982 *Inorg. Chem.* **1994**, *33*, 982–993

Multicomponent Polyanions. 46. Characterization of the Isomeric Keggin Decamolybdodivanadophosphate Ions in Aqueous Solution by ^{31}P and ^{51}V NMR

Lage Pettersson,[*,†] **Ingegärd Andersson,**[†] **Anna Selling,**[†] **and John H. Grate**[*,‡]

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden, and Catalytica Inc.,
430 Ferguson Drive, Mountain View, California 94043

Received July 8, 1993[●]

The Keggin decamolybdodivanadophosphate ions have been studied in aqueous 0.6 M Na(Cl) medium by potentiometry and ^{31}P (202.5 MHz) and ^{51}V (131.55 MHz) NMR spectrometry. An assignment of all detected resonances of decamolybdodivanadophosphate species to individual Keggin isomers is proposed. The five positional isomers of α-$[Mo_{10}V_2PO_{40}]^{5-}$ were identified and characterized. Two minor $[Mo_{10}V_2PO_{40}]^{5-}$ species, probably β-Keggin isomers, were also observed. The pK_a values of the conjugate monoprotonated species, $[HMo_{10}V_2PO_{40}]^{4-}$, have been precisely determined from the ^{31}P and ^{51}V chemical shift vs pH behavior, using α-$[Mo_{11}VPO_{40}]^{4-}$ as internal standard. These pK_a values are in the range 0–0.5 at 25 °C and in the range 0.8–1.1 at 90 °C. From quantitative NMR integral data the relative abundances of the α isomers at equilibrium were evaluated. The distribution among them is close to statistical, with little measurable change between 25 and 90 °C.

Introduction

As part of an ongoing study of the equilibrium speciation in the aqueous molybdovanadophosphate system, the decamolybdodivanadophosphate ions have been studied in 0.6 M Na(Cl) medium by potentiometry and ^{31}P and ^{51}V NMR spectrometry. The ionic formula,[1] $[Mo_{10}V_2PO_{40}]^{5-}$, and α-Keggin structure for these anions are well established.[2a,b]

Figure 1 shows polyhedral representations of the α- and β-Keggin structures. Keggin polyoxoanions, XMO_{40}^{n-} (presently, X = P and M = Mo, V), contain a central XO_4 tetrahedron surrounded by twelve MO_6 octahedra arranged in four M_3O_{13} groups of edge-sharing octahedra. The edge-sharing M_3O_{13} groups are linked to each other and to the central tetrahedron by shared corners. There are five possible Keggin structures, called α, β, γ, δ, and ϵ. The α structure has the T_d symmetry shown in Figure 1. In the other structures, one (β), two (γ), three (δ), and four (ϵ) of the edge-sharing M_3O_{13} groups in the α structure have been rotated by 60° on their X–O axis. The β structure, also shown in Figure 1, has C_{3v} symmetry.

The α-Keggin structure is by far the most common. The β-form appears to have lower stability due to its less obtuse corner-sharing M–O–M bonds to the rotated M_3O_{13} group.[2a] With less obtuse corner-sharing M–O–M bonds, the corresponding M⋯M distances are shortened, increasing internal electrostatic repulsions, and $p\pi \rightarrow d\pi$ bonding may be weakened. The γ, δ, and ϵ forms are increasingly disfavored by internal electrostatic repulsions, having increasing numbers of short edge-shared M⋯M distances, and are rarely observed. Those that are reported tend to be synthetically constructed tungstate species and do not appear as significant equilibrium species.

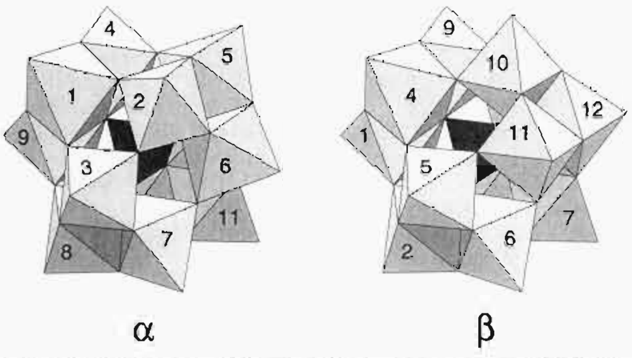


Figure 1. Polyhedral representations of α- and β-Keggin polyoxoanion structures, with the recommended IUPAC numbering schemes.

When α-Keggin molybdates are partially reduced, isomerization to β structures commonly occurs.[2c] Substituting V(V) in place of Mo(VI) in the parent α-$[PMo_{12}O_{40}]^{3-}$ structure is electrostatically similar to such reduction of Mo(VI) to Mo(V) and so might likewise lead to formation of β isomers at equilibrium.

For the parent T_d α-Keggin XMO_{40}^{n-} structure, all MO_6 sites are symmetrically equivalent, so that one isomorphous substitution, at any site, results in a single α-Keggin structure. Accordingly, α-$[Mo_{11}VPO_{40}]^{4-}$ is a single structure. For two or more such substitutions, however, positional isomers are possible. For two substitutions, as in $[Mo_{10}V_2PO_{40}]^{5-}$, five positional α-Keggin isomers are possible,[3] shown in Figure 2. This positional isomer count considers the enantiomorphs of the dissymmetric isomers as single positional isomers.

[†] University of Umeå.

[‡] Catalytica Inc.

[●] Abstract published in *Advance ACS Abstracts*, February 1, 1994.

(1) The ionic formula of the decamolybdodivanadophosphates is more commonly written $[PMo_{10}V_2O_{40}]^{5-}$. We usually denote the composition of a solution species by the stoichiometric integers of the components used in our potentiometric study of its equilibrium formation. Thus, a decamolybdodivanadophosphate pentaanion is written as (21,10,2,1) with reference to the ordered component set shown in the following equilibrium equation:

$$21H^+ + 10MoO_4^{2-} + 2HVO_4^{2-} + HPO_4^{2-} = (H^+)_{21}(MoO_4^{2-})_{10}(HVO_4^{2-})_2(HPO_4^{2-})$$

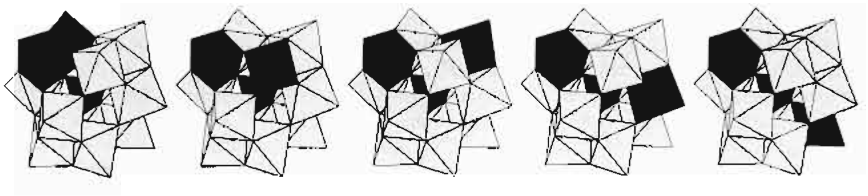
The actual ionic formula can differ from the so-indicated composition by the gain or loss of water, which cannot be ascertained by potentiometry alone. For the decamolybdodivanadophosphates, their Keggin structure and, hence, ionic formula are well established.[2] We find it convenient to also use our standard component order—H, Mo, V, P—when writing ionic formula, in this case $Mo_{10}V_2PO_{40}^{5-}$, as represented by the following equilibrium equation, a special case of the preceding one:

$$21H^+ + 10MoO_4^{2-} + 2HVO_4^{2-} + HPO_4^{2-} = Mo_{10}V_2PO_{40}^{5-} + 12H_2O$$

(2) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983: (a) pp 23–27. (b) p 78. (c) p 107.

(3) Pope, M. T.; Scully, T. F. *Inorg. Chem.* **1975**, *14*, 953. The numbering scheme adopted by these authors to describe the positional isomers predates and differs from the IUPAC proposal later adopted by Pope[7] and used in this paper. The translation between these numbering schemes is straightforward using the figures provided in these references.

0020-1669/94/1333-0982$04.50/0



designation (enantiomer)	α-1,4	α-1,2	α-1,5 (α-1,8)	α-1,6 (α-1,7)	α-1,11
symmetry	C_s	C_s	C_2	C_1	C_{2v}
degeneracy	12	12	12	24	6
statistical abundance	18.2%	18.2%	18.2%	36.4%	9.1%

Figure 2. The five possible isomers of α-$[Mo_{10}V_2PO_{40}]^{5-}$, counting enantiomer pairs as single positional isomers. The VO_6 octahedra are dark gray. The degeneracies and statistically predicted relative abundances listed for the dissymmetric isomers include both enantiomorphs. The statistically predicted relative abundance is among these α isomers only and is the percent of their total degeneracy.

Multiple ^{31}P and ^{51}V NMR resonances for the decamolybdodivanadophosphates and the decatungstodivanadophosphates in aqueous solution evidence the coexistence of multiple positional isomers. In the first[4,5] and ensuing[6] reports observing such isomerism, using NMR instruments of lower field than that used in the present study, the resonances of the positional isomers were inadequately resolved to attempt their assignment to the individual isomers. Pope and collaborators[4] did note that the relative intensities of two composite ^{31}P resonances observed for the decamolybdodivanadophosphates species were consistent with the presence of all five α isomers in their expected relative abundances. (The statistically predicted relative abundances are given in Figure 2.) More recent studies of the deca*tungsto*divanadophosphates, using higher field NMR instruments, have provided more resolved spectra and at least partial assignments of the ^{51}V resonances to individual α isomers.[7,8]

Equilibration kinetics in molybdate polyoxoanion systems are well-known to be rather rapid, in contrast to the corresponding tungstate polyoxoanion systems in which they are relatively slow. The interconversion of the decatungstodivanadophosphate positional isomers is sufficiently slow to allow partial separation of α-$[H_zW_{10}V_2PO_{40}]^{(5-z)-}$ positional isomers by fractional extractions of their etherates from acidic aqueous solution.[8] Specific positional isomers of tungstovanadophosphate can even be synthetically constructed and isolated.[9,10] In the present molybdovanadophosphate system, the equilibrium kinetics proved sufficiently rapid to conveniently allow its equilibrium analysis.[11]

Nomenclature and Designations. Compositions given in brackets, as in $[HMo_{10}V_2PO_{40}]^{4-}$, designate the ionic formulas of discrete Keggin ions. To designate Keggin structures without regard to their protonation state and charge, the abbreviation $Mo_{10}V_2P$ is sometimes used.

To designate the positional isomers of α- and β-Keggin species, the recommended IUPAC numbering schemes,[12] shown in Figure 1, are used. Like Pope[7] and most other authors, however, we indicate the vanadium positions in Keggin $M_{10}V_2P$ species (M = Mo, W) by the lowest possible numbers (1,x for the α isomers, as shown in Figure 2), not by the highest possible numbers (12,x for the α isomers) as in the recommended IUPAC schemes. In this paper, all references to dissymmetric positional isomers are meant to refer to both enantiomorphs. Thus, references to the α-1,5 isomer (C_2 symmetry) apply to the α-1,5 and α-1,8 enantiomers together. References to the α-1,6 isomer (C_1 symmetry) apply to the α-1,6 and α-1,7 enantiomers together.

Compositions given in braces, as in $\{Na_5Mo_{10}V_2PO_{40}\}$, designate the macroscopic elemental compositions of solutions and solids of Keggin salts. Rigorously, they specify the known mole ratios among Na, P, Mo, and V present. In the solids and solutions of this study, Mo, V, and P are always present in Keggin proportions, (Mo + V) = 12 P, and are predominantly incorporated into $[H_zMo_{(12-x)}V_xPO_{40}]^{(3+x-z)-}$ anions. Accordingly, the macroscopic elemental composition in braces corresponds, essentially, to the average polyanion formula and the countercations present that balance its average anionic charge. These average formulas can have nonintegral ratios of the elements but still the overall Keggin ratio.

A 0.6 M Na(Cl) ionic medium is 0.600 M Na^+ with Cl^- providing counteranion balance not provided by the oxometalate anions. The acidity measurements are on the concentration scale, where pH = $-\log [H^+]$, and *not* on the activity scale, pH = $-\log a_{H^+}$.

