recently confirmed by 2-D ^{183}W NMR.[4d] When a solution of this anion (pH 2) is heated to 80 °C, the single resonance splits into several (at least four between −520 and −550 ppm), and this may indicate the generation of other α-based isomers. Such isomers, and others derived from β- and/or γ-dodecametalate structures, will be discussed in a subsequent paper.

The trivanadium species α- and β-$SiW_9V_3O_{40}^{7-}$ are known to contain adjacent corner-shared VO_6 octahedra (α- and β-1,2,3 isomers) from ^{183}W NMR and precursor anion structure.[4d,33] No evidence for isomerization of these species was observed, and the pH dependence of δ could be fitted to a simple titration curve (Figure 4) by assuming monoprotonation of the anions. The values of pK_a estimated from these curves were 4.97 ± 0.10 (α) and 4.99 ± 0.15 (β).

Tungstophosphates. The ^{51}V and ^{31}P NMR data for $PW_{11}VO_{40}^{4-}$ were in satisfactory agreement with literature values.[3c,4d,34] Our values are as follows: for the potassium salt in aqueous buffers at pH 2.5 and 3.0, δ_V −554.6 ($\Delta\nu_{1/2}$ = 31 Hz), δ_P −14.83; for the tetrabutylammonium salt in CD_3CN, δ_V −548.4 ($\Delta\nu_{1/2}$ = 37 Hz), δ_P −14.47.

Our method of synthesis of α-$PW_{10}V_2O_{40}^{5-}$ leads to a mixture of stereoisomers as we and others have shown some years ago.[35] The resolution and sensitivity provided by high-field spectrometers permits us to modify our earlier conclusions. The ^{51}V NMR spectrum at 131.4 MHz of a solution of $K_5PW_{10}V_2O_{40}$ is shown in Figure 5. Besides the resonance from a $PW_{11}VO_{40}^{5-}$ impurity

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Table IV. ^{51}V NMR Data for $K_{3+x}PV_xW_{12-x}O_{40}$

	30 °C		80 °C	
sample[a]	$-\delta^b$	$\Delta\nu_{1/2}$	$-\delta^c$	$\Delta\nu_{1/2}$
K_4PVW_{11}[d]	554.34[e]	41 ± 3		
$K_5PV_2W_{10}$[f]	525.41 [1.0][g]	93 ± 5	521.72 [1.0]	43 ± 6
	545.72 [1.5]	190 ± 10	542.21 [1.5]	86 ± 9
	551.67 } [2.0]		548.11 } [1.9]	
	552.25 }		548.56 }	
	552.47 }		549.19 }	47 ± 6
	554.37[h]		551.25[h]	37 ± 6[h]
	556.38 [1.0]	69 ± 4	552.96 [1.0]	47 ± 6
$K_5PV_2W_{10}$[f,i]			521.72 [1.0]	50 ± 5
			542.24 [1.8]	92 ± 9
			548.11	
			548.6 (2) [2.4]	
			549.19	56 ± 5
			552.96 [1.2]	59 ± 5

[a] In 0.2 M $LiCO_2CH_2Cl$ buffer (98% D_2O, pH 2.5). [b] Measured at 131.394099 MHz; SW = 30000 Hz (8K real points); acqt = 0.27 s; NS = 1000–3128. [c] Measured at 131.394927 MHz; SW = 30000 Hz (8K real points); acqt = 0.27 s; NS = 272–728. [d] $[V]_t$ = 0.01 M. [e] ±0.03 ppm; with respect to $SiVW_{11}$ at room temperature (assigned as −548.30 ppm) in 0.25 M NaOAc (50% D_2O, pH 4.7), by external substitution referencing. [f] $[V]_t$ = 0.004 M. [g] Relative integrated intensities in brackets. [h] Resonance of $PVW_{11}O_{40}^{4-}$ impurity. [i] Batch without impurity of $PVW_{11}O_{40}^{4-}$.

