Inorganic Chemistry

Dawson Type Heteropolyanions. 3.[†] Syntheses and ^{31}P, ^{51}V, and ^{183}W NMR Structural Investigation of Octadeca(molybdo–tungsto–vanado)diphosphates Related to the [H$_2$P$_2$W$_{12}$O$_{48}$]$^{12-}$ Anion

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The synthesis and multinuclear NMR characterization of mixed molybdenum–vanadium–tungsten polyoxometalates [P$_2$Mo$_x$V$_y$W$_{18-(x+y)}$O$_{62}$]$^{n-}$ ($x + y \leq 8$) related to the Dawson structure are reported. The mixed species are obtained from the hexavacant anion [H$_2$P$_2$W$_{12}$O$_{56}$]$^{12-}$ by successive condensation and hydrolysis reactions. The strategy of synthesis is mainly based on the steric control of hydrolysis reactions by the nature and the strength of the base, the relative kinetic lability of molybdenum and tungsten in hydrolysis reactions, and the conservation of the framework when vacant sites are refilled by new metal atoms. Rather good values of ^{31}P chemical shift variations can be predicted by an additive model taking into account the contribution of substituting groups, depending on their position in the structure. The influence of Mo/W and V/W substitutions on ^{183}W chemical shifts of the remaining W atoms has been discussed and seems to be preferentially passed on through corner junctions.

Introduction

The acid−base and redox behaviors of polyoxometalates play an important role in synthesis and applications, especially in homogeneous and heterogeneous catalysis. These properties are dependent on the nature and the relative positions of the metal cations in the framework. Vanadium, molybdenum, and tungsten are the main constitutive metals in polyoxometalates, and the acid strengh decreases in the order W > Mo > V but the oxidizing ability in the order V > Mo > W. Moreover, additional electrons introduced in homometallic heteropolyanions with unequivalent d^0 metal atoms can be localized on preferential sites.[1,2] The development of methods of synthesis leading to well-defined mixed species is thus important.

One strategy is to use polyvacant species and to insert the "addenda atoms" into the vacant sites without modification of the host structure. This strategy has been utilized for Keggin type polyoxometalates in order to obtain [XM$_x$W$_{12-x}$O$_{40}$]$^{n-}$ [3] or [X(MM′)$_x$W$_{12-x}$O$_{40}$]$^{n-}$ [4] anions (M ≠ M′, $x = 1$ to 3). The same strategy has been utilized for Wells−Dawson heteropolyanions[5] which result from the association of two A-{PW$_9$O$_{34}$} subunits. Two metallic sites can be distinguished (Figure 1): polar sites when the metal belongs to a trimetallic group {M$_3$O$_{13}$} (numbers 1 to 3 and 16 to 18) and equatorial sites when the metal belongs to a ditungstic group {M$_2$O$_{10}$} (numbers 4 to 15). The trivacant species [P$_2$W$_{15}$O$_{56}$]$^{12-}$, in which a polar trimetallic group is

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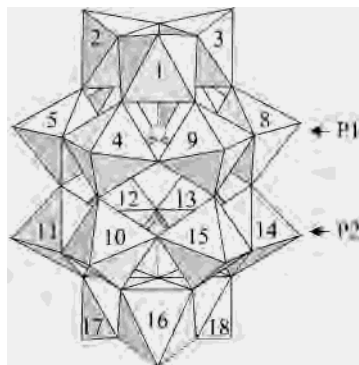(5) Dawson, B. *Acta Crystallogr.* **1953**, *6*, 113.

Figure 1. Polyhedral representation of the structure of the Dawson polyanion $[P_2W_{18}O_{62}]^{6-}$ and numbering of the metallic atoms according to the IUPAC rules (Jeannin, Y.; Fournier, M. *Pure Appl. Chem.* **1987**, *59*, 1529).

missing,[6,7] is the precursor of mixed $[P_2(MM')_xW_{18-x}O_{62}]^{n-}$ anions (M,M' = Mo, V, Nb..., x = 1 to 3)[8–10] and tetranuclear sandwich complexes $[(M,M')_4(H_2O)_2(P_2W_{15}O_{56})_2]^{12-}$ (M' can be an alkaline cation such as Na$^+$).[11,12] In some cases, addition of the metal cations to the polyvacant species leads to a partial substitution of the tungsten atoms and a structural rearrangement.[13]

The hexavacant anion $[H_2P_2W_{12}O_{48}]^{12-}$ has been previously obtained by selective hydrolysis of $[P_2W_{18}O_{62}]^{6-}$.[6] No X-ray structure determination of the unstable $[H_2P_2W_{12}O_{48}]^{12-}$ anion has been published up to now, and its molecular structure is known only from indirect observations. Actually, the hexavacant site can be refilled by molybdenum atoms, giving rise again to the complete Dawson species $[P_2Mo_6W_{12}O_{62}]^{6-}$, and the relative positions of the six molybdenum atoms were initially deduced from its behavior toward alkaline degradation.[14] This assumption was later confirmed by analysis of the ^{183}W NMR solution spectrum of $[P_2Mo_6W_{12}O_{62}]^{6-}$.[15] Moreover the X-ray structure of K_2-$Li_5[H_7P_8W_{48}O_{184}]\cdot92H_2O$ was shown to contain the crown heteropolyanion $[H_7P_8W_{48}O_{184}]^{40-}$ obtained by condensation of four $[H_2P_2W_{12}O_{48}]^{12-}$ anions.[16]

The saturated $[P_2Mo_6W_{12}O_{62}]^{6-}$ anion can be used itself as a precursor of mono- and trivacant mixed Mo–W anions obtained by selective hydrolysis reactions, and, in this paper, we show that these vacant species can be used to prepare

V/Mo/W Dawson heteropolyanions containing no more than fourteen tungsten atoms. All the compounds have been characterized by ^{31}P and ^{183}W NMR spectroscopy.