Experimental Section

Concentrated Molybdovanadophosphate Solutions and Solids. Molybdovanadophosphate sodium salt solutions were prepared, as described below, by the methods developed at Catalytica.[13a] Free molybdovanadophosphoric acid solutions were prepared, as described below, by the method developed by Onoda,[14] with modifications.[13a,b] These methods yields aqueous solutions containing only the molybdovanadophosphate components and countercations in Keggin proportions. Solid salts and free acids were recovered from them by evaporation and drying. All the described solids redissolve rapidly and completely in water to give solutions identical (^{31}P and ^{51}V NMR) to their parent solutions.

Starting materials were MoO_3 (Climax Molybdenum Pure Grade M, ~99.95%), V_2O_5 (Kerr-McGee "low alkali", ≥99.6%), H_3PO_4 (Mallincrodt 85% AR), anhydrous Na_2CO_3 (Mallincrodt AR), and

---

(4) (a) Pope, M. T.; O'Donnell, S. E.; Prados, R. A. *J. Chem. Soc., Chem. Commun.* **1975**, 22. (b) Pope, M. T.; O'Donnell, S. E.; Prados, R. A. *Adv. Chem. Ser.* **1976**, *No. 150*, 85. (c) O'Donnell, S. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **1976**, 2290.

(5) Kazanskii, L. P.; Fedetov, M. A.; Ptushkina, M. N.; Spitsyn, V. I. *Dokl. Phys. Chem. (Engl. Transl.)* **1975**, *224*, 1029.

(6) Maksimovskaya, R. I.; Fedetov, M. A.; Mastikhin, V. M.; Kuznetsova, L. I.; Matveev, K. I. *Dokl. Phys. Chem. (Engl. Transl.)* **1978**, *240*, 422.

(7) Leparulo-Loftus, M. A.; Pope, M. T. *Inorg. Chem.* **1987**, *26*, 2112.

(8) Maksimovskaya, R. I.; Subocheva, O. A.; Kuznetsova, L. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1986**, 1977.

(9) *Inorganic Syntheses*; Ginsberg, A. P., Ed.; Wiley: New York, 1990; Vol. 27, pp 98–103. There is a misprint in Table I on p. 98: γ in the bottommost formula should be β.

(10) Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677.

(11) Pettersson, L.; Andersson, I.; Selling, A.; Grate, J. H. Unpublished results.

(12) Jeannin, Y.; Fournier, M. *Pure Appl. Chem.* **1987**, *59*, 1529.

(13) (a) Grate, J. H.; Hamm, D. R.; Saxton, R. J. International Patent Application Publication Number WO 91/13681, 1991. (b) Grate, J. H.; Hamm, D. R.; Klingman, K. A.; Saxton, R. J.; Downey, S. L. International Patent Application Publication Number WO 91/13854, 1991. (c) Grate, J. H.; Mahajan, S.; Hamm, D. R.; Klingman, K. A.; Downey, S. L. International Patent Application Publication Number WO 91/13853, 1991. (d) Grate, J. H.; Hamm, D. R.; Saxton, R. J.; Muraoka, M. T. International Patent Application Publication Number WO 91/13851, 1991. (e) Grate, J. H.; Hamm, D. R.; Mahajan, S. In *Catalysis of Organic Reactions*; Kosak, J., Johnson, T., Eds.; Marcel Dekker: New York, in press. (f) Grate, J. H.; Hamm, D. R.; Mahajan, S. In *Polyoxometallates: From Platonic Solids to Antiretroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer: Dordrecht, The Netherlands, 1994; pp 213–264.

(14) Onoda, T.; Otake, M. U.S. Patent 4,156,574, 1979 (assigned to Mitsubishi Chemical Industries).

distilled water. The solution preparations were conducted in 3-necked Morton flasks, of 5-L or 12-L capacity, each equipped with an electric heating mantle, efficient reflux condenser, powder addition funnel, and high torque overhead mechanical stirrer. Water rinses were used for all solution transfers to ensure quantitative recoveries into the final solutions.

Solution of 0.30 M {$Na_5Mo_{10}V_2PO_{40}$}. A 218.26-g amount of V_2O_5 (1.20 mol) was suspended in 2.0 L of water in a 5-L Morton flask with stirring, and the mixture was heated to about 60 °C. A 127.19-g amount of Na_2CO_3 (1.20 mol) was slowly added in portions to the rapidly stirred mixture, causing CO_2 liberation and dissolution of the V_2O_5 to give an essentially homogeneous solution. The solution was heated at the reflux for 1 h. The solution was then a lime green color due to dissolved V^{IV} which was originally present in the V_2O_5. Approximately 1 mL of 30% H_2O_2 was added dropwise, leaving a slightly turbid, pale orange-tan sodium metavanadate solution. The solution was maintained at reflux for an additional 1 h to ensure the decomposition of excess peroxide and then cooled to room temperature. The solution was clarified by vacuum filtration to remove a brown solid (<0.1 g) which contained almost all the iron and silica impurities originally present in the V_2O_5. The clear, orange vanadate solution was then returned to a Morton flask, and 1727.28 g of MoO_3 (12.00 mol) was added with rapid stirring. The mixture was heated to reflux, an additional 190.78 g of Na_2CO_3 (1.80 mol) was slowly added in portions to the stirred suspension, causing CO_2 liberation, and then 137.7 g of 85.4% (w/w) H_3PO_4 (1.20 mol) was added. After 3 h at reflux, the resulting homogeneous burgundy-red solution was cooled to room temperature and volumetrically diluted with water to a total volume of 4.00 L, giving 0.30 M {$Na_5Mo_{10}V_2PO_{40}$}.

{$Na_5Mo_{10}V_2PO_{40}$}·$13.6H_2O$. A 1.000-L volume of 0.30 M {$Na_5Mo_{10}V_2PO_{40}$} (0.30 mol) in a tared 2-L round-bottom flask was evaporated to visual dryness by rotating-film evaporation at 50 °C under vacuum. The solid was further dried in the flask under pump vacuum for 24 h. The mass in the flask after drying was 627.7 g, corresponding to an equivalent weight of 2092 g/mol of anion. The water content of the solid was calculated as the difference between this equivalent weight and the formula weight for anhydrous salt. The recovered solid was pulverized to a fine powder and mixed to blend any inhomogeneities in its composition.

Solution of 0.10 M {$Na_4Mo_{11}VPO_{40}$} (4.00 L) and {$Na_4Mo_{11}VPO_{40}$}·$12.4H_2O$ (209 g from 1.000 L of a 0.10 M solution) were prepared analogously from the corresponding mole ratios of components.

Solution of 0.317 M {$H_{4.9}Mo_{10.1}V_{1.9}PO_{40}$}. Preparation of a desired 0.30 M {$H_5Mo_{10}V_2PO_{40}$} (0.60 mol/L of V) solution was attempted by adapting the procedure of ref 14: 545.64 g of V_2O_5 (3.00 mol) and 4318.20 g of MoO_3 (30.00 mol) were suspended in 4.0 L of water with moderate stirring. A 344.23-g amount of 85.4% (w/w) H_3PO_4 (3.00 mol) was added, the mixture was diluted to a total volume of 10.0 L with an additional 4.7 L of water, and the stirring mixture was heated to reflux. The mixture was maintained at reflux for 7 days, after which it was cooled to room temperature, the stirring was stopped, and the undissolved solids were allowed to fall for 5 days. The burgundy-red supernatant solution was decanted from the yellow residue. Repeatedly, the residue was suspended in water, the suspension was centrifuged, and the supernatant was decanted. The wash supernatants were combined with the original supernatant, and the resulting solution was clarified by vacuum filtration. The volume of the solution was reduced to about 9 L by rotating-film evaporation at 50 °C under vacuum.

The yellow residue was dried over $CaCl_2$ desiccant under vacuum to a dry mass of 39.46 g and was analyzed as 86% V_2O_5 and 10.5% MoO_3 by quantitative elemental analyses for P, Mo, and V. The incorporations of Mo, V, and P into the polyoxoacid solution were determined by difference: 99.9%, 93.8%, and 100.0%, respectively. The solution was volumetrically diluted with water to a total volume of 9.38 L to provide a vanadium concentration of 0.60 mol/L.

The composition of this solution is designated 0.317 M {$H_{4.9}Mo_{10.1}V_{1.9}PO_{40}$} + 0.003 M H_3PO_4. Alternatively, the solution may be viewed as 0.285 M {$H_5Mo_{10}V_2PO_{40}$} + 0.032 M {$H_4Mo_{11}VPO_{40}$} + 0.003 M H_3PO_4.

{$H_5Mo_{10}V_2PO_{40}$}·$10.1H_2O$. A 4.0-L volume of 0.050 M {$H_5Mo_{10}V_2PO_{40}$} was prepared analogously to the 0.30 M preparation above. On the basis of the dry weight and analysis of the undissolved yellow residue (97.2% V_2O_5), the incorporations of Mo, V, and P into the polyoxoacid solution were >99.99%, 99.3%, and >99.99%, respectively. (More dilute free molybdovanadophosphoric acid preparations proceed with greater V_2O_5 incorporation.) The entire solution was evaporated to visual dryness by rotating-film evaporation at 40 °C under vacuum, and the resulting solid was further dried under pump vacuum for 24 h. The recovered solid was pulverized to a fine powder. Elemental analyses (Mo, V) established the equivalent weight of 1920 g/mol of anion. The water content of the solid was calculated as the difference between this equivalent weight and the formula weight for anhydrous salt.

Solution of 0.30 M {$H_4Mo_{11}VPO_{40}$}. The solution was prepared at ~0.05 M concentration and concentrated to 0.30 M: 45.47 g of V_2O_5 (0.25 mol) and 791.67 g of MoO_3 (5.50 mol) were suspended in 5.0 L of water with moderate stirring. A 57.37-g amount of 85.4% (w/w) H_3PO_4 (0.50 mol) was added, the mixture was diluted to a total volume of 10.0 L with an additional 4.5 L of water, and the mixture was heated to reflux. After 2 days at reflux, 15 drops of 30% H_2O_2 was added dropwise to the mixture. The mixture was maintained at reflux for a total of 7 days, giving a slightly turbid light burgundy-red mixture. The mixture was cooled to room temperature and clarified by vacuum filtration. The volume of the solution was reduced to about 1.5 L by rotating-film evaporation at 50 °C under vacuum. The resulting homogeneous, clear, burgundy-red solution was volumetrically diluted to a total volume of 1.667 L, giving 0.30 M {$H_4Mo_{11}VPO_{40}$}.

{$H_4Mo_{11}VPO_{40}$}·$21.5H_2O$. A 100-mL volume of 0.30 M {$H_4Mo_{11}VPO_{40}$} (0.030 mol) was evaporated to visual dryness by rotating-film evaporation at 50 °C under vacuum, and the resulting solid was further dried under pump vacuum. The recovered solid was pulverized to a fine powder. Elemental analyses for vanadium established the equivalent weight of 2169 g/mol of anion. The water content of the solid was calculated as the difference between this equivalent weight and the formula weight for anhydrous salt.

Solutions for Potentiometric and NMR Studies. The solutions for the potentiometric and NMR studies were mixed from stock solutions of the components (HCl, Na_2MoO_4, $NaVO_3$, NaH_2PO_4), from the concentrated stock solutions (0.30 M {$Na_5Mo_{10}V_2PO_{40}$} and 0.317 M {$H_{4.9}Mo_{10.1}V_{1.9}PO_{40}$}), or from the solid Keggin molybdovanadophosphoric acids ({$H_4Mo_{11}VPO_{40}$} and {$H_5Mo_{10}V_2PO_{40}$}) and sodium salts ({$Na_4Mo_{11}VPO_{40}$} and {$Na_5Mo_{10}V_2PO_{40}$}), above. Boiled distilled water was used to prepare all the solutions. All solutions for potentiometric and NMR study were prepared to contain 0.6 M Na(Cl) at 25 °C. Sodium chloride (E. Merck pa) was dried at 180 °C and used without any further purification.