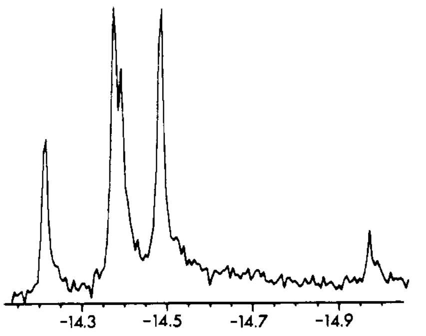

Figure 6. 202.44-MHz ^{31}P NMR spectrum of α-$K_5PV_2W_{10}O_{40}$ (pH 2.5). A correction factor of 0.75 ppm has been added to the experimental δ.[37] The resonance at 14.97 ppm is from an impurity of $PVW_{11}O_{40}^{4-}$.

in this particular sample, six other resonances are observed, three of which are clustered near −548 ppm (the poorly resolved shoulder at −548.1 ppm appears in the spectrum of each sample examined). The chemical shifts and line widths are given in Table IV and are in satisfactory agreement with previously reported spectra from lower field instruments.[6c] Of the five possible stereoisomers[36] of $PW_{10}V_2O_{40}^{5-}$, three (1,2, 1,4, and 1,11) have C_s symmetry, one (1,5) has C_2 symmetry, and one (1,6) has C_1 symmetry. If all five isomers were present, six ^{51}V resonances should be observed, assuming adequate resolution of the two resonances for the 1,6-isomer. Plausible assignments of the ^{51}V resonances will be given later on the basis of chemical shift, line width, and the pH dependence of δ. Only the two lowest field lines are affected by pH: (30 °C, 23.67-MHz data): pH 4.7, −525.2, −545.9 pp; pH 2.5, −525.8, −546.7 ppm; pH 0.3, −529.6, −547.0 ppm. The 202.44-MHz ^{31}P NMR spectrum of the same sample as that shown in Figure 5 has four resolved peaks at −14.21, −14.37, −14.39, and −14.48 ppm as well as a resonance at −14.98 ppm from the impurity of $PW_{11}VO_{40}^{4-}$[37] (see Figure 6). Since the ^{51}V spectrum indicated the presence of five isomers, we conclude that the fifth ^{31}P line is unresolved. In earlier spectra[35] only three resonances were resolved.

Table V. ^{51}V NMR Data for $K_5VV_2W_{10}O_{40}$[a]

$-\delta^b$	integral		$\Delta\nu_{1/2}$, Hz
505.3	3.8	0.38	76 ± 5
527.3	1	} 1.2	180 ± 30
530.2	9.7	}	43 ± 5
532.3	1.3	}	76 ± 5
536.0	5.4	0.54	67 ± 5
558.2		1	32 ± 4
558.8			
559.1			22 ± 4
559.4 (sh)			
559.9 (sh)			

[a] In 0.5 M HSO_4^-/SO_4^{2-} (50% D_2O, pH 2.0). Measured at 131.3940990 MHz; SW = 33000 Hz (8K real points); acqt = 0.27 s; T = 30 °C; $[V]_t$ = 0.06 M; NS = 592. [b] ±0.1 ppm; measured with respect to $SiVW_{11}$ (assigned as −548.30 ppm) in 0.25 M NaOAc (pH 4.7, 50% D_2O) by external substitution referencing.

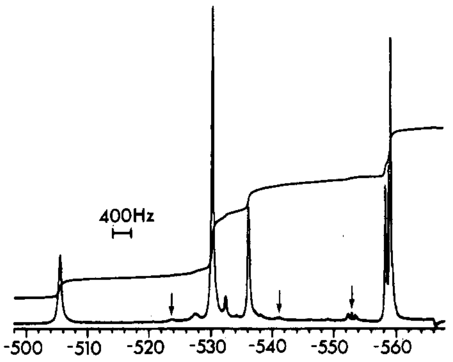

Figure 7. 131.4-MHz ^{51}V NMR spectrum of $K_5VV_2W_{10}O_{40}$ (pH 2.0). The arrows indicate the impurity of $VV_3W_9O_{40}^{6-}$.