Experimental Section

Materials. Potassium dodecatungstodiphosphate[17] and compounds **1** and **5**,[6] **2**, **3**, **6**, **9**, **11**, and **14**[14] have been prepared according to literature procedures. Numbering of the compounds is defined in Figure 2. Molybdenum and vanadium numbers in the structure are indicated successively, according to Figure 1.

1,9,10,15,16-4-K$_7$[P$_2$Mo$_5$VW$_{12}$O$_{62}$]·19H$_2$O (4). A sample of 33 g (7.5 mmol) of α_1-K$_9$Li[P$_2$Mo$_5$W$_{12}$O$_{61}$]·18H$_2$O (**3**) was added to a mixture of 150 mL of 1 M LiCl, 15 mL (7.5 mmol) of 0.5 M NaVO$_3$ and 20 mL of concentrated HCl (d = 1.19). The clear solution was treated with 30 g of KCl. The reddish precipitate was filtered and then air-dried. Anal. Calcd for K$_7$[P$_2$Mo$_5$VW$_{12}$O$_{62}$]· 19H$_2$O: K, 6.22; P, 1.41; Mo, 10.90; V, 1.16; W, 50.2; H$_2$O, 7.57. Found: K, 6.37; P, 1.42; Mo, 10.22; V, 1.20; W, 50.5; H$_2$O, 7.52.

4,9,10,15,16-Na$_{12}$[P$_2$Mo$_5$W$_{10}$O$_{56}$]·23H$_2$O (7). A suspension of 30 g of K$_6$[P$_2$Mo$_6$W$_{12}$O$_{62}$]·14H$_2$O (**5**) in 60 mL of water was treated with 25 g of NaClO$_4$·H$_2$O. After vigorous stirring, the potassium perchlorate was filtered off and 150 mL of 1 M Na$_2$CO$_3$ was added to the filtrate. The precipitate was filtered after 15 mn, washed with methanol, and air-dried. Anal. Calcd for Na$_{12}$[P$_2$Mo$_5$W$_{10}$O$_{56}$]· 23H$_2$O: Na, 6.96; P, 1.56; Mo, 12.10; W, 46.4; H$_2$O, 10.44. Found: Na, 7.34; P, 1.54; Mo, 11.85; W, 47.0; H$_2$O, 10.39.

4,9,10,15,16-1-K$_7$[P$_2$Mo$_5$VW$_{12}$O$_{62}$]·17H$_2$O (8). A mixture of 25 mL of 0.5 M NaVO$_3$ and 250 mL of 1 M HCl was treated with 55 g of α_2-K$_{10}$[P$_2$Mo$_5$W$_{12}$O$_{61}$]·18H$_2$O (**6**). Then 35 g of KCl was added to the solution. The yellow precipitate was filtered and then air-dried. Anal. Calcd for K$_7$[P$_2$Mo$_5$VW$_{12}$O$_{62}$]·17H$_2$O: K, 6.26; P, 1.42; Mo, 10.97; V, 1.07; W, 50.5; H$_2$O, 7.00. Found: K, 6.42; P, 1.42; Mo, 10.47; V, 1.10; W, 50.0; H$_2$O, 7.02.

4,9,10,15,16-1,2,3-K$_8$[HP$_2$Mo$_5$V$_3$W$_{10}$O$_{62}$]·18H$_2$O (10). Na$_{12}$[P$_2$-Mo$_5$W$_{10}$O$_{56}$]·23H$_2$O (**7**) (20 g) was added to a mixture of 30 mL of 0.5 M NaVO$_3$, 40 mL of 1 M HCl, and 80 mL of water. Then 30 g of KCl was added to the clear solution. The red precipitate was filtered and then dissolved in 250 mL of warm water for crystallization. Anal. Calcd for K$_8$[HP$_2$Mo$_5$V$_3$W$_{10}$O$_{62}$]·18H$_2$O: K, 7.51; P, 1.48; Mo, 11.47; V, 3.66; W, 44.0; H$_2$O, 7.78. Found: K, 7.4; P, 1.45; Mo, 11.59; V, 3.48; W, 43.4; H$_2$O, 7.82.

4,9,10,15-Na$_{12}$[P$_2$Mo$_4$W$_{11}$O$_{56}$]·23H$_2$O (12). This compound was prepared from K$_6$[P$_2$Mo$_4$W$_{14}$O$_{62}$]·14H$_2$O (**14**) by the same procedure as **7** from **5**. Anal. Calcd for Na$_{12}$[P$_2$Mo$_4$W$_{11}$O$_{56}$]·23H$_2$O: K, 6.81; P, 1.53; Mo, 9.47; W, 49.9; H$_2$O, 10.21. Found: K, 7.18; P, 1.50; Mo, 9.17; W, 49.3; H$_2$O, 10.33.

4,9,10,15-1-K$_7$[P$_2$Mo$_4$VW$_{13}$O$_{62}$]·16H$_2$O (13). A solution of 25 mL of 0.5 M NaVO$_3$ was acidified with 150 mL of 0.35 M HCl, and 56 g of K$_{10}$[P$_2$Mo$_4$W$_{13}$O$_{61}$]·19H$_2$O (**11**) was added. A yellow precipitate was obtained by addition of 56 g of KCl and was filtered and air-dried. Anal. Calcd for K$_7$[P$_2$Mo$_4$VW$_{13}$O$_{62}$]·16H$_2$O: K, 6.11; P, 1.38; Mo, 8.57; V, 1.14; W, 53.4; H$_2$O, 6.43. Found: K, 6.71; P, 1.34; Mo, 8.06; V, 1.15; W, 53.3; H$_2$O, 6.37.