The stock solutions of the components were prepared and analyzed as follows: Diluted solutions of hydrochloric acid (E. Merck pa) were standardized against TRIS (tris(hydroxymethyl)aminomethane). Dilute sodium hydroxide was prepared from "oljelut" (50% NaOH and 50% H_2O) and standardized against hydrochloric acid. Sodium metavanadate (E. Merck pa) was dissolved in hot water, and the solution was cooled to room temperature, filtered through porous glass G4, and standardized by evaporation to the solid. Sodium dihydrogen phosphate monohydrate (E. Merck pa) was used as received, and solutions were standardized by evaporation to the solid. Sodium molybdate stock solution was prepared as previously described.[15]

After the components were mixed, the molybdovanadophosphate solutions required up to 24 h at 25 °C to reach equilibrium. For measurements at 90 °C, solutions in tightly capped 8-mm NMR sample tubes were equilibrated by heating 2–3 h in a water bath. The increase in volume from 25 to 90 °C was estimated to be 3%, with a corresponding decrease in concentrations. Since the relative abundances of different Keggin species would not be measurably changed by a 3% decrease in concentration, especially not among isomeric species, no corrections for the concentration decrease from 25 to 90 °C were made.

NMR Measurements. The ^{31}P and ^{51}V NMR measurements were obtained using a Bruker AM500 spectrometer at 202.5 and 131.55 MHz, respectively. The probe temperature was thermostated at (25.0 ± 0.5) °C or (90.0 ± 1.0) °C. The field frequency stabilization was locked to deuterium by placing the 8-mm sample tubes into 10-mm tubes containing D_2O. The samples were spinning in all experiments.

The spin–lattice relaxation times (T_1) were evaluated using the inversion recovery method. For determination of the relative abundances of species from their resonance intensities, spectra were recorded quantitatively with the relaxation delay set to at least $5T_1$, and the free induction decay (FID) was multiplied by an exponential line-broadening function (LB = 1), using the Bruker software, to improve the signal/noise ratio. For recording chemical shifts for determining pK_a values, the relaxation delay was decreased to about $1T_1$ to speed data collection, and a Gaussian–Lorentzian double apodization was applied to the FID, using the Bruker software, to enhance resolution to obtain more accurate chemical shifts of overlapping resonances.

The ^{51}V chemical shifts are not measurably dependent on the concentration of Keggin ions, but the ^{31}P chemical shifts are. Presumably, this is a bulk susceptibility effect. (The ^{31}P chemical shifts are also dependent on the ionic medium concentration, which is held constant at

---

(15) Pettersson, L. *Acta Chem. Scand.* **1971**, *25*, 1959.

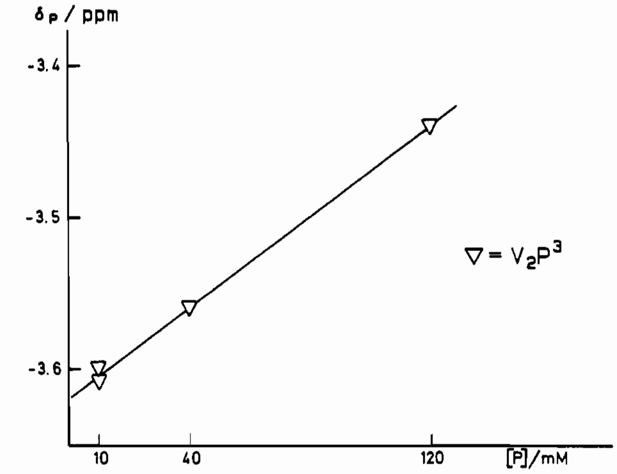


Figure 3. ^{31}P chemical shift dependence on total Keggin ion concentration, as [P], for the resonance V_2P^3 (see Figures 6 and 7) in solutions with [Mo] = 10[P], [V] = 2[P], and pH = 2.5–3.5 in 0.6 M Na(Cl) at 25 °C.

0.6 M Na(Cl) in the present study.) The ^{31}P chemical shift dependence on total Keggin ion concentration is illustrated for the dominant $[Mo_{10}V_2PO_{40}]^{5-}$ isomer (V_2P^3) in Figure 3. The ^{31}P chemical shifts of the other Keggin species, including $[Mo_{11}VPO_{40}]^{4-}$, show parallel linear behavior. A solution of 10 mM [Keggin ions] was chosen as the reference state, and shifts recorded at other Keggin ion concentrations were corrected to this reference state.

$[Mo_{11}VPO_{40}]^{4-}$ was used as an internal ^{31}P and ^{51}V chemical shift standard. (See below.) At 25 °C, $[Mo_{11}VPO_{40}]^{4-}$ present in 10 mM $\{Na_4Mo_{11}VPO_{40}\}$ in 0.6 M Na(Cl) has its $\delta_P = -3.540$ ppm toward higher frequency from capillary 85% H_3PO_4 and its $\delta_V = -533.6$ ppm toward higher frequency from capillary $VOCl_3$. The spectral range set at 25 °C was used at 90 °C. This gave the chemical shifts for 10 mM $[Mo_{11}VPO_{40}]^{4-}$ in 0.6 M Na(Cl) at 90 °C at $\delta_P = -2.83$ ppm and $\delta_V = -528.6$ ppm.

Emf Measurements. The acidity measurements are on the concentration scale, where $-\log [H^+] = pH$, and *not* on the activity scale, $-\log a_{H^+} = pH$, and from now on we will for simplicity use pH instead of $-\log [H^+]$. The pH values were measured with an Orion Research 81-03 Semimicro Ross combination electrode. The small diameter of this electrode made it possible to measure pH in solutions stored in the 8-mm NMR sample tubes. The electrode was calibrated against buffer solutions of known $[H^+]$ in 0.6 M Na(Cl) medium at 25 °C and against NBS standards at 90 °C. In tests where pH was measured in solutions of known $[H^+]$ at 90 °C, the measured pH values were in accordance with those calculated from the known $[H^+]$. Thus, the two scales essentially coincide.

Computer Programs. Resonance intensities were computed by integration using the Bruker software or, for severely overlapping resonances, by line shape analysis using the program NMRi,[16] inputting the chemical shifts determined by resolution enhancement (see above). The chemical shifts of the individual Keggin species and the pK_a values for the protonated species were computed from the chemical shift vs pH data using the least-squares program LAKE.[17]

Results

Undecamolybdomonovanadophosphate as an NMR Chemical Shift Reference. Solutions of synthetic $\{H_4Mo_{11}VPO_{40}\}$, $\{Na_4Mo_{11}VPO_{40}\}$, and mixtures thereof exhibit a single ^{51}V NMR resonance and a single ^{31}P NMR resonance arising from a Keggin species, each at the same chemical shift in all such solutions. Acidic solutions (pH < $\sim$2) prepared from the components (HCl, Na_2MoO_4, $NaVO_3$, NaH_2PO_4) in the Mo:V:P ratio of 11:1:1 exhibit the same single ^{51}V resonance and single ^{31}P resonance arising from a Keggin species, whose chemical shifts do not change with pH down to pH < 0.

Equilibrium analysis of the system H^+–MoO_4^{2-}–HVO_4^{2-}–HPO_4^{2-} established the composition (22,11,1,1)[1] for this species, corresponding to $[Mo_{11}VPO_{40}]^{4-}$, and confirmed that this anion does not protonate in solution down to pH values < 0.[11,18] $[Mo_{11}VPO_{40}]^{4-}$ is commonly presumed to have the α-Keggin structure. $[Mo_{12}PO_{40}]^{3-}$ and $[Mo_{10}V_2PO_{40}]^{5-}$ each have the α-Keggin structure in hydrous crystals.[2ab,19,20] For $[W_{11}VPO_{40}]^{4-}$ in aqueous solution, 2-dimensional ^{183}W NMR connectivity patterns establish its α-Keggin structure.[10]

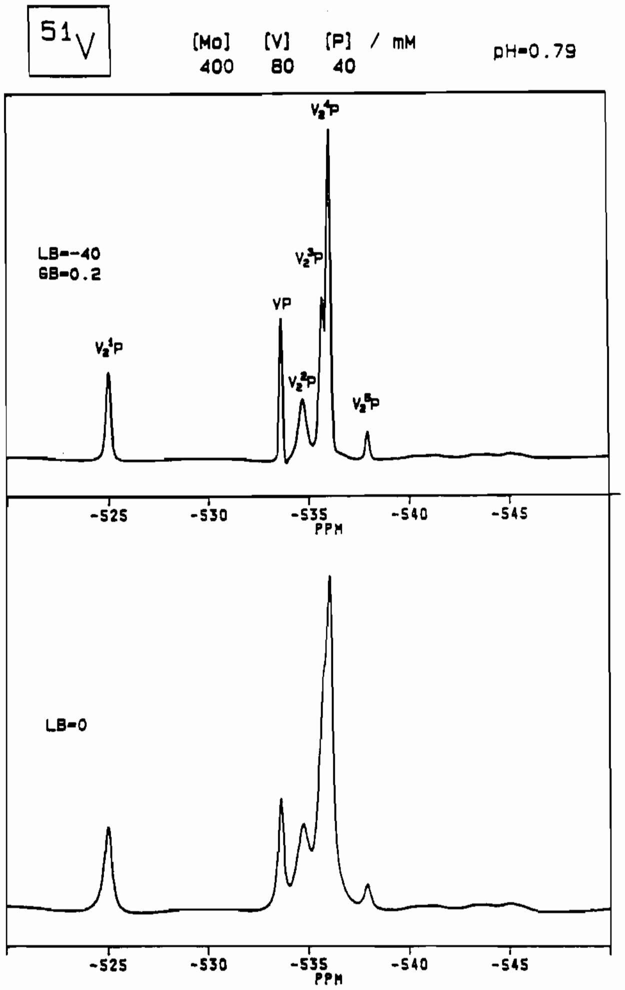


Figure 4. ^{51}V NMR spectrum of a solution of 40 mM P, 400 mM Mo, and 80 mM V, at pH = 0.79 in 0.6 M Na(Cl) at 25 °C, with (top) and without (bottom) resolution enhancement. (See the Experimental Section.) The resonance labeled VP is of $[Mo_{11}VPO_{40}]^{4-}$. The resonances labeled $V_2{}^1P$, $V_2{}^2P$, ..., $V_2{}^5P$ are of the $[H_zMo_{10}V_2PO_{40}]^{(5-z)-}$ species.

Since the ^{31}P and ^{51}V chemical shifts of $[Mo_{11}VPO_{40}]^{4-}$ are invariant over pH, it could be used as an internal chemical shift standard for both nuclei. The chemical shifts of $[Mo_{11}VPO_{40}]^{4-}$ in 10 mM $\{Na_yH_{(4-y)}Mo_{11}VPO_{40}\}$ solutions in 0.6 M Na(Cl) at 25 °C are $\delta_P = -3.540$ and $\delta_V = -533.6$ ppm. See the Experimental Section. The ^{51}V resonance line width is $\Delta\nu_{1/2} = 34$ Hz at 25 °C and 12 Hz at 90 °C. (The unsubstituted Keggin $[Mo_{12}PO_{40}]^{3-}$ has its $\delta_P = -3.20$ under corresponding conditions.[21])

Decamolybdodivanadophosphates at 25 °C. Equilibrated solutions containing decamolybdodivanadophosphates exhibited identical ^{31}P and ^{51}V NMR spectra, when at the same concentration and pH in 0.6 M Na(Cl) medium, whether prepared from synthetic $\{Na_5Mo_{10}V_2PO_{40}\}$ or $\{H_5Mo_{10}V_2PO_{40}\}$ or from the components (HCl, Na_2MoO_4, $NaVO_3$, and NaH_2PO_4). In all cases, equilibrium was established within 24 h at 25 °C, and all NMR and pH data reported herein are from fully equilibrated solutions.