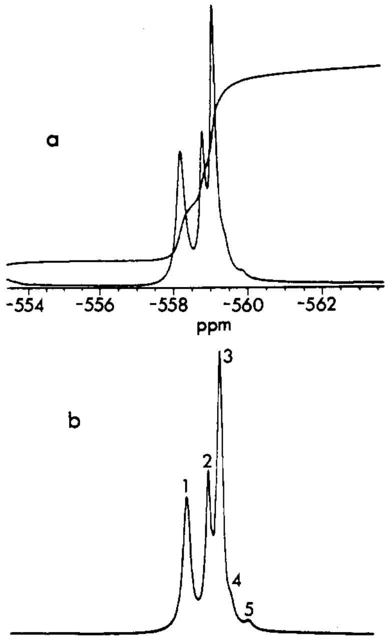

Figure 8. (a) Expansion of the region between −554 and −563 ppm of the spectrum shown in Figure 7. (b) Simulation of (a) with lines at −558.2, −558.8, −559.1, −559.4, and −559.9 ppm and relative integrated intensities of (1) 30.4%, (2) 21.9%, (3) 41.7%, (4) 4.0%, and (5) 2.0%.

Vanadium-Centered Keggin Anions. The tungstovanadate anions $VW_{12-x}V_xO_{40}^{(3+x)-}$ (x = 2–4) are known to contain a central vanadium atom in the Keggin structure.[17,39,40] Our early ^{51}V CW-NMR spectra indicated that the compounds with x = 2 and

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Table VI. ^{51}V NMR Data for $K_6VV_3W_9O_{40}$[a]

$-\delta$[b]	integral	$\Delta\nu_{1/2}$, Hz
480.5	<0.1	110 ± 10
502.5	1	160 ± 10
505.2		130 ± 10
507 ± 1 (sh)		
508.1		
509.0		90 ± 10
522.0	2	290 ± 50
525.8		
526.9 (sh)		
527.7		
530.0		
531.0		
533.4		58 ± 4
552.5 ± 0.2 (sh)	1	
552.8		20–30
553.0 ± 0.2 (sh)		
553.1		20–30
553.4 ± 0.2 (sh)		
554.0		20 ± 4

[a] In 0.25 M NaOAc (pH 4.0); measured at 131.394099 MHz; SW = 33 000 Hz (8K real points); acqt = 0.27 s; T = 30 °C; $[V]_t$ = 0.08 M, NS = 656. [b] ±0.1 ppm; measured with respect to $SiVW_{11}$ (assigned as −548.30 ppm) in 0.25 M NaOAc (pH 4.7, 50% D_2O) by external substitution referencing.

3 were formed as mixtures of stereoisomers.[6c] Current FT-NMR data at 131.39 MHz for $VW_{10}V_2O_{40}{}^{5-}$ are summarized in Table V, and a spectrum is shown in Figure 7. With the exception of the cluster of narrow lines at high field (ca. −559 ppm), the spectrum has a pattern similar to that of $PW_{10}V_2O_{40}{}^{5-}$, namely one line significantly downfield from a group of at least four others. The lines at −559 ppm are therefore assigned to the central tetrahedral vanadium atoms (the ratio of the integrated intensities of these lines to the remainder of the spectrum is 1:2.1). An expansion of these lines (Figure 8) shows the presence of the five possible isomers, although two of these are present in small amounts (estimated by simulation to be ca. 2 and 4%). This conclusion is confirmed by the remainder of the spectrum, which shows three major resonances (−505.3, −530.2, and −536.0 ppm) and two minor ones. Since the 1,6-isomer should have two V-(octahedral) lines (see above), we assume that it is present as one of the minor isomers and that its second line is overlapped by a more intense one.

NMR data for $VW_9V_3O_{40}{}^{6-}$ are summarized in Table VI, and the 131.39-MHz spectrum at pH 4 is shown in Figure 9. A spectrum of the same anion at 78.88 MHz has recently been reported[29] and is in general agreement but is less well-resolved than that shown in Figure 9. The interpretation of the spectrum is based on comparison with that of $VW_{10}V_2O_{40}{}^{5-}$. The lines at ca. −553 ppm are attributed to the central vanadiums, and expansion of this region reveals resonances corresponding to at least 7 of the 13 possible isomers. The ratio of the integrated intensity of these resonances to that of the remainer of the spectrum is 1:3.