4,9,10,15-1,2,3-K$_8$[P$_2$Mo$_4$V$_3$W$_{11}$O$_{62}$]·18H$_2$O (15). This compound was prepared from **12** by the same procedure as **10** from **7**. Anal. Calcd for K$_8$[P$_2$Mo$_4$V$_3$W$_{11}$O$_{62}$]·18H$_2$O: K, 7.34; P, 1.46; Mo, 9.01; V, 3.39; W, 47.5; H$_2$O, 7.82. Found: K, 7.23; P, 1.45; Mo, 8.97; V, 3.50; W, 47.3; H$_2$O, 7.75.

1,4,9,10,15,16-K$_9$[H$_3$P$_2$V$_6$W$_{12}$O$_{62}$]·18H$_2$O (18). The potassium salt K$_{12}$[H$_2$P$_2$W$_{12}$O$_{48}$]·24H$_2$O (32 g, 8 mmol) was dissolved in a

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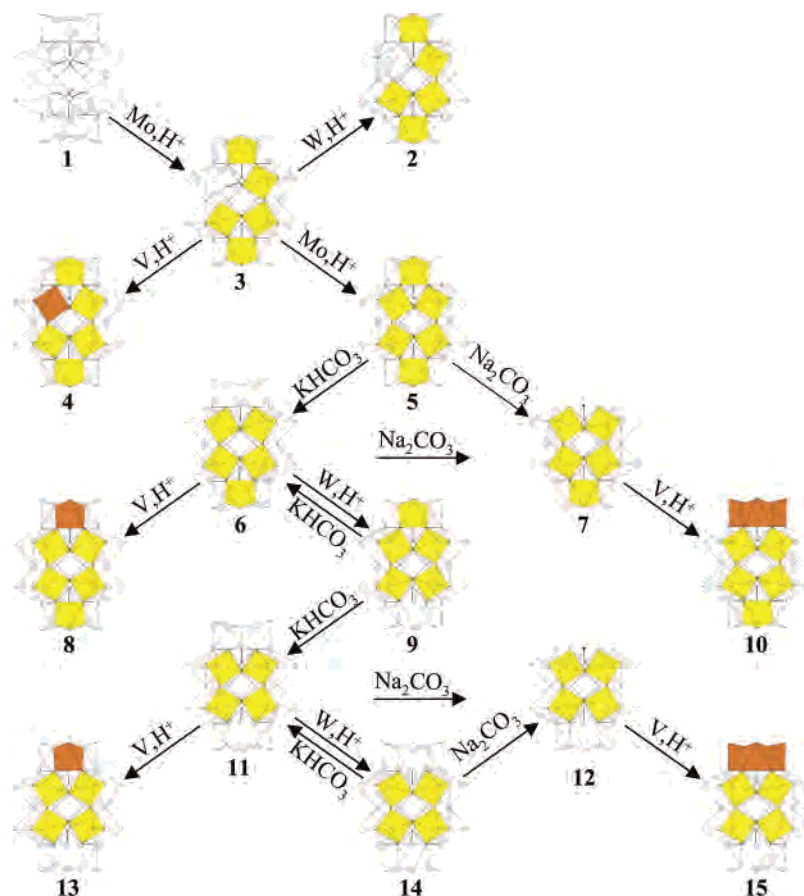
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Figure 2. Routes of formation of the Mo−V−W Dawson heteropolyanions by successive selective hydrolysis and condensation reactions. Hydrolyses by KHCO$_3$ or Na$_2$CO$_3$ give the polar monovacant or trivacant species, respectively.

solution obtained by addition of 10 mL of 1 M HCl in 400 mL of water. Then 100 mL (50 mmol) of 0.5 M NaVO$_3$ was added and, immediately, 70 mL of 1 M HCl. The pH was about 3. A saturated KCl solution (200 mL) was added and the precipitate separated by filtration. It was dissolved in 600 mL of warm water (40 °C) and allowed to crystallize at room temperature. Anal. Calcd for K$_9$-[H$_3$P$_2$V$_6$W$_{12}$O$_{62}$]·18H$_2$O: K, 8.29; P, 1.46; V, 7.21; W, 52.0; H$_2$O, 7.63. Found: K, 8.12; P, 1.47; V, 7.26; W, 51.8; H$_2$O, 7.56.

Analyses. Tungsten, molybdenum, and vanadium were determined by polarography in an acetate buffer of their respective pyrocatechol complexes. Potassium was determined by gravimetry of the tetraphenylborate salt, sodium by atomic absorption spectroscopy, and phosphorus by spectrophotometry of the molybdovanadophosphate.[18] Water was determined by thermogravimetric analysis.

NMR Characterizations. The very concentrated solutions required for [183]W NMR were prepared by dissolving the potassium salts in an aqueous saturated LiClO$_4$ solution, filtering off the KClO$_4$ precipitate, and adding 10% D$_2$O for field frequency lock. [183]W NMR spectra were recorded at room temperature in 10-mm-o.d. tubes on a Bruker WM250, a Bruker AC300, or a Bruker AM500 apparatus operating at 10.4, 12.5, or 20.8 MHz, respectively. The spectral width was chosen to ca. 150 ppm (1500, 2000, and 3000 Hz respectively). Depending on the symmetry of the species and on the spectrometer, high quality spectra, with good signal-to-noise ratio to observe tungsten satellites, required between 2000 and 50000 transients corresponding to 1-h to 1-day spectrometer time.