---

(16) Dumoulin, C. L.; Levy, G. C. *J. Mol. Struct.* **1984**, *113*, 299.

(17) Holmström, K. Thesis, University of Umeå, Umeå, Sweden, 1988.

(18) Reference 8 reports that the ^{31}P and ^{51}V chemical shifts of undecamolybdomonovanadophosphate remain unchanged with increasing acidity to 3.5 N HCl but begin to shift slightly in 5 N HCl.

(19) D'Amour, H.; Allmann, R. *Z. Krist.* **1976**, *143*, 1.

(20) Sergienko, V. S.; Detusheva, L. G.; Yurchenko, E. N.; Porai-Kosihts, M. A. *J. Struct. Chem.* (*Engl. Transl.*) **1981**, *22*, 831.

(21) Pettersson, L.; Andersson, I. Unpublished results.

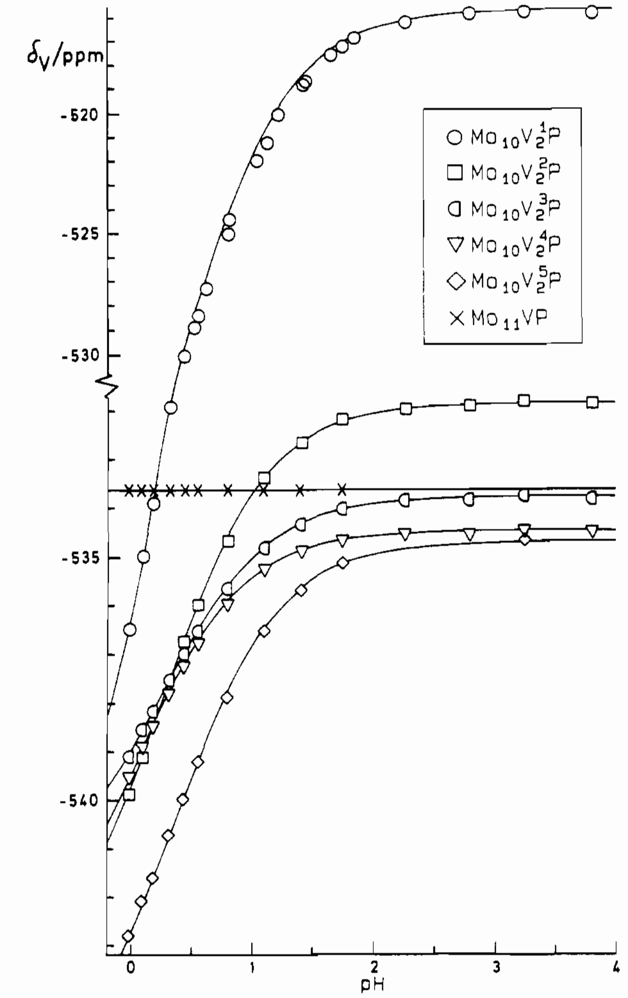


Figure 5. ^{51}V chemical shifts of the resonances VP and $V_2{}^1P$–$V_2{}^5P$ plotted vs pH, in 0.6 M Na(Cl) at 25 °C. The lines through the data for the resonances $V_2{}^1P$–$V_2{}^5P$ are the monoprotonation titration curves calculated to fit the data.

Figure 4 shows the ^{51}V NMR spectrum of an acidic solution (pH = 0.79) having Mo:V:P = 10:2:1 with 40 mM P. In such acidic solutions, the vanadium exists in an equilibrium distribution among $[Mo_{11}VPO_{40}]^{4-}$ (resonance labeled VP in the figure), $[H_zMo_{10}V_2PO_{40}]^{(5-z)-}$ species (resonances labeled $V_2{}^1P$, $V_2{}^2P$, ..., $V_2{}^5P$), $[H_zMo_9V_3PO_{40}]^{(6-z)-}$ species, and $VO_2{}^+$. The $[H_zMo_9V_3PO_{40}]^{(6-z)-}$ and $VO_2{}^+$ resonances are hardly perceptible in the spectrum at $\delta_V < -540$ ppm. The five resonances labeled $V_2{}^1P$–$V_2{}^5P$ were confirmed to be $[H_zMo_{10}V_2PO_{40}]^{(5-z)-}$ species by varying the Mo:V ratio among solutions while maintaining the Keggin proportions (Mo + V):P = 12:1. These resonances exhibited constant relative intensities among them, variable intensities relative to the other resonances, and maximum intensities relative to the sum of all other resonances when Mo:V = 10:2.

Figure 5 shows the ^{51}V chemical shifts of the five resonances $V_2{}^1P$–$V_2{}^5P$ plotted vs pH over the range 0–4. While their shifts converged and diverged over this pH range, no additional resonances corresponding to $[H_zMo_{10}V_2PO_{40}]^{(5-z)-}$ species were revealed.

Equilibrium analysis established the composition (21,10,2,1),[1] corresponding to fully unprotonated $[Mo_{10}V_2PO_{40}]^{5-}$, for the species present at pH > ~2, where the ^{51}V chemical shifts in Figure 5 plateau.[11] All the isomers begin to become protonated at pH ≈ 2. Four of the resonances show a similar magnitude of chemical shift dependence on pH. The fifth, $V_2{}^1P$, exhibits an exceptionally greater change of chemical shift with protonation state (note the break and change in scale on the δ_V axis in Figure 5).

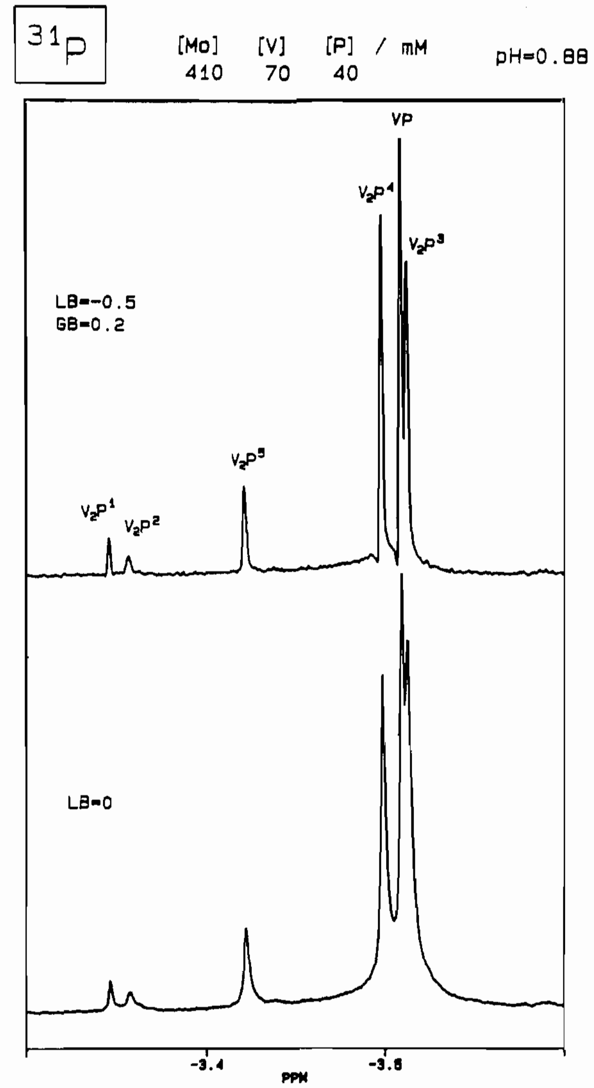


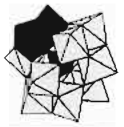
Figure 6. ^{31}P NMR spectrum of a solution of 40 mM P, 410 mM Mo, and 70 mM V, at pH = 0.88 in 0.6 M Na(Cl) at 25 °C, with (top) and without (bottom) resolution enhancement. The resonance labeled VP is of $[Mo_{11}VPO_{40}]^{4-}$. The resonances labeled V_2P^1, V_2P^2, ..., V_2P^5 are of $[H_zMo_{10}V_2PO_{40}]^{(5-z)-}$ species.

The pK_a values of the protonated species $[HMo_{10}V_2PO_{40}]^{4-}$ as well as the chemical shifts for the unprotonated and protonated species were determined from the experimental points in Figure 5 by using the LAKE least-squares program[17] and are compiled in Table 1 with the standard deviations of these determinations, reported as 3σ values. The precision of these determinations are, in our judgement, remarkably high considering that only half of the titration "S-curve" could be covered by experimental points and that the ionic medium could not be held constant into the most acidic solutions. (The effects of the ionic medium variation on the chemical shifts was, however, corrected by referencing to $[Mo_{11}VPO_{40}]^{4-}$ as internal shift standard.) Table 1 also reports the relative intensities (as percent abundance) and line widths of the five resonances $V_2{}^1P$–$V_2{}^5P$ at pH 3 and 0.

Figure 6 shows the ^{31}P spectrum of an acidic solution (pH = 0.88) having Mo:V:P = 10.25:1.75:1 with 40 mM P at 25 °C. The solution is essentially 10 mM $[Mo_{11}VPO_{40}]^{4-}$ and 30 mM $[H_zMo_{10}V_2PO_{40}]^{(5-z)-}$ species. Five resonances arising from $[H_zMo_{10}V_2PO_{40}]^{(5-z)-}$ species were observed (labeled V_2P^1, V_2P^2, ..., V_2P^5 in Figure 6). Figure 7 shows the ^{31}P chemical shifts, at 25 °C, of these five resonances plotted vs pH over the range 0–3.5. While their shifts converged and diverged over this pH range, no additional resonances corresponding to $[H_zMo_{10}V_2PO_{40}]^{(5-z)-}$ species were revealed.

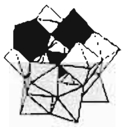
As in the ^{51}V spectra, all the $[Mo_{10}V_2PO_{40}]^{5-}$ isomers observed in the ^{31}P spectra begin to become protonated at pH ≈ 2. The

Table 1. ^{51}V-NMR Data, Analyses, and Assignments for the $[Mo_{10}V_2PO_{40}]^{5-}$ Isomers at 25 °C

^{51}V-NMR resonance	Composition	pK_a (3σ)	δ (3σ) (ppm)	Δδ^a (ppm)	Δν$_{1/2}$ (Hz)	Abundance^b pH 3	pH 0	Assignment
$V_2{}^1P$	$Mo_{10}V_2PO_{40}{}^{5-}$		−515.74 (.11)	27.5	60	11%	15%	 α-1,4
○	$HMo_{10}V_2PO_{40}{}^{4-}$	0.48 (.02)	−543.20 (.44)					
$V_2{}^2P$	$Mo_{10}V_2PO_{40}{}^{5-}$		−531.83 (.03)	12.3	100	21%		 α-1,2
□	$HMo_{10}V_2PO_{40}$	0.26 (.02)	−544.09 (.22)					
$V_2{}^3P$	$Mo_{10}V_2PO_{40}{}^{5-}$		−533.76 (.03)	8.1	60	21%		 α-1,5
ᗡ	$HMo_{10}V_2PO_{40}{}^{4-}$	0.26 (.02)	−541.87 (.21)					
$V_2{}^4P$	$Mo_{10}V_2PO_{40}{}^{5-}$		−534.46 (.04)	9.6	50	45%	39%	 α-1,6 +  α-1,11
▽	$HMo_{10}V_2PO_{40}{}^{4-}$	0.04 (.04)	−544.05 (.51)					
$V_2{}^5P$	$Mo_{10}V_2PO_{40}{}^{5-}$		−534.68 (.08)	11.7	40	4%		 β-4,11
◇	$HMo_{10}V_2PO_{40}{}^{4-}$	0.35 (.03)	−546.42 (.32)					

^{a} $\delta(Mo_{10}V_2PO_{40}{}^{5-}) - \delta(HMo_{10}V_2PO_{40}{}^{4-})$. ^{b} Relative abundance among the detected $Mo_{10}V_2P$ resonances.