Chemical Shifts and Line Widths. Chemical shifts and line widths of ^{51}V NMR lines are both temperature- and solvent-dependent. Within the temperature range 30–80 °C δ increases (i.e. the line moves toward higher frequency) by 3–7 ppm and line widths typically decrease by about 60%. The latter change reflects the decreased rotational correlation time of the polyanion (see eq 1 and 2). Some solvent effects, e.g. the 16 ppm shift for $VW_5O_{19}{}^{3-}$ in water and acetonitrile, are not simply accounted for by volume susceptibility differences and must indicate specific interactions. In aqueous solutions chemical shifts are not highly sensitive ($\Delta\delta < 2$) to counterion identity and concentration, polyanion concentration, and buffer identity, *unless* the anion is susceptible to protonation. The later process always results in both increased (more positive) δ and increased line width. In Table VII we summarize chemical-shift and line-width data for groups of isostructural polyanions, recorded as far as possible under comparable conditions. The data agree to within a few ppm with those of others[4d,29] when account is taken of protonation. Chemical shifts and line widths in Table VII are for the fully deprotonated anions. We note that not only do line widths and chemical shifts increase as more adjacent vanadium atoms are incorporated into the polyanion structures[41] but also that there are quantitative differences in these trends according to whether the VO_6 octahedra share edges or corners. The relative increase for $V_1 \cdots V_2 \cdots V_3$ species is greater for the Keggin anions in which VO_6 octahedra share corners than for the hexametalate and Dawson anions in which VO_6 groups share edges. In contrast, the changes in δ for the last two groups of anions is greater than for the first.

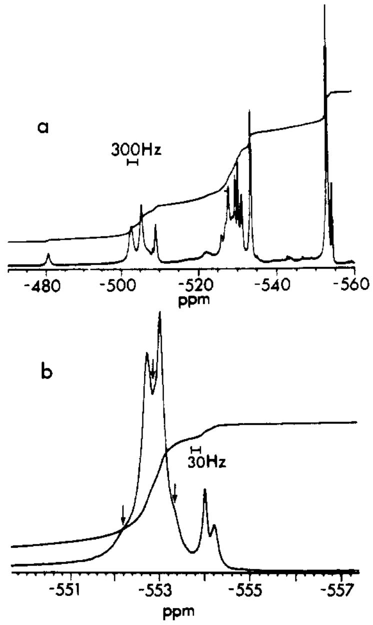

Figure 9. (a) 131.4-MHz ^{51}V NMR spectrum of $K_6VV_3W_9O_{40}$ (pH 4). (b) Expansion of the region between −550 and −557 ppm. Arrows indicate unresolved shoulders.

Table VII. Chemical Shifts and Line Widths for Isostructural Tungstovanadates[a]

no.	anion	$-\delta$	$\Delta\nu_{1/2}$, Hz
1	$VW_5O_{19}{}^{3-}$	522.9	13 (2)
2	$V_2W_4O_{19}{}^{4-}$	508.3[b]	24 (5)[b]
3	$V_3W_3O_{19}{}^{5-}$	496.7[c]	43 (5)[c]
4	α-$SiVW_{11}O_{40}{}^{5-}$	548.3	40 (5)
5	α-1,2-$SiV_2W_{10}O_{40}{}^{6-}$	544.8	160 (10)
6	α-1,2,3-$SiV_3W_9O_{40}{}^{7-}$	536[d]	300 (10)
7	α-$PVW_{11}O_{40}{}^{4-}$	554.7	31 (5)
8	α-1,2-$PV_2W_{10}O_{40}{}^{5-}$	548.6[e]	122[e]
9	α-1,2,3-$PV_3W_9O_{40}{}^{6-}$	532.5[e]	275[e]
10	α_2-$P_2VW_{17}O_{62}{}^{7-}$[f]	554.7	33 (5)
11	α-1,2-$P_2V_2W_{16}O_{62}{}^{8-}$[f]	528.3	67 (5)
12	α-1,2,3-$P_2V_3W_{15}O_{62}{}^{8-}$[f]	502.6	130 (5)

[a] In 0.25 M HOAc/NaOAc (pH 4.7); T = 30 °C unless noted otherwise. [b] In 0.25 M $CH_2ClCOOH/CH_2ClCOONa$, pH 2.5. [c] In 0.5 M NH_3, pH 8.5. [d] pH 7.3. [e] pH 2.0 (V_2); 5.7 (V_3).[4d] [f] Data from ref 31.