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The highest resolution, for the determination of $^2J_{W-P}$ coupling constants, was obtained at the lowest field (WM250) whereas the highest field (AM500) gave the highest sensitivity spectra for determination of $^2J_{W-W}$ coupling constants. Chemical shifts are reported with respect to WO$_4^{2-}$ ($\delta = 0$ ppm) according to the IUPAC recommendation: positive δ corresponds to high frequency shift (deshielding) with respect to the reference. They were measured by the substitution method, using a saturated aqueous solution (in D$_2$O) of dodecatungstosilicic acid (H$_4$SiW$_{12}$O$_{40}$) as a secondary standard ($\delta = -103.8$ ppm).

For each species, ^{31}P spectra (101.5, 121.5, and 202.5 MHz respectively) were measured, for control, prior to [183]W spectra on the same NMR tubes, using the same tunable VSP probehead. For the vanadium-containing species, [51]V spectra were also measured, at 65.7 and 131.4 MHz, under the same conditions on the WM250 and AM500 spectrometers, respectively.

Better quality spectra, especially for the quadrupolar [51]V nucleus, were nevertheless obtained using less concentrated solutions (0.02 M) in 1 M aqueous LiCl.

The ^{31}P and [51]V chemical shifts were referenced to external 85% H$_3$PO$_4$ and to neat VOCl$_3$, respectively, using the substitution method. No bulk magnetic susceptibility correction was applied.

Taking into account the experimental conditions and the NMR line widths, the accuracy for the chemical shift measurements amounts to ca. 0.1, 0.03, and 0.5−1 ppm for [183]W, ^{31}P, and [51]V, respectively. For the dissymmetrical anions, however, the chemical shift difference between the two nonequivalent ^{31}P nuclei is obtained at ±0.01 ppm.

Results and Discussion

Strategy of Syntheses. Figure 2 illustrates the successive hydrolysis and condensation steps involved in the synthesis of some mixed W/Mo/V Dawson heteropolyanions. The strategy was mainly based on the selectivity of hydrolysis reactions. Some empirical rules which have been mostly previously reported[9] have to be considered: (i) Moderate alkaline hydrolysis of a complete ("saturated") Mo/W mixed anion $[P_2Mo_xW_{18-x}O_{62}]^{6-}$ by $KHCO_3$ leads to monovacant ("lacunary") α_2 species (vacant site in a polar group). (ii) Alkaline hydrolysis of a complete Mo/W mixed anion $[P_2Mo_xW_{18-x}O_{62}]^{6-}$ by Na_2CO_3 leads to trivacant $[P_2Mo_yW_{15-y}O_{56}]^{12-}$ species. (iii) Everything being otherwise identical, the rate of alkaline hydrolysis at a site occupied by molybdenum is about 10-fold higher than the rate at a site occupied by tungsten. (iv) The rate of hydrolysis of M atoms of a $\{M_3O_{13}\}$ polar group is higher if the neighboring metal atoms in equatorial position are molybdenum. (v) Addition of vanadate to the trivacant $[P_2Mo_yW_{15-y}O_{56}]^{12-}$ or hexavacant $[H_2P_2W_{12}O_{48}]^{12-}$ species with moderate acidification leads to a complete Dawson structure in one step. The behavior of vanadium is clearly related to the great stability of the complete vanadium compounds at high pH values due to their high negative charge. (vi) On the contrary, addition of tungsten or molybdenum under the same conditions occurs in two steps leading first to a monovacant species, then to a saturated one. The monovacant α_2 isomer (polar vacancy) is always obtained from the trivacant species, but the α_1 isomer (equatorial vacancy) is obtained in the presence of lithium cations from the hexavacant species. With sodium and potassium cations, the α_1 isomer quickly gives the α_2 isomer.

Let us illustrate these rules, considering some examples (Figure 2). The 1,9,10,15,16-4-$[P_2 Mo_5VW_{12}O_{62}]^{7-}$ species **4** (Mo atoms are in sites 1, 9, 10, 15, and 16 and vanadium in site 4, α_1 isomer) was synthesized from α_1-$[P_2$-$Mo_5W_{12}O_{61}]^{10-}$ **3** first obtained by reaction of molybdenum with the hexavacant $[H_2P_2W_{12}O_{48}]^{12-}$ anion **1** in the presence of lithium (rule v). A different way has to be considered for the synthesis of the corresponding 4,9,10,15,16-1-$[P_2Mo_5$-$VW_{12}O_{62}]^{7-}$ **8** (α_2 isomer): the monovacant α_2-$[P_2$-$Mo_5W_{12}O_{61}]^{10-}$ compound **6** was obtained by specific hydrolysis of $[P_2Mo_6W_{12}O_{62}]^{6-}$ **5** by $KHCO_3$ (rules i and iii), and then vanadium was added.