Table 2. ^{31}P-NMR Data, Analyses, and Assignments for the $[Mo_{10}V_2PO_{40}]^{5-}$ Isomers at 25 °C

^{31}P-NMR resonance	Composition	pK_a (3σ)	δ (3σ) (ppm)	Δδ^a (ppm)	Δν$_{1/2}$ (Hz)	Abundance^b (pH 3)	Assignment
V_2P^1	$Mo_{10}V_2PO_{40}{}^{5-}$		−3.433 (.002)	0.26	0.75	~3%	 β-4,10 and  β-4,11
D	$HMo_{10}V_2PO_{40}{}^{4-}$	0.33 (.05)	−3.168 (.014)				
V_2P^2	$Mo_{10}V_2PO_{40}{}^{5-}$		−3.508 (.001)	0.53	1.50	~4%	
◇	$HMo_{10}V_2PO_{40}{}^{4-}$	0.37 (.02)	−2.980 (.009)				
V_2P^3	$Mo_{10}V_2PO_{40}{}^{5-}$		−3.596 (.003)	0.44	0.85	~40%	 α-1,6 +  α-1,11
▽	$HMo_{10}V_2PO_{40}{}^{4-}$	0.03 (.08)	−3.159 (.043)				
V_2P^4	$Mo_{10}V_2PO_{40}{}^{5-}$		−3.627 (.003)	0.54	0.70	~40%	 α-1,2 +  α-1,5
□	$HMo_{10}V_2PO_{40}{}^{4-}$	0.24 (.05)	−3.090 (.027)				
V_2P^5	$Mo_{10}V_2PO_{40}{}^{5-}$		−3.650 (.005)	0.70	0.95	~13%	 α-1,4
○	$HMo_{10}V_2PO_{40}{}^{4-}$	0.49 (.04)	−2.948 (.023)				

^{a} $\delta(HMo_{10}V_2PO_{40}{}^{4-}) - \delta(Mo_{10}V_2PO_{40}{}^{5-})$. ^{b} Relative abundance among the detected $Mo_{10}V_2P$ resonances.

^{31}P spectral data were analyzed in the same manner as the ^{51}V spectral data, and the results are compiled in Table 2. Again, the pK_a values of the protonated species $[HMo_{10}V_2PO_{40}]^{4-}$ were determined with precision that, in our judgement, is remarkably high.

Decamolybdodivanadophosphates at 90 °C. In view of the utility of aqueous molybdovanadophosphates in oxidation reactions at temperatures of ~100 °C and above,[13] we have also examined their speciation in solutions at 90 °C (below the atmospheric boiling point for experimental convenience).

Figure 8 shows the ^{51}V NMR spectrum at 90 °C of the same solution (Mo:V:P = 10:2:1, 40 mM P) whose spectrum at 25 °C is shown in Figure 4. (At 90 °C, the pH of the solution is 0.85, compared to 0.79 at 25 °C.) The ^{51}V resonances exhibit much

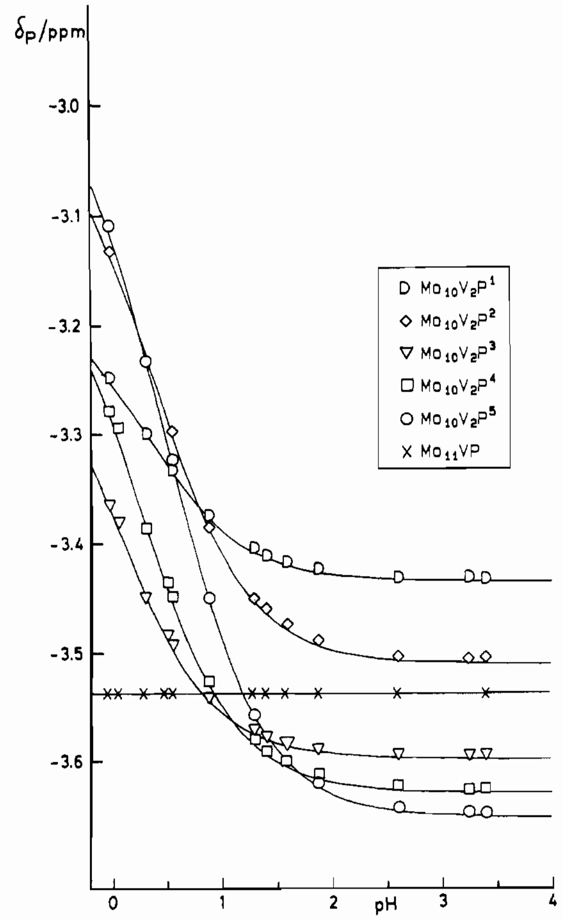


Figure 7. ^{31}P chemical shifts of the resonances VP and V_2P^1–V_2P^5 plotted vs pH, in 0.6 M Na(Cl) at 25 °C. The lines through the data for the resonances V_2P^1–V_2P^5 are the monoprotonation titration curves calculated to fit the data.

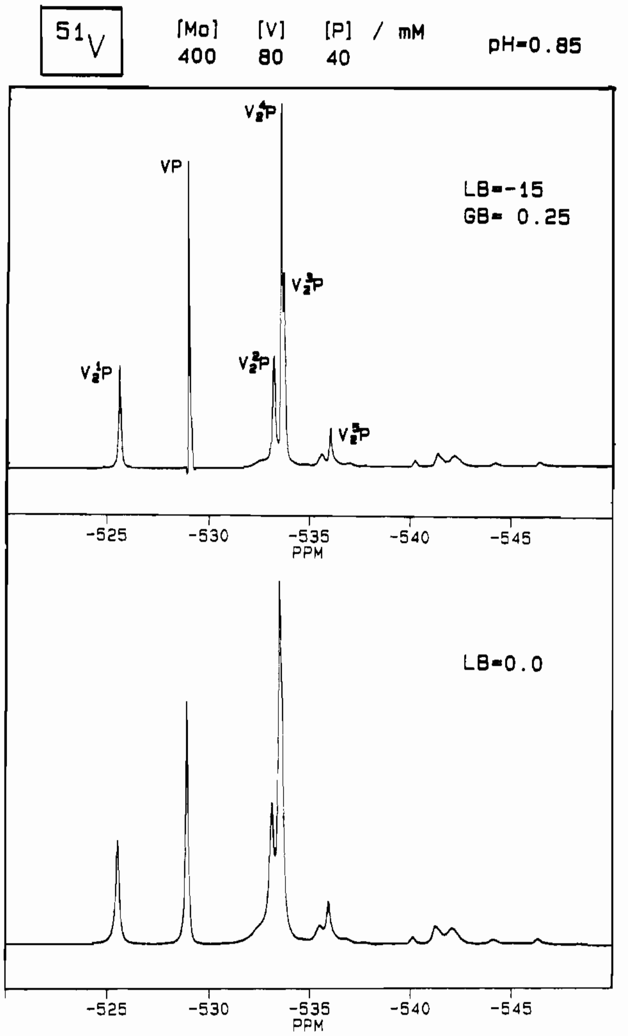


Figure 8. ^{51}V NMR spectrum of the solution of Figure 4 at 90 °C, with (top) and without (bottom) resolution enhancement. The resonance labels correspond to those in Figure 4. Resonance $V_2{}^6P$, seen in less acidic solutions at 90 °C, is not resolved from other V_2P resonances in this spectrum. (See Figure 9.)

narrower line widths at the higher temperature, reflecting the polyanions' decreased rotational correlation times.[7] The resonances of $[H_zMo_9V_3PO_{40}]^{(6-z)-}$ species and $VO_2{}^+$, which were too broad to readily discern at 25 °C, are more distinct in the 90 °C spectra. The vanadium is seen to remain predominantly incorporated into Keggin molybdovanadophosphates at this temperature.

Six resonances of $[H_zMo_{10}V_2PO_{40}]^{(5-z)-}$ species were identifiable in the 90 °C spectra. The five more intense correspond to the five resonances observed in the 25 °C spectra and are correspondingly labeled $V_2{}^1P$–$V_2{}^5P$ in Figure 8. The sixth, least intense resonance, $V_2{}^6P$, was not resolved at 25 °C.

Figure 9 shows the ^{51}V chemical shifts, at 90 °C, of the six resonances $V_2{}^1P$–$V_2{}^6P$ plotted vs pH over the range 0–5. No additional resonances corresponding to $[H_zMo_{10}V_2PO_{40}]^{(5-z)-}$ species were revealed over this pH range. The spectrophotometric titration curves are similar to those at 25 °C (Figure 5) but shifted to higher pH. The pK_a values of the protonated species $[HMo_{10}V_2PO_{40}]^{4-}$, determined by LAKE least-squares analysis, are included in Table 3. (The data were insufficient to determine the pK_a value corresponding to resonance $V_2{}^6P$ with any reliable confidence.) The pK_a values corresponding to resonances $V_2{}^1P$–$V_2{}^5P$ at 90 °C were all 0.6–0.7 pH units higher than the corresponding values determined at 25 °C (Table 2).

The relative intensities among the $[H_zMo_{10}V_2PO_{40}]^{(5-z)-}$ resonances, shown in Table 3 as percent abundances, are similar to those at 25 °C. (The relative intensities between resonances $V_2{}^3P$ and $V_2{}^4P$ were difficult to determine due to severe overlap over the entire pH range. The percent abundances given for them in Table 3 are approximate, but their sum is well determined.)

^{31}P NMR spectra at 90 °C exhibit the same five resonances of $[H_zMo_{10}V_2PO_{40}]^{(5-z)-}$ species observed at 25 °C, in approximately the same relative intensities. At 90 °C, the resonances are shifted ~+0.75 ppm relative to their chemical shifts at 25 °C and their line widths are nearly twice as broad. Figure 10 shows the ^{31}P chemical shifts, at 90 °C, of these five resonances plotted vs pH over the range 0–3.5. These titration curves are similar to those at 25 °C (Figure 7) and, as in the ^{51}V spectra, shifted to higher pH. Table 4 includes the pK_a values of the protonated species $[HMo_{10}V_2PO_{40}]^{4-}$ determined by LAKE least-squares analysis.