Under certain simplifying assumptions a linear correlation between δ and the square root of the line width is expected (and observed[42]) for quadrupolar nuclei. The origin of the correlation can be traced to equations for the line widths of quadrupolarly broadened lines (eq 1) and for paramagnetic nuclear shielding (eq 4),[5] where k' is an orbital reduction (nephelauxetic) factor,

$$\sigma_p = -(\text{const})\langle r^{-3}\rangle k'^2(\Delta E)^{-1} \qquad (4)$$

ΔE is the LUMO–HOMO separation, and the other terms have

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(41) Domaille,[4d] has also noted this.

(42) (a) ^{35}Cl: Saito, Y. *Can. J. Chem.* **1965**, *43*, 2530. (b) ^{55}Mn: Bancroft, G. M.; Clark, H. C.; Kidd, R. G.; Rake, A. T.; Spinner, H. G. *Inorg. Chem.* **1973**, *12*, 728.

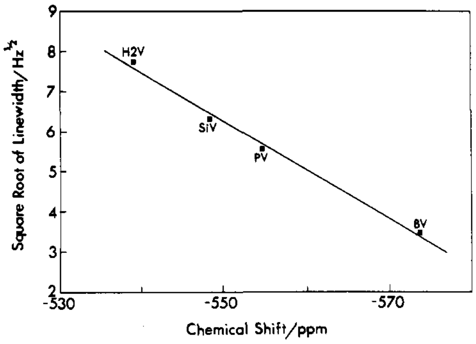

Figure 10. Plot of the square root of the line width vs. ^{51}V chemical shift for α-RVW$_{11}$O$_{40}^{n-}$ anions.

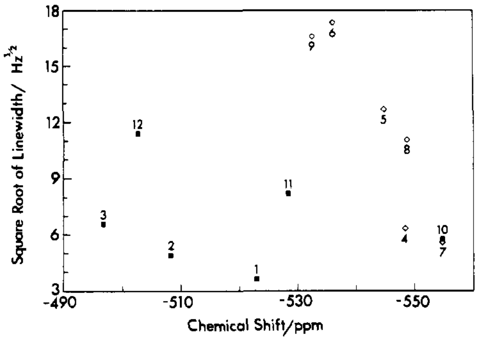

Figure 11. Plot of the square root of the line width vs. ^{51}V chemical shift for the tungstovanadate anions listed in Table VII.

their usual significance. The electric field gradient for transition-metal nuclei can be represented by eq 5,[43] where R is a

$$q = {}^4\!/_7(1 - R)\langle r^{-3}\rangle \times [-n(d_{z^2}) + n(d_{x^2-y^2}) + {}^1\!/_2 n(d_{xy}) - {}^1\!/_2\{n(d_{xz}) + n(d_{yz})\}] \quad (5)$$

Sternheimer antishielding factor and the n's are effective electronic populations of the metal's d orbitals. If comparisons are made between species of similar size and structure (therefore similar τ_c's), the square root of the line width is proportional to q. Data for monovanadium-substituted Keggin anions are plotted in Figure 10 and show a rather good correlation with a slope of 0.12 Hz$^{1/2}$ ppm^{-1}.[44,45] Data for the anions listed in Table VII are plotted in Figure 11 and fall on (or close to) three lines of slopes 0.11, 0.45, and 0.11 Hz$^{1/2}$ ppm^{-1} for anions **1–3**, **4–9**, and **10–12**, respectively. These lines quantitate the differences between anions with adjacent VO$_6$ octahedra sharing edges (**1–3**, **10–12**) and those with VO$_6$ octahedra sharing corners (**4–9**). That the effect on line width (field gradient) is more dramatic when the VO$_6$ octahedra share corners (V–O–V angle ~150°) is consistent with the greater extent of V–O–V π interaction compared with the case of edge-shared octahedra (V–O–V $\approx$ 100°).[46]