Synthesis of **15** in which four molybdenum atoms are in neighboring equatorial positions on one face of the Dawson structure and three vanadium atoms constitute a trioxometallic polar group is a good example to illustrate the application of the rules i to v**.** This compound has to be synthesized from the trivacant compound **12** in one step by addition of vanadium (rule v), but selective formation of **12** is possible only from the symmetric complete framework **14** or the corresponding monovacant α_2 species **11** by reaction with Na_2CO_3 (rule ii). The obtention of pure **11** sample from **9** is then the critical step since hydrolysis of the unsymmetrical anion **9** by $KHCO_3$ can lead, a priori, to a mixture of four compounds (Figure 3): **11** (the desired
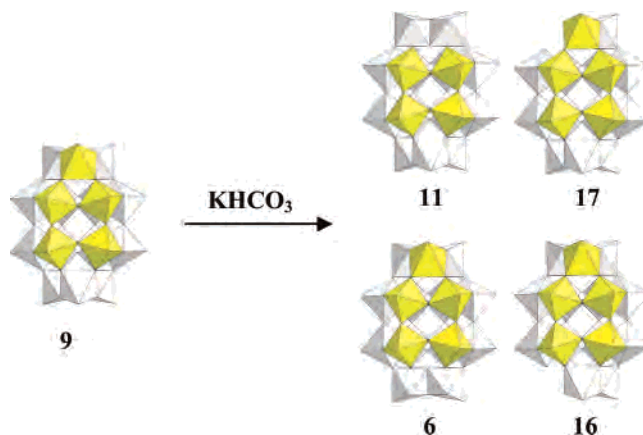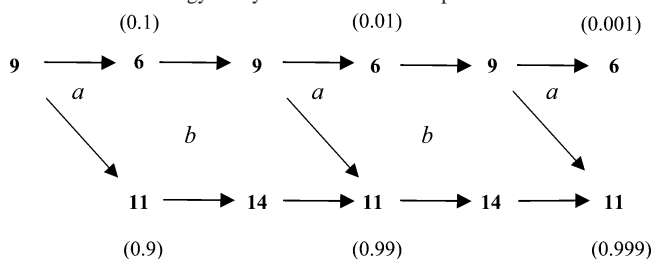
Figure 3. The four possible monovacant anions resulting from hydrolysis of **9** by $KHCO_3$. Actually, only a mixture of **6** (about 10%) and **11** (about 90%) was obtained.

Scheme 1. Strategy of Synthesis of Pure Compound **11**[a]

[a] Proportions of **6** and **11** after each cycle of hydrolysis and condensation reactions are indicated in parentheses. Reactants: step *a*, $KHCO_3$; step *b*, $WO_4^{2-} + H^+$.

product) and **6** (from which **9** was obtained) if a metallic atom near to the four equatorial molybdebum atoms is eliminated (molybdenum or tungsten, respectively), but also **16** and **17** if a tungsten atom of a polar group and not directly bound to these molybdenum atoms is eliminated. Actually, the ^{31}P NMR analysis of the solution showed that only two compounds are obtained, about 90% of **11** and 10% of **6**. This means that the rate of hydrolysis on sites near the equatorial molybdenum atoms is much greater than the rate at the other polar sites (rule iv). The relative proportions of **11** and **6** are due to the higher hydrolytic lability of molybdenum compared to tungsten (rule iii).

In order to obtain a pure **11** sample, addition of tungstate to the mixture **11** + **6** with moderate acidification followed again by hydrolysis by $KHCO_3$ was performed two times. The first reaction yielded to a mixture of **14** and **9** in the same proportions, the second to a mixture of **11** and **6** in a ratio 99/1. A second cycle of reactions gave **11** with 99.9% purity (Scheme 1).

^{183}W NMR Characterization. Relative positions of V, Mo, and W atoms in the structure have been confirmed by ^{183}W NMR spectroscopy. Establishment of the structure and assignment of the resonance lines to the different kinds of tungsten atoms has been made according to the following considerations: (i) The number and relative intensities of lines gives the symmetry of the molecule. (ii) Values of homonuclear coupling constants indicate the presence of neighboring tungsten atoms linked by sharing either corners (about 20 Hz) or edge (about 10 Hz). Unfortunately, they
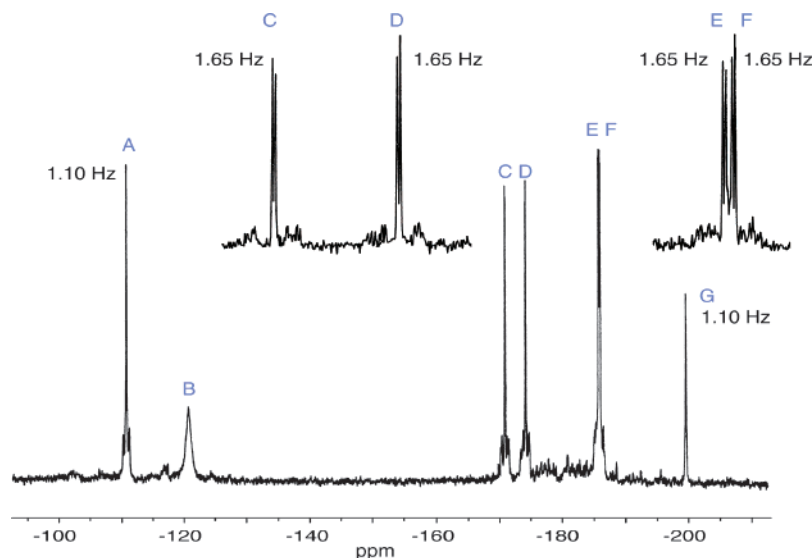
Figure 4. 20.8 MHz ^{183}W NMR spectrum of a ca. 0.3 M aqueous solution of 4,9,10,15-1-$[P_2Mo_4VW_{13}O_{62}]^{7-}$, **13**. Total spectrometer time, 7 h. Assignment of resonance peaks: A, W17, W18; B, W2, W3; C, D, E, F, equatorial W atoms; G, W16. The insets represent the abscissa expansion of lines C, D, E, and F, after resolution enhancement. This shows the splitting due to heteronuclear coupling with the phosphorus atom. For these lines the $^2J_{W-P}$ coupling values are indicated and are characteristic of equatorial W nuclei.

are frequently degenerated and do not allow an unambiguous assignment. (iii) Polar tungsten atoms are less strongly coupled to the phosphorus nucleus than equatorial ones ($^2J_{P-W}$ about 1 and 2 Hz, respectively). (iv) Tungsten atoms in the vicinity of vanadium give broader resonance lines than the other ones.