Discussion

Assignment of Resonances and Characterization of α-Isomers. The five α-$[Mo_{10}V_2PO_{40}]^{5-}$ positional isomers will exhibit, among them, five potentially resolvable ^{31}P NMR resonances (one each) and six potentially resolvable ^{51}V NMR resonances. The α-1,6 isomer has symmetrically inequivalent vanadiums (C_1 symmetry) and thereby two potentially resolvable ^{51}V resonances. In each of the other four α isomers, the two vanadiums are related by symmetry elements and are thereby magnetically equivalent. The symmetry in some of the α-$[Mo_{10}V_2PO_{40}]^{5-}$ isomers (α-1,2, α-1,5, α-1,11; see below) is reduced upon monoprotonation to α-$[HMo_{10}V_2PO_{40}]^{4-}$ species. Symmetry-related protonation sites are protonated with equal frequency, however, and the α-$[HMo_{10}V_2PO_{40}]^{4-}$ species equilibrate with their conjugate α-$[Mo_{10}V_2PO_{40}]^{5-}$ isomers, and hence each other, rapidly relative to the NMR time scale. Consequently, only equilibrium exchange-averaged resonances are observed—evidenced by the

Table 3. ^{51}V-NMR Data, Analyses, and Assignments for the $[Mo_{10}V_2PO_{40}]^{5-}$ Isomers at 90 °C

^{51}V-NMR resonance	Composition	pK_a (3σ)	δ (3σ) (ppm)	$\Delta\delta^a$ (ppm)	$\Delta\upsilon_{1/2}$ (Hz)	Abundance^b pH 3 pH 0	Assignment
$V_2{}^1P$	$Mo_{10}V_2PO_{40}{}^{5-}$		−509.75 (.30)	24.8	23	12% 17%	 α-1,4
○	$HMo_{10}V_2PO_{40}{}^{4-}$	1.08 (.05)	−534.52 (.77)				
$V_2{}^2P$	$Mo_{10}V_2PO_{40}{}^{5-}$		−526.10 (.15)	12.2	32	21%	 α-1,2
□	$HMo_{10}V_2PO_{40}{}^{4-}$	0.94 (.06)	−538.33 (.47)				
$V_2{}^3P$	$Mo_{10}V_2PO_{40}{}^{5-}$		−528.61 (.12)	8.6	19	~20%	 α-1,5
ᗡ	$HMo_{10}V_2PO_{40}{}^{4-}$	0.94 (.06)	−537.26 (.40)				
$V_2{}^4P$	$Mo_{10}V_2PO_{40}{}^{5-}$		−528.87 (.10)	9.4	17	~37% ~32%	 α-1,6 +  α-1,11
▽	$HMo_{10}V_2PO_{40}{}^{4-}$	0.78 (.06)	−538.27 (.43)				
$V_2{}^5P$	$Mo_{10}V_2PO_{40}{}^{5-}$		−528.82 (.15)	11.8	24	6%	 β-4,11
◇	$HMo_{10}V_2PO_{40}{}^{4-}$	0.98 (.06)	−540.63 (.45)				
$V_2{}^6P$	$Mo_{10}V_2PO_{40}{}^{5-}$		−526.73 (.12)		~40	4%	 β-4,10
△	$HMo_{10}V_2PO_{40}{}^{4-}$						

^{a} $\delta(Mo_{10}V_2PO_{40}{}^{5-}) - \delta(HMo_{10}V_2PO_{40}{}^{4-})$. ^{b} Relative abundance among the detected $Mo_{10}V_2P$ resonances.

chemical shift vs pH curves—and the number of potentially resolvable resonances is unchanged as the α-$[Mo_{10}V_2PO_{40}]^{5-}$ isomers become monoprotonated.

While no more than five ^{31}P resonances and six ^{51}V resonances of $Mo_{10}V_2P$ species were observed resolved in this study, we ultimately assigned them to seven isomers, including the five α-Keggin positional isomers as the most abundant species and two other Keggin isomers, thought to be β-Keggin isomers, in low relative abundance. This assignment is presented in Tables 1–4, and the reasons for it follow. In this assignment, the two ^{51}V resonances of the α-1,6 isomer are unresolved in a single observed resonance.

The assignment is based, in part, on comparisons of the relative intensities of the $Mo_{10}V_2P$ resonances to the statistically predicted relative abundances of the α isomers. The statistically predicted relative abundances correspond to the α isomers' degeneracies, and are typically cited herein as percents of the total of their degeneracies. (The degeneracy of each isomer equals the number of ways two vanadiums can be substituted for two molybdenums in the parent T_d α-$[Mo_{12}PO_{40}]^{3-}$ structure to provide that isomer. For the dissymmetric isomers, α-1,5 and α-1,6, the degeneracies of their enantiomorphs are summed. See Figure 2 and ref 3.) The degeneracies predict one α isomer in high abundance (α-1,6, 36% among α isomers), three in medium abundance (α-1,2, α-1,4, and α-1,5, each 18%), and one in low abundance (α-1,11, 9%). The five observed ^{31}P resonances and six observed ^{51}V resonances of $Mo_{10}V_2P$ species cannot be assigned to only the five α isomers in any reasonable agreement with these statistically predicted relative abundances. For example, in the ^{31}P spectra at 25 °C, there are two high-intensity resonances (each ~40% of observed $Mo_{10}V_2P$ ^{31}P resonances), one medium-intensity resonance (~13%), and two very low-intensity resonances (each ~3–4%).

The assignment is also based, in part, on the responses of the resonances' chemical shifts to protonation of the α-$[Mo_{10}V_2PO_{40}]^{5-}$ isomers. Keggin polyoxometalates protonate at bridging oxygens, and the most basic of these should be the surface edge-shared oxygens (O_e) within the edge-sharing M_3O_{13} groups.[22] In the Keggin molybdovanadophosphates, the more basic of these oxygens are those bound to a vanadium(V) instead of two molybdenum(VI). Accordingly, the basicity among such oxygens decreases in the following order: V–O_e–V, V–O_e–Mo, Mo–O_e–Mo. Among the α-$[Mo_{10}V_2PO_{40}]^{5-}$ isomers, only the α-1,4 isomer has an V–O_e–V oxygen, and it has only one of them. It is expected to be the most basic (highest pK_a) of the α isomers.[23]

---

(22) Protonation at the edge-shared oxygens of Keggin polyoxometalates is generally accepted in the field (personal communication, M. Pope), but we have been unable to locate any reference making such a general statement or any reference specifically indicating the site of protonation of a α-Keggin structure. For the preference for protonation at bridging oxygens rather than terminal oxygens, see: Barcza, L.; Pope, M. T. *J. Phys. Chem.* **1975**, *79*, 92. Protonation at edge-shared oxygens rather than corner-shared oxygens is expected on the basis of bond angle and orbital hybridization considerations and has been found in closely related structures. The structure of the β-Keggin anion β-$[H_xPMo^{VI}{}_8Mo^{V}{}_4O_{40}]^{(7-x)-}$ indicates that three protons are bound at three equivalent edge-shared oxygens: Barrows, J. N.; Jameson, G. B.; Pope, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 1771. The structure of the "bicapped α-Keggin" anion $[H_4PV_{14}O_{42}]^{5-}$ shows its four protons bound at "uncapped" edge-shared oxygens: Khan, M. I.; Zubieta, J.; Toscano, P. *Inorg. Chim. Acta* **1992**, *193*, 17. The assignments of ^{51}V NMR resonances to $[Mo_{10}V_2PO_{40}]^{5-}$ isomers in the present work may be taken as further evidence for protonation at edge-shared oxygens. If protonation instead occurred at corner-shared oxygens, the most basic isomer would then be the α-1,2 instead of the α-1,4. However, the ^{51}V resonance having the highest pK_a and the one having the broad line width characteristic of corner-shared VO_6 octahedra are not the same. See the text and ref 7.

(23) Statistical factors affecting the isomers' relative basicities should also be considered. The 1,4-α isomer has only one most basic V–O_e–V oxygen. The other α-isomers protonate at less basic V–O_e–Mo oxygens, but each such isomer has four of them. The 1,4-α isomer also has two V–O_e–Mo sites, however, diminishing any significant contribution of this statistical difference in determining the relative order of basicity.

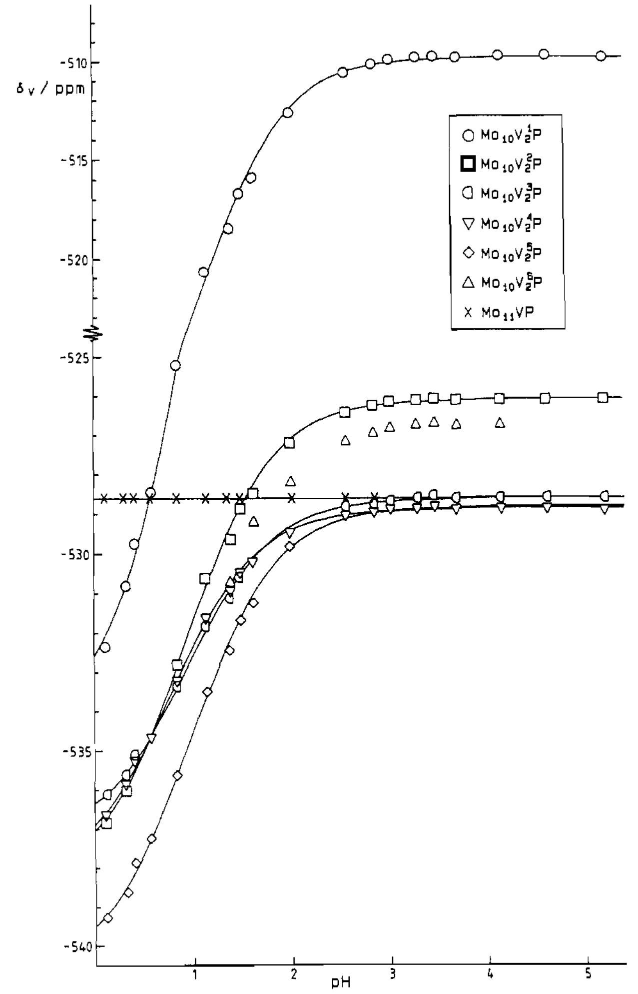


Figure 9. ^{51}V chemical shifts of the resonances VP and $V_2{}^1P$–$V_2{}^6P$ plotted vs pH, in 0.6 M Na(Cl) at 90 °C. The lines through the data for the resonances $V_2{}^1P$–$V_2{}^5P$ are the monoprotonation titration curves calculated to fit the data.

The other four α-$[Mo_{10}V_2PO_{40}]^{5-}$ isomers will protonate at V–O_e–Mo sites, of which there are four in each such isomer. In the α-1,11 isomer, the four V–O_e–Mo sites are equivalent by symmetry. In each of the α-1,2 and α-1,5 isomers, the four V–O_e–Mo sites exist in two pairs by symmetry. In the α-1,6 isomer, the four V–O_e–Mo sites are all inequivalent. Nonetheless, the chemical shift vs pH data could be explained with high precision by a single pK_a for each resonance observed in the ^{31}P and ^{51}V spectra. We are inclined to believe this manifests indistinguishable pK_a values for the symmetrically inequivalent V–O_e–Mo sites in each of the α-1,2, α-1,5, and α-1,6 isomers, rather than preferential protonation at only one type of V–O_e–Mo site in each isomer.

The resonances $V_2{}^1P$ in the ^{51}V spectra and V_2P^5 in the ^{31}P spectra have the same and uniquely highest pK_a value (~0.5 at 25 °C) in their respective spectra and matching unique intensities relative to other $Mo_{10}V_2P$ resonances (11–15% of all detected resonances at 25 °C). They are assigned to the α-1,4 isomer, unique in having a V–O_e–V protonation site. $V_2{}^1P$ and V_2P^5 each exhibit, in their respective spectra, the greatest change in chemical shift on protonation. In the ^{31}P spectra this distinction is modest, but in the ^{51}V spectra it is exceptionally conspicuous. $V_2{}^1P$ shifts upfield on protonation by more than twice the amount of any other $Mo_{10}V_2P$ ^{51}V resonance. Protonation of the α-1,4 isomer at its single V–O_e–V site occurs adjacent to both vanadiums simultaneously. In contrast, monoprotonation of the other α isomers, at V–O_e–Mo sites, occurs adjacent to only one vanadium at a time. Accordingly, the substantially greater chemical shift change of $V_2{}^1P$ on protonation reinforces its assignment to the α-1,4 isomer.