The patterns shown in Figure 11 allow us to make some statements about the assignment of ^{51}V NMR lines in the spectra of isomer mixtures. We begin with PV$_2$W$_{10}$O$_{40}^{5-}$ (Table IV and Figure 5) and assign the broadest line, at −545.7 ppm, to the 1,2-isomer; Domaille has independently prepared this species (his data are recorded in Table VII and confirm this particular assignment). The line at −525.4 ppm is assigned to the 1,4-isomer on account of its extreme δ, 29 ppm downfield from that of PVW$_{11}$O$_{40}^{4-}$. We note here that the local environment of V in the latter anion is identical with that in α_2-P$_2$VW$_{17}$O$_{62}^{7-}$ (δ −554.7) and that 1,4-PV$_2$W$_{10}$O$_{40}^{5-}$ is analogous to α-1,2-P$_2$V$_2$W$_{16}$O$_{62}^{8-}$ (δ −528.3). The remaining lines in Figure 5 must be assigned to the three isomers with isolated V atoms; note that the chemical shifts are close to that of PVW$_{11}$O$_{40}^{4-}$ and that all are upfield from those of the "adjacent" isomers. Of the three remaining isomers only one (1,6) has inequivalent V atoms, and we tentatively assign the lines at −552.5 and −556.4 ppm to this species on the basis of their apparent equal integrals.

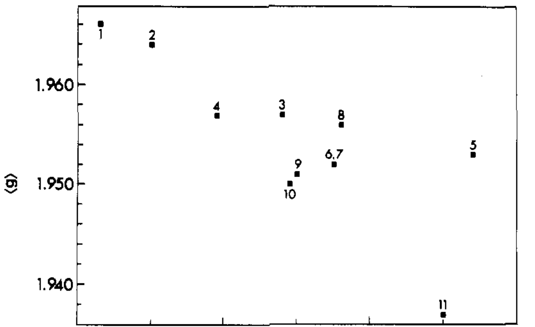

Figure 12. ⟨g⟩ for metallovanadates(IV) vs. δ(^{51}V) for the corresponding metallovanadates(V). Anions: (1) VW$_5$O$_{19}^{3-}$; (2) α-PVMo$_{11}$O$_{40}^{4-}$; (3) α-SiVW$_{11}$O$_{40}^{5-}$; (4) H$_2$VW$_{11}$O$_{40}^{7-}$; (5) α-BVW$_{11}$O$_{40}^{6-}$; (6) α-PVW$_{11}$O$_{40}^{4-}$; (7) α_2-P$_2$VW$_{17}$O$_{62}^{7-}$; (8) β_1-SiVW$_{11}$O$_{40}^{5-}$; (9) β_2-SiVW$_{11}$O$_{40}^{5-}$; (10) β_3-SiVW$_{11}$O$_{40}^{5-}$; (11) α_1-P$_2$VW$_{17}$O$_{62}^{7-}$.

Analogous arguments can be applied to the spectrum of VV$_2$W$_{10}$O$_{40}^{5-}$ (Table V and Figure 7) although the relative abundances of the different isomers are different from those observed for the sample of PV$_2$W$_{10}$O$_{40}^{5-}$. Thus the broad line at −527.3 ppm attributed to the 1,2-isomer is only a minor component of the spectrum. The line at low field (−505.3 ppm) is assigned to the 1,4-isomer, but the attribution of the remaining major resonances at −530.2 and −536.0 ppm among the other isomers cannot be made.

If an α Keggin structure is assumed, there are 13 possible isomers of VV$_3$W$_9$O$_{40}^{6-}$. Three of these (1,2,3; 1,4,9; 1,6,12) have equivalent "octahedral" V atoms, two (1,5,8; 1,6,7) have C_s symmetry, and the remainder have C_1 symmetry. If all 13 isomers are formed and all resonances resolved, a total of 31 lines would be observed for "octahedral" vanadiums plus 13 for "tetrahedral" vanadiums. Only 7 of the latter are resolved. Examination of Figure 9 reveals (in addition to the "tetrahedral" lines at −552 to −555 ppm)[47] an isolated line at −480.5 ppm (A), a group of lines between −502.5 and −509.0 ppm (B), and a broad (290-Hz) line at −522.0 ppm (C) just downfield from another group of lines between −525.8 and −533.4 ppm (D). Assignment of A to the 1,4,9-isomer is consistent with previous arguments; it is 25 ppm downfield from the signal assigned to 1,4-VV$_2$W$_{10}$O$_{40}^{5-}$, and these two species have local vanadium symmetries identical with those of α-1,2,3-P$_2$V$_3$W$_{15}$O$_{62}^{9-}$ and α-1,2-P$_2$V$_2$W$_{16}$O$_{62}^{8-}$, respectively. The last two anions also have chemical shifts differing by ~25 ppm. There are five possible isomers (1,2,4; 1,3,4; 1,4,6; 1,4,7; 1,4,8) that contain pairs of edge-shared VO$_6$ octahedra, and these vanadiums might be expected to contribute to the B lines, which have chemical shifts close to that of 1,4-VV$_{W10}$O$_{40}^{5-}$. Resonance C is the broadest resolved line in the spectrum. This fact, together with a δ value 6 ppm downfield from the line attributed to 1,2-VV$_2$W$_{10}$O$_{40}^{5-}$, suggests that C might identify the 1,2,3-isomer, although it is also certainly possible that the latter (if indeed it is present in this particular sample) has a resonance obscured in the B group of lines. The final group (D) of resonances is attributed to corner-shared and isolated VO$_6$ octahedra. Little more can be said with any certainty about the assignments of the