A table collecting the data for the saturated compounds is given as Supporting Information. All ^{183}W NMR spectra show unambiguously that the heteropolyanions **2** to **14** have been obtained by the strategy illustrated in Figure 2. NMR spectra and elemental analysis showed that all compounds were obtained with a purity higher than 90%. As a typical example the ^{183}W NMR spectrum of **13** is presented Figure 4.

The variations of the chemical shifts when molybdenum atoms are substituted for tungsten atoms are illustrated in Figure 5. Resonance lines of polar and equatorial tungsten atoms of $[P_2W_{18}O_{62}]^{6-}$ (-126.5 and -172 ppm, respectively[9]) can be taken as a starting point to discuss the influence of the Mo/W substitution on the chemical shift values of the remaining tungsten atoms. As a general rule, only small variations are observed for the Mo/W substitution. For example, the presence of four equatorial molybdenum atoms in **14** leads to variations less than 2 ppm for all the tungsten atoms, except for the W1,W16 pair which is shielded by 7 ppm. As already noted,[9] this is likely due to the similarity between Mo(VI) and W(VI), their substitution inducing neither strong geometric nor electronic perturbations. The most influenced W1 and W16 atoms are linked to two molybdenum atoms by corner junctions. We can thus expect that corner junctions are more effective than edge junctions to pass on the perturbation resulting from the Mo/W substitution. The same observation holds for the pentasubstituted compound **9** (Figure 5).

Influence of the V/W substitution in a polar position has been previously discussed.[9] Variations of the chemical shifts
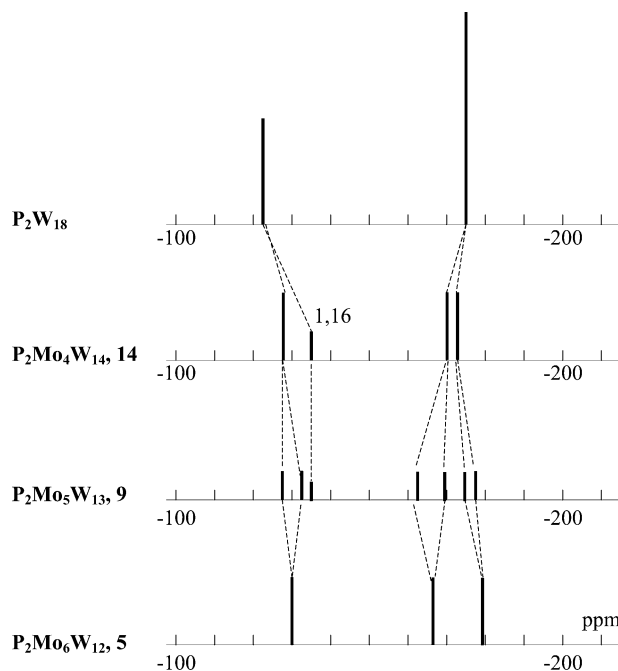

Figure 5. Variations of ^{183}W chemical shifts with substitution of molybdenum for tungsten atoms in $[P_2W_{18}O_{62}]^{6-}$.

are larger than for the Mo/W substitution, and the main change is a large shielding of the equatorial and polar tungsten atoms which are on the same face of the Dawson structure and opposite to the V/W polar substitution site. For example, for $[P_2V_3W_{15}O_{62}]^{9-}$, the V/W substitution leads to a shielding of the six opposite equatorial tungsten atoms by 53 ppm and of the three polar opposite tungsten atoms by 30 ppm (Figure 6). On the contrary, the chemical shift of the six equivalent equatorial tungsten atoms near the perturbated site is not much modified. For α_2-$[P_2VW_{17}O_{62}]^{7-}$, only the opposite tungsten atoms on the same face as V are strongly shielded, the equatorial W10,W15 pair by 33 ppm and the polar W16 by 41 ppm (Figure 7). The higher
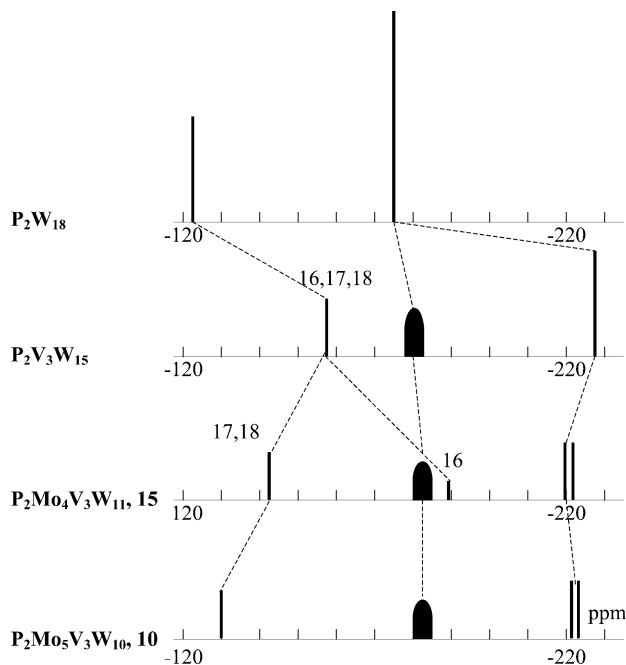
Figure 6. Variations of [183]W chemical shifts with substitution of molybdenum for tungsten atoms in $[P_2V_3W_{15}O_{62}]^{9-}$.
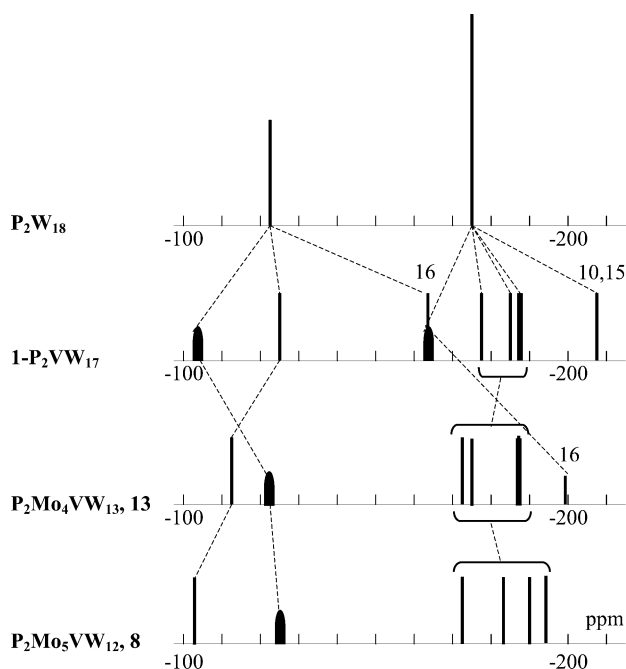