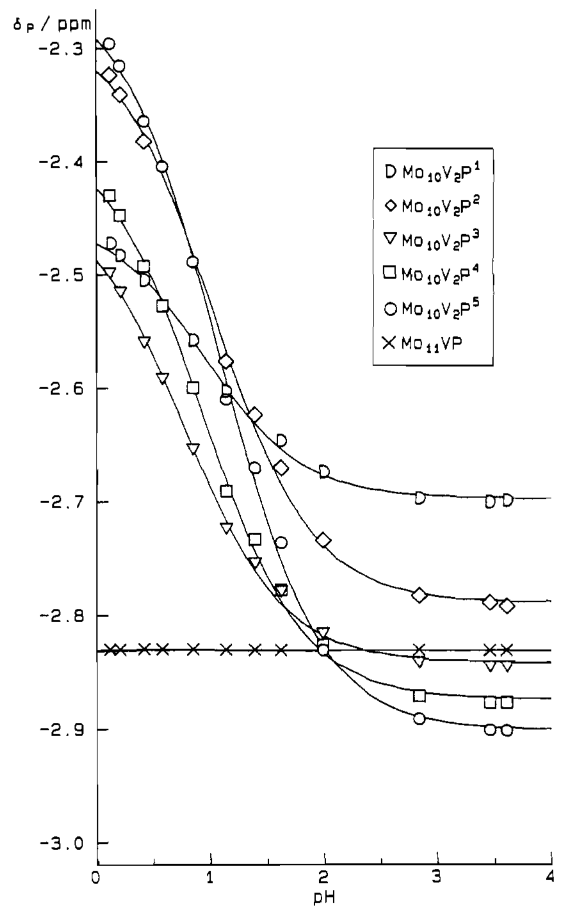


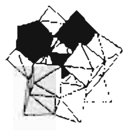
Figure 10. ^{31}P chemical shifts of the resonances VP and V_2P^1–V_2P^5 plotted vs pH, in 0.6 M Na(Cl) at 90 °C. The lines through the data for the resonances V_2P^1–V_2P^5 are the monoprotonation titration curves calculated to fit the data.

When the $Mo_{10}V_2P$ species are fully deprotonated, $V_2{}^1P$ is 16 ppm from the nearest of the other $Mo_{10}V_2P$ resonances in the ^{51}V spectra, which are all grouped within a 3 ppm range. This is consistent with the edge-shared vanadiums in the α-1,4 isomer experiencing the environment most distinct from the vanadium environments in the several α isomers in which the two VO_6 octahedra share no oxygens. The large chemical shift change of $V_2{}^1P$ on protonation brings its chemical shift into the range of the other $Mo_{10}V_2P$ resonances. From electrostatic considerations, the V–OH–V environment in α-1,4-$[HMo_{10}V_2PO_{40}]^{4-}$ is more similar to the V–O–Mo environment in the other isomers.

There are two plausible alternative assignments of the remaining major $Mo_{10}V_2P$ resonances in the ^{51}V and ^{31}P spectra. Their differentiation focuses on the assignment of $V_2{}^2P$ in the ^{51}V spectra. The alternative assignment that is not shown in the tables recognizes that resonances $V_2{}^2P$ and $V_2{}^3P$ in the ^{51}V spectra have identical intensities, each 21% of the total abundance (sum of intensities) of detected $Mo_{10}V_2P$ resonances, and the same pK_a (0.26 at 25 °C). There is only a single ^{31}P resonance having this pK_a, V_2P^4, and its relative abundance, ~40% of all detected $Mo_{10}V_2P$ ^{31}P resonances, is about equal to the sum of the relative abundances of $V_2{}^2P$ and $V_2{}^3P$ in the ^{51}V spectra. This is close to the statistically predicted relative abundance of the α-1,6 isomer, 36% among α isomers. The α-1,6 isomer is unique in having this high statistically predicted relative abundance, twice that of any other α isomer, and in being capable of exhibiting two resolved ^{51}V resonances.

Nonetheless, such assignment of $V_2{}^2P$ to the α-1,6 isomer is disfavored for one set of reasons, and its assignment to the α-1,2 isomer instead is preferred for yet another. Moreover, there is still another ^{51}V resonance ($V_2{}^4P$) and another ^{31}P resonance (V_2P^3) with sufficient relative intensities, and having the same pK_a, to account for the α-1,6 isomer.

Table 4. ^{31}P-NMR Data Analyses, and Assignments for the $[Mo_{10}V_2PO_{40}]^{5-}$ Isomers at 90 °C

^{31}P-NMR resonance	Composition	pK_a (3σ)	δ (3σ) (ppm)	Δδ[a] (ppm)	Δ$\upsilon_{1/2}$ (Hz)	Abundance[b] (pH 3)	Assignment
V_2P^1 D	$Mo_{10}V_2PO_{40}^{5-}$ $HMo_{10}V_2PO_{40}^{4-}$	 0.94 (.11)	−2.696 (.008) −2.445 (.016)	0.25	1.3	4%	 β-4,10 and  β-4,11
V_2P^2 ◇	$Mo_{10}V_2PO_{40}^{5-}$ $HMo_{10}V_2PO_{40}^{4-}$	 1.02 (.09)	−2.787 (.014) −2.273 (.026)	0.51	2.3	6%	
V_2P^3 ▽	$Mo_{10}V_2PO_{40}^{5-}$ $HMo_{10}V_2PO_{40}^{4-}$	 0.77 (.09)	−2.840 (.009) −2.426 (.027)	0.41	1.8	~37%	 α-1,6 +  α-1,11
V_2P^4 □	$Mo_{10}V_2PO_{40}^{5-}$ $HMo_{10}V_2PO_{40}^{4-}$	 0.93 (.08)	−2.872 (.012) −2.369 (.026)	0.50	1.4	~40%	 α-1,2 +  α-1,5
V_2P^5 ○	$Mo_{10}V_2PO_{40}^{5-}$ $HMo_{10}V_2PO_{40}^{4-}$	 1.08 (.08)	−2.889 (.017) −2.239 (.029)	0.65	1.4	~13%	 α-1,4

[a] $\delta(HMo_{10}V_2PO_{40}^{4-}) - \delta(Mo_{10}V_2PO_{40}^{5-})$. [b] Relative abundance among the detected $Mo_{10}V_2P$ resonances.

The assignment of $V_2{}^2P$ to the α-1,6 isomer is disfavored as neither its chemical shift nor its line width appear consistent with that assignment when compared to other ^{51}V resonances. Like the α-1,6 isomer, the α-1,5 and α-1,11 isomers each contain separated VO_6 octahedra—respectively less and more separated than those in the α-1,6 isomer. Consequently, both the possible ^{51}V resonances of the unprotonated α-1,6 isomer could be expected to fall in the same chemical shift range as the resonances of the unprotonated α-1,5 and α-1,11 isomers. *If* $V_2{}^2P$ and $V_2{}^3P$ are assigned to the α-1,6 isomer, *then* the α-1,5 and α-1,11 isomers must have their ^{51}V resonances within $V_2{}^4P$ and possibly $V_2{}^5P$, having chemical shifts when unprotonated within a narrow ~0.2 ppm range at 25 °C. Not only are unprotonated $V_2{}^2P$ and unprotonated $V_2{}^3P$ both well outside this narrow chemical shift range but $V_2{}^2P$ is even more shifted from $V_2{}^3P$ (by 1.9 ppm at 25 °C) than $V_2{}^3P$ is from the range of $V_2{}^4P$ and $V_2{}^5P$ (by 0.7 ppm from $V_2{}^4P$ at 25 °C). Accordingly, it seems unlikely that these two resonances can both correspond to the α-1,6 isomer.

Likewise, the line widths of the two possible ^{51}V resonances of the α-1,6 isomer are expected to be similar to those of the α-1,5 and α-1,11 isomers. *If* $V_2{}^2P$ and $V_2{}^3P$ are assigned to the α-1,6 isomer, *then* the resonances remaining available for assignment to the α-1,5 and α-1,11 isomers ($V_2{}^4P$ and $V_2{}^5P$) have line widths of $\nu_{1/2}$ = 40–50 Hz at 25 °C. The resonance $V_2{}^3P$ is not too dissimilar, with $\nu_{1/2}$ = 60 Hz at 25 °C, but $V_2{}^2P$ has a uniquely broad line width, $\nu_{1/2}$ = 100 Hz at 25 °C. Again, it seems unlikely that $V_2{}^2P$ and $V_2{}^3P$ can both correspond to the α-1,6 isomer.

The preferred assignment of the $V_2{}^2P$ resonance to the α-1,2 isomer is based on its uniquely broad line width. Leparulo-Loftus and Pope established[7] that among isostructural tungstovanadate polyanions, including the α-Keggin *tungsto*vanadophosphates, ^{51}V resonance line widths are substantially broader in structures having corner-shared VO_6 octahedra. On the basis of this criterion, they assigned the uniquely broad resonance in the ^{51}V spectrum of a mixture of α-$[W_{10}V_2PO_{40}]^{5-}$ positional isomers to the α-1,2 isomer. They confirmed this assignment by comparison to the reported ^{51}V spectral data for isolated, individual α-1,2-$[W_{10}V_2PO_{40}]^{5-}$, independently synthesized and structurally characterized (1- and 2-dimensional ^{183}W and ^{51}V NMR) by Domaille.[10]

The $V_2{}^2P$ resonance in the present spectra of $Mo_{10}V_2P$ isomers is likewise assigned to the α-1,2 isomer. Moreover, this assignment places the unprotonated α-1,2 resonance upfield (by 1.8 ppm at 25 °C) from α-$[Mo_{11}VPO_{40}]^{4-}$, as is the unprotonated α-1,4 resonance, while all the resonances remaining available for assignment to all the unprotonated α isomers having separated VO_6 octahedra are closely grouped slightly downfield (within 1.1 ppm at 25 °C) from α-$[Mo_{11}VPO_{40}]^{4-}$.

As a consequence of this assignment of $V_2{}^2P$ in the ^{51}V spectra to the α-1,2 isomer, V_2P^4 in the ^{31}P spectra must contain the unresolved ^{31}P resonances of the α-1,2 isomer and another isomer whose ^{51}V resonance is $V_2{}^3P$. As previously noted, V_2P^4 is the only ^{31}P resonance exhibiting the same pK_a as both $V_2{}^2P$ and $V_2{}^3P$, and its abundance among to all detected $Mo_{10}V_2P$ ^{31}P resonances (~40%) corresponds to the sum of the coequal abundances (each 21%) of $V_2{}^2P$ and $V_2{}^3P$ among all detected $Mo_{10}V_2P$ ^{51}V resonances. The only remaining α isomer having the same statistically predicted relative abundance (18%) as the α-1,2 isomer (recalling that the α-1,4 isomer is already assigned to $V_2{}^1P$ and V_2P^5) is the α-1,5 isomer. Accordingly, $V_2{}^3P$ is assigned to the α-1,5 isomer and V_2P^4 is assigned to the unresolved ^{31}P resonances of the α-1,2 and α-1,5 isomers.

Also as a consequence of the assignment of $V_2{}^2P$, and hence V_2P^4, to the α-1,2 isomer, the only remaining ^{31}P resonance with sufficient intensity to assign to the α-1,6 isomer in reasonable agreement with its statistically predicted relative abundance among α isomers (36%) is V_2P^3 (~40% abundance among all detected $Mo_{10}V_2P$ ^{31}P resonances). The *only* observed ^{51}V resonance having the same pK_a as V_2P^3 is $V_2{}^4P$ (0.04 at 25 °C), and its intensity (45% among all detected unprotonated $Mo_{10}V_2P$ ^{51}V resonances) is sufficient to account for the *unresolved* ^{51}V resonances of the α-1,6 isomer. Accordingly, V_2P^3 in the ^{31}P spectra and $V_2{}^4P$ in the ^{51}V spectra are assigned, at least in part, to the α-1,6 isomer.