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[43] Bancroft, G. M.; Mays, M. J.; Prater, B. E. *J. Chem. Soc. A* **1970**, 956.

[44] The data for H$_2$VW$_{11}$O$_{40}^{7-}$ are taken from: Flynn, C. M., Jr.; Pope, M. T.; O'Donnell, S. E. *Inorg. Chem.* **1974**, *13*, 831.

[45] The remarkably narrow line for BVW$_{11}$O$_{40}^{6-}$ has also been noted by Domaille.[44] Coupling of 24 Hz to ^{183}W is resolvable.

[46] The greater two-bond coupling across corner-shared junctions (e.g. for ^{183}W–^{183}W 15–30 Hz vs. 5–15 Hz for edge-shared junctions) is probably a further indication.

[47] Note that these are quite resolved from the "tetrahedral" lines in the spectrum of VV$_2$W$_{10}$O$_{40}^{5-}$, which appear above −558 ppm. Indeed, when the spectrum of VV$_3$W$_9$O$_{40}^{6-}$ is recorded in acidic solution (pH 0–1), lines at ~−560 ppm slowly develop and indicate the presence of the VV$_2$ anion.

$VV_2W_{10}O_{40}{}^{5-}$ and $VV_3W_9O_{40}{}^{6-}$ spectra until or unless individual isomers can be separated and identified by 2-D W NMR. We can however extrapolate from our assignments for the 1,4- and 1,4,9-isomers to estimate the chemical shifts of the currently unknown $VVW_{11}O_{40}{}^{4-}$: V(tetrahedral), −564 ppm; V(octahedral), −530 ppm. The 1,4,9-isomer of $PV_3W_9O_{40}{}^{6-}$ should have δ near −500 ppm, i.e. ~25 ppm downfield from 1,4-$PV_2W_{10}O_{40}{}^{5-}$,[47] and this has recently been confirmed by Domaille and Watunya.[38]

Chemical Shifts and ESR *g* Values. Some years ago Kazanskii[48] reported a linear correlation between $\delta(^{51}V)$ of four tungstovanadates, $VW_5O_{19}{}^{3-}$, $PVMo_{11}O_{40}{}^{4-}$, $PVW_{11}O_{40}{}^{4-}$, and $H_2VW_{11}O_{40}{}^{7-}$, and $\langle g \rangle$ for the corresponding anions reduced by one electron to contain vanadium(IV). Both paramagnetic nuclear shielding of V^V and the g value of V^{IV} are dependent upon excitation energies and orbital angular momentum, and *changes* in $\langle g \rangle$ and δ might be expected to be roughly parallel. A plot of all currently available data for polyanions that contain a single vanadium (Figure 12) shows that there is some correlation but with considerable scatter.[47]. There is no correlation for ions containing two or more vanadiums, nor is there a correlation between $\delta(^{183}W)$ for dodecatungstates and $\langle g \rangle$ for the corresponding one-electron heteropoly blues.[49]

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Preparation and Structural Examination of a Series of New, Low-Valent Iron Phosphine Isocyanide Complexes with Bent C–N–C Linkages