Figure 7. Variations of [183]W chemical shifts with substitution of molybdenum for tungsten atoms in $1-[P_2VW_{17}O_{62}]^{7-}$ (α_2 isomer).

W−O−W angles of the corner junctions (about 160°) and corresponding homonuclear $^2J_{W-W}$ coupling constants (20−30 Hz) compared to edge junctions (about 120° and 10 Hz, respectively) are likely responsible of the preferential transmission of the vanadium effect on tungsten atoms of the same face.

We can now discuss the influence of an additional Mo/W substitution in the four equatorial sites 4, 9, 10, and 15 of a face of the Dawson structure. Two main observations can be drawn from Figures 6 and 7: (i) The polar W_{16} atom on the same face as molybdenum atoms is further shielded by 36 ppm in **15** and 32 ppm in **13**. (ii) On the contrary,

chemical shifts of the equatorial tungsten atoms of the two other faces of the structure are only slightly modified. Thus, equatorial molybdenum atoms, which do not lead to important variations of tungsten chemical shifts when they are alone, enhance the effect of vanadium in a polar site, once again only for tungsten atoms linked by successive corner junctions. The additional molybdenum substitution effect can be related to the electronic structure of mixed V/W and V/Mo Dawson heteropolyanions. It has been shown by Lopez et al.[19] that the lowest unoccupied molecular orbital (LUMO) in $[P_2V_3W_{15}O_{62}]^{10-}$ corresponds to the three polar vanadium atoms. On the contrary, in the hypothetical molybdenum analogue $[P_2V_3Mo_{15}O_{62}]^{10-}$, the LUMO is not localized in one of the regions of the molecule and the participation of polar V and equatorial Mo is similar. It can be expected that there is also a competition between V and Mo orbitals when four equatorial W are replaced by four Mo on a face of the molecule. The LUMO corresponds to metal atoms in sites 1, 4, 9, 10, and 15, and the electronic influence of the polar V atom on the opposite W16 atom of the same face would be enhanced.

[51]V NMR Characterization. For the vanadium containing compounds, [51]V NMR agrees also with the postulated structures: monovanadium polar substituted species exhibit a relatively narrow line (less than 100 Hz), depending on the concentration, at −536 and −537 ppm for **8** and **13**, respectively. For the equatorial substituted anion **4**, the relatively broad line (ca. 700 Hz) shifts to high frequency by about 20 ppm. A similar shielding was already observed for the monovanadium derivatives of $P_2W_{18}O_{62}^{6-}$.[9] For the trivanadium compounds **10** and **15**, two resonances, with relative intensity 1:2, are observed, in agreement with C_s symmetry. According to its intensity, the high frequency signal at −488 ppm for both species is assigned to the V atom in the plane of symmetry, in the vicinity of two equatorial Mo atoms. This resonance is significantly broader (ca. three times) than the second one (−513 for **10**, −510 ppm for **15**): this reflects the quicker relaxation rate for the V atoms adjacent to Mo than for those adjacent to W. As the nuclear relaxation of [51]V is dominated by quadrupolar mechanism, the relaxation rate is proportional to the electric field gradient at the nucleus and strongly depends on the symmetry of the V coordination sphere. This means that the VO_6 octahedron is likely less distorted for vanadium V2 and V3 (near W) than for V1, in agreement with the higher flexibility of the Mo−oxo groups with respect to W−oxo groups.

^{31}P NMR Characterization. Mixed W/Mo/V Dawson heteropolyanions are well characterized by ^{31}P NMR spectroscopy. Symmetric species where the two half-anions are identical show one signal, and unsymmetrical species show two signals, the chemical shift values depending on the composition and on the relative positions of the W, Mo, and V atoms in the framework. Chemical shift values observed for the mixed species stable in solution are indicated in the Table 1, where P1 and P2 are the phosphorus atoms of the

(19) Lopez, X.; Bo, C.; Poblet, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 12574.

Table 1. Observed and Calculated ^{31}P NMR Chemical Shifts for Molybdo−Tungsto−Diphosphates and Molybdo−Tungsto−Vanado−Diphosphates[a]

no.	compound	P1			P2			$\Delta\delta_{obsd}$	$\Delta\delta_{calcd}$	$\Delta(\Delta\delta)$
		δ_{obsd}	δ_{calcd}	$\Delta = \delta_{obsd} - \delta_{calcd}$	δ_{obsd}	δ_{calcd}	$\Delta = \delta_{obsd} - \delta_{calcd}$			
1	1,4,9,10,15,16-P$_2$□$_6$W$_{12}$									
2	1,9,10,15,16-P$_2$Mo$_5$W$_{13}$	−10.43	−10.76	+0.33	−9.58	−9.85	+0.27	−0.85	−0.91	+0.06
3	1,9,10,15,16-4-P$_2$Mo$_5$□W$_{12}$	−7.56	−6.85	−0.71	−10.02	−10.27	+0.25	+2.46	+3.42	−0.96
4	1,9,10,15,16-4-P$_2$Mo$_5$VW$_{12}$	−9.51	−10.15	+0.64	−9.79	−10.31	+0.52	+0.28	+0.16	+0.12
5	1,4,9,10,15,16-P$_2$Mo$_6$W$_{12}$	−9.47	−9.84	+0.37	−9.47	−9.84	+0.37			
6	4,9,10,15,16-1-P$_2$Mo$_5$□W$_{12}$	−5.6	−4.94	−0.66	−10.66	−11.02	+0.36	+5.06	+6.08	−1.02
7	4,9,10,15,16-1,2,3-P$_2$Mo$_5$□$_3$W$_{10}$									
8	4,9,10,15,16-1-P$_2$Mo$_5$VW$_{12}$	−8.88	−8.99	+0.11	−9.86	−10.31	+0.45	+0.98	+1.32	−0.34
9	1,4,9,10,15-P$_2$Mo$_5$W$_{13}$	−9.52	−9.83	+0.31	−10.24	−10.59	+0.35	+0.72	+0.76	−0.04
10	4,9,10,15,16-1,2,3-P$_2$Mo$_5$V$_3$W$_{10}$	−4.5	−4.40	−0.1	−10.96	−11.28	+0.32	+6.46	+6.88	−0.42
11	4,9,10,15-1-P$_2$Mo$_4$□W$_{13}$	−5.62	−4.93	−0.69	−11.45	−11.77	+0.32	+5.83	+6.84	−1.01
12	4,9,10,15-1,2,3-P$_2$Mo$_4$□$_3$W$_{11}$									
13	4,9,10,15-1-P$_2$Mo$_4$VW$_{13}$	−9.02	−8.98	−0.04	−11.62	−11.06	−0.56	+2.6	+2.08	+0.52
14	4,9,10,15-P$_2$Mo$_4$W$_{14}$	−10.30	−10.58	+0.28	−10.30	−10.58	+0.28			
15	4,9,10,15-1,2,3-P$_2$Mo$_4$V$_3$W$_{11}$	−4.57	−4.39	−0.18	−11.75	−12.03	+0.28	+7.18	+7.64	−0.46
18	1,4,9,10,15,16-P$_2$V$_6$W$_{12}$	−10.57	−11.02	+0.45	−10.57	−11.02	+0.45			

[a] P1 is in the half-anion with atom numbering from 1 to 9 and P2 in the half-anion with atom numbering from 10 to 18. $\Delta\delta = \delta(P1) - \delta(P2)$, $\Delta(\Delta\delta) = \Delta\delta_{obsd} - \Delta\delta_{calcd}$. In the lacunary species, the vacancies are symbolized as □ in the formula.

Table 2. ^{31}P Chemical Shifts of Dawson MoW and VW Heteropolyanions and Variations by Reference to α-[P$_2$W$_{18}$O$_{62}$]$^{6-}$ [a]

species	$\delta(P1)$	$\delta(P2)$	$\Delta\delta(P1)$	$\Delta\delta(P2)$	perturbation	$\Delta\delta = \delta(P1) - \delta(P2)$
[P$_2$W$_{18}$O$_{62}$]$^{6-}$	−12.44	−12.44				
1-[P$_2$□W$_{17}$O$_{61}$]$^{10-}$	−6.79	−13.63	+5.65	−1.19	polar lacuna (pl)	6.84
4-[P$_2$□W$_{17}$O$_{61}$]$^{10-}$	−8.53	−12.86	+3.91	−0.42	equatorial lacuna (el)	4.33
1-[P$_2$MoW$_{17}$O$_{62}$]$^{6-}$	−11.69	−12.45	+0.75	−0.01	polar Mo (pm)	0.76
4-[P$_2$MoW$_{17}$O$_{62}$]$^{6-}$	−11.52	−12.43	+0.92	+0.01	equatorial Mo (em)	0.91
1-[P$_2$VW$_{17}$O$_{62}$]$^{7-}$	−10.84	−12.92	+1.60	−0.48	polar V (pv)	2.08
4-[P$_2$VW$_{17}$O$_{62}$]$^{7-}$	−11.83	−12.90	+0.61	−0.46	equatorial V (ev)	1.07
1,2,3-[P$_2$V$_3$W$_{17}$O$_{62}$]$^{9-}$	−6.25	−13.89	+6.19	−1.45	polar V3 (pv3)	7.64

[a] P1 is in the half-anion with atoms numbering from 1 to 9 and P2 in the half-anion with atoms numbering from 10 to 18. $\Delta\delta(Pi) = \delta(Pi)$ (compound) $- \delta(Pi)(P_2W_{18})$. The perturbation will be noted pl, pl′; el, el′; pm, pm′, etc. for the P atom in the same or the opposite subunit, respectively.

half-anions with metallic atoms numbered 1 to 9 and 10 to 18, respectively (Figure 1).

We have previously reported for the 1,2,3-4-[P$_2$M$_3$-M′W$_{14}$O$_{62}$]$^{n-}$ anions (M, M′ = Mo, V), where {M$_3$O$_{13}$} is a polar trimetallic group and M′ is localized in an equatorial site, that fairly good chemical shift values can be predicted by an additive model taking into account the independent contributions of {M$_3$O$_{13}$} and M′ on the chemical shifts of the two phosphorus