The only α-$Mo_{10}V_2P$ isomer remaining to have resonances assigned to it is the α-1,11 isomer. Among the α isomers, it most resembles the α-1,6 isomer in having well-separated VO_6 octahedra. While the α-1,6-$[HMo_{10}V_2PO_{40}]^{4-}$ isomer is the most acidic among the observed isomers ($pK_a = 0.04$ at 25 °C for $V_2{}^4P$ and V_2P^3), the only resonances remaining unassigned in the ^{51}V and ^{31}P spectra are among the least acidic (pK_a values $\sim$0.35 for $V_2{}^5P$, V_2P^1, and V_2P^2 at 25 °C), second only to the α-1,4 isomer. Accordingly, none of these remaining unassigned resonances appear appropriate for assignment to the α-1,11 isomer. In view of its low statistically predicted abundance among α isomers (9%) and the expected similarity of its chemical shifts and pK_a value to the α-1,6 isomer, the observed resonances assigned to the α-1,6 isomer ($V_2{}^4P$ and V_2P^3) are also assigned to contain the unresolved resonances of the α-1,11 isomer.

This overall assignment of NMR resonances to the α isomers is further supported by the overall trends it exhibits. The unprotonated α isomers' ^{31}P chemical shifts, their ^{51}V chemical shifts, and their conjugate acids' pK_a values all show the same relative order (to the extent they are resolved), which is the order of the distance between the two vanadiums. In the ^{51}V spectra, the unprotonated α isomers' chemical shifts appear to reflect the extent to which each vanadium's environment is perturbed by the other vanadium (relative to molybdenum). Notably, those isomers with separated VO_6 octahedra (α-1,5, α-1,6, α-1,11) have unprotonated ^{51}V resonances shifted relatively close to each other and to the α-$[Mo_{11}VPO_{40}]^{4-}$ resonance. In the ^{31}P spectra, the unprotonated α isomers' chemical shifts appear to reflect the degree of polarity in the charge distribution surrounding phosphorus. Notably, the α-1,4 isomer, which has the most unbalanced charge distribution among the unprotonated α isomers, but the most uniform charge distribution among the monoprotonated α isomers, exhibits the greatest change in chemical shift upon monoprotonation, from one extreme of the unprotonated α isomers to the other extreme of the monoprotonated α isomers.

The so-assigned distribution of the α isomers satisfactorily agrees, at both 25 °C and 90 °C, with that statistically predicted. (Albeit, only the sum of the abundances of the α-1,6 and α-1,11 could be determined since their resonances were unresolved in both the ^{51}V and ^{31}P spectra.) The abundance of the unprotonated α-1,4 isomer (11% at 25 °C, 12% at 90 °C), however, is substantially depressed relative to that statistically predicted (18%). Its decreased stability relative to the statistical level can be ascribed to its most unbalanced charge distribution and its uniquely weaker bonding of two oxygens between two vanadium(V) nuclei. Notably, its relative abundance increases toward that statistically predicted as it becomes monoprotonated (to 15% at pH 0 at 25 °C, where it is 75% monoprotonated, and to 17% at pH 0 at 90 °C, where it is 92% monoprotonated). This occurs at the expense of one or both of the α isomers with the most even charge distribution when unprotonated (α-1,6, α-1,11).

Assignment of Resonances to β-Isomers. The resonances remaining to be assigned in the ^{51}V spectra ($V_2{}^5P$, $V_2{}^6P$) and ^{31}P spectra (V_2P^1, V_2P^2) are the least intense of the detected $Mo_{10}V_2P$ resonances. On the basis of their similar abundances and similar pK_a values, these two ^{51}V resonances and two ^{31}P resonances are supposed to arise from the same two species.

These least intense of the observed resonances are tentatively assigned to β isomers. The two ^{31}P resonances so assigned have the most downfield chemical shifts among the $Mo_{10}V_2P$ ^{31}P resonances. This accords with the reported downfield ^{31}P shift of a β-$[W_{10}V_2PO_{40}]^{5-}$ (−12.85 ppm) compared to two α-$[W_{10}V_2PO_{40}]^{5-}$ isomers (−13.46, −13.61 ppm).[9]

There are 14 possible β-$[Mo_{10}V_2PO_{40}]^{5-}$ positional isomers (counting enantiomorphs as single positional isomers).[2a] Eight possible β isomers can arise by rotation of the edge-sharing Mo_3O_{13} groups in the five α isomers. Their degeneracies do not predict a substantial statistically preferred predominance for any two or few of them. (The statistically predicted abundance ratios among these eight are 6:6:6:4:3:3:3:2.) Moreover, it appears unlikely that the relative stabilities among them (factoring out statistical factors) would be much different than among their corresponding α isomers, since the relationships between the vanadiums are not significantly changed by rotation of the edge-sharing Mo_3O_{13} groups. For the same reason, they appear poor candidates for exhibiting ^{51}V resonances resolved from their corresponding α isomers. Accordingly, the two observed apparent β isomers more likely result from rotation of an edge-sharing $Mo_{3-x}V_xO_{13}$, where x is 1 or 2. There are six such β isomers. The statistically predicted abundance ratios among these six are 2:2:2:2:1:1, so they cannot be further discriminated on that basis.

A further winnowing of the likely structures for these two apparent β isomers is based, in part, on their pH behavior. The two apparent β resonances have pK_a values $\sim$0.35 at 25 °C, between those of the most basic α-1,4 isomer (0.48 at 25 °C) and the next most basic α isomers, α-1,2 and α-1,5 (both 0.26 at 25 °C). Although second only to the α-1,4 isomer in basicity, they do not exhibit an exceptionally large change in ^{51}V chemical shift on protonation similar to the α-1,4 isomer, which has a single protonation site adjacent to both its edge sharing vanadiums. Instead, their changes in chemical shifts on protonation are similar to those of the other α isomers, which protonate at V–O_e–Mo sites, adjacent to only one vanadium at a time. Accordingly, these β isomers are not likely to be ones having edge-shared VO_6 octahedra, related to the α-1,4 isomer by rotation of one edge-sharing M_3O_{13} groups on its P–O axes. (This rules out the β-10,-11 isomer, resulting from 60° rotation of the edge-sharing MoV_2O_{13} group in the α-1,4 isomer, and also the two β isomers resulting from rotation of the edge-sharing Mo_3O_{13} groups in the α-1,4 isomer.) On the basis of their pK_a values of $\sim$0.35 at 25 °C, they more likely contain either corner-sharing VO_6 octahedra similar to the α-1,2 isomer (pK_a 0.26 at 25 °C) or separated VO_6 octahedra connected similar to the α-1,5 isomer (pK_a 0.26 at 25 °C). They are not likely to contain VO_6 octahedra as separated as in the much less basic α-1,6 and α-1,11 isomers (pK_a values 0.04 at 25 °C).

There are only two β isomers meeting these criteria. Only the β-4,10 isomer (with its β-9,10 enantiomer) has corner-sharing VO_6 octahedra with one of them in the rotated edge-sharing Mo_2VO_{13} group. (See Figure 1 for numbering scheme.) Only the β-4,11 isomer (with its β-9,12 enantiomer) has the same type of connectivity between the vanadiums as does the α-1,5 isomer: *cis*-V–O_c–Mo–O_e–V. (O_c is a corner-shared oxygen. O_e is an edge-shared oxygen. *cis* refers to the relationship of the oxygens in the connecting MoO_6 octahedron.) In the α-1,5 isomer there are two such connections through different MoO_6 octahedra. In the β-4,11 isomer, the second connection through a different MoO_6 octahedron is *cis*-V–O_c–Mo–O_c–V. Among the remaining β isomers with a rotated edge-sharing Mo_2VO_{13} group, the shortest connectivity between the two vanadiums (through molybdenum) is *trans*-V–O–Mo–O–V and each such β isomer has only one such connection through a single molybdenum. This is analogous to the connectivity in the much less basic α-1,6 isomer. Consequently, the two observed apparent β isomers are tentatively assigned to the β-4,10 and β-4,11 isomers and their enantiomers. (For each, the symmetrically inequivalent vanadiums are presumed to exhibit a single unresolved resonance.)

When resolved in the ^{51}V spectra of solutions at 90 °C, the resonance $V_2{}^6P$ exhibits a line width ($\sim$40 Hz) comparable to, if not broader than, that of the α-1,2 isomer at 90 °C (32 Hz). This is indicative of corner-sharing VO_6 octahedra. (See above and ref 7.) In comparison, the line width of $V_2{}^5P$ (24 Hz at 90 °C, 40 Hz at 25 °C) is comparable to the narrower line widths of the other α isomers, all lacking corner-shared VO_6 octahedra (17–23 Hz at 90 °C, 50–60 Hz at 25 °C). Consequently, $V_2{}^6P$ is plausibly assigned to the β-4,10 isomer and $V_2{}^5P$ to the β-4,11 isomer.

These are the two β isomers that can be derived from the α-1,2 isomer by 60° rotation (+ or −) of one edge-sharing Mo_2VO_{13} group. As the α-1,2 isomer is the only α isomer with corner-sharing between the VO_6 octahedra in different edge-sharing Mo_2VO_{13} groups, it seems reasonable that it might be uniquely destabilized relative to its corresponding β isomers. This would reflect weaker bonding across a $V^V–O_c–V^V$ corner relative to $V^V–O_c–Mo^{VI}$ or $Mo^{VI}–O_c–Mo^{VI}$ corners. Thus, the overall corner-shared bonding in the β-4,11 isomer, which lacks any $V–O_c–V$ corner, would be stronger than that in the α-1,2 isomer. In the β-4,10 isomer, however, the remaining $V–O_c–V$ corner will have a less obtuse bond angle than in the α-1,2 isomer (~145° vs ~155°)[2a] and thus weaker $p\pi \rightarrow d\pi$ bonding at the same bond distances. If present, as tentatively assigned, shorter $V–O_c–V$ bonds in this β isomer, to overcompensate for the less obtuse bond angle, must be invoked to complete this rationalization. The concept that the α-1,2 isomer is unique among α isomers in being destabilized relative to corresponding β isomers, however, does not find any support in its abundance relative to other α isomers, which is close to that predicted statistically. (It appears in the same abundance as the α-1,5 isomer, with which it has equal statistically predicted abundance.)

Concluding Remarks. Only by using a constant ionic medium, an internal chemical shift standard, a combination electrode calibrated on the concentration pH scale (pH = $-\log [H^+]$), a high-field NMR instrument (500 MHz ^1H), and corrections for bulk susceptibility effects (Figure 3), *all in combination*, did it prove possible to precisely track the $Mo_{10}V_2P$ ^{31}P and ^{51}V resonances as their chemical shifts converged and diverged with increasing acidity to pH 0. This made it possible to precisely determine their pK_a values in the 0–0.5 range even though only about half of each titration "S-curve" could be experimentally covered. This capability was essential to enable the assignment and characterization of the $[Mo_{10}V_2PO_{40}]^{5-}$ isomers reported herein. A partial assignment of $[H_zMo_9V_3PO_{40}]^{(6-z)-}$ resonances to individual positional isomers has been completed and will be reported subsequently.

Acknowledgment. Financial support from Catalytica Inc. and the Swedish Natural Science Research Council for the work at University of Umeå is hereby gratefully acknowledged. We thank David R. Hamm and Shannan L. Downey for the synthetic molybdovanadophosphate solutions and solids.