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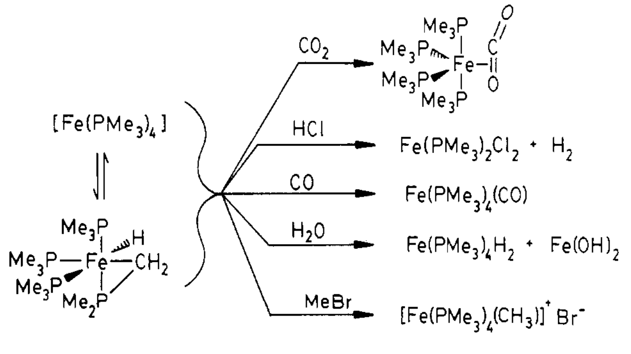
A general synthesis for the preparation of complexes with the formula $Fe(PMe_3)_2(CNR)_3$ where R = Me, Et, *i*-Pr, *t*-Bu, CH_2CMe_3, Ph, and 2,6-xylyl (2,6-xyl) is reported from the reaction of $Fe(PMe_3)_4$ with isocyanides. The derivatives with R = CH_2CMe_3, Ph, and 2,6-xyl have been structurally characterized. $Fe(PMe_3)_2(CNCH_2CMe_3)_3$ crystallizes in monoclinic space group $C2$ with $Z = 4$ and with $a = 28.645$ (13) Å, $b = 9.590$ (4) Å, $c = 11.983$ (4) Å, $\beta = 101.36$ (3)°, and $V = 3227.0$ (4.2) Å^3. $Fe(PMe_3)_2(CNPh)_3$ crystallizes in monoclinic space group $C2/c$ with $Z = 4$ and with $a = 14.136$ (9) Å, $b = 11.559$ (12) Å, $c = 17.343$ (9) Å, $\beta = 98.19$ (4)°, and $V = 2804.9$ (6.4) Å^3. $Fe(PMe_3)_2(CN\text{-}2,6\text{-}xyl)_3$ crystallizes in monoclinic space group $P2_1/c$ with $Z = 4$ and with $a = 9.542$ (2) Å, $b = 24.086$ (5) Å, $c = 15.473$ (5) Å, $\beta = 105.61$ (2)°, and $V = 3424.9$ (2.9) Å^3. These complexes undergo equilibrium exchange reactions with added RNC in solution, giving products with the stoichiometry $Fe(PMe_3)(CNR)_4$ and $Fe(CNR)_5$. The complex $Fe(PMe_3)(CN\text{-}2,6\text{-}xyl)_4$ has been structurally characterized and crystallizes in space group $P2_1/c$ with $Z = 4$ and with $a = 21.655$ (4) Å, $b = 9.901$ (3) Å, $c = 19.609$ (3) Å, $\beta = 113.30$ (1)°, and $V = 3861.6$ (3.3) Å^3. These structures are compared and contrasted with other known structures of $Ru(PPh_3)(CNR)_4$ and $Fe(CNR)_5$ complexes. A general feature observed is the markedly increased bending of the C–N–C linkage upon decreasing the number of π-acceptor RNC ligands.

Introduction

Many inorganic and organometallic complexes of metals in low oxidation states are known in which the ligand set is comprized of good π-acceptor ligands. Delocalization of electron density into the ligands tends to render the metal less reducing (lowering its reduction potential) and consequently less reactive toward air, water, and other small unsaturated molecules. While carbon monoxide is a π-acceptor that is commonly used for this purpose, the isoelectronic isocyanide ligand also "stabilizes" metals in low oxidation states by lowering their reduction potentials.

In 1975, simultaneous reports appeared from Muetterties and Klein regarding the reduction of $FeCl_2$ in the presence of PMe_3.[1,2] An unstable complex could be isolated and characterized with the empirical formula $[Fe(PMe_3)_4]$. Further studies of this complex revealed a dynamic process in which this 16-electron Fe(0) species was in fact in equilibrium with the intramolecular oxidative-addition adduct $H\overline{Fe(PMe_2CH_2})(PMe_3)_3$. Evidence for the presence of a facile equilibrium was also provided by a series of reactions of the incipient coordinatively unsaturated complex with σ-donor ligands and oxidative-addition substrates (Scheme I).[3]

Scheme I



In this paper, we report the preparation and structures of a series of new, low-valent iron(0) complexes containing both PMe_3 and RNC ligands that are active in C–H bond functionalization reactions.[4] Earlier studies of the reduction of iron(II) isocyanide

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[†] A. P. Sloan Fellow, 1984–1986. Camille and Henry Dreyfus Teacher Scholar, 1985–1987.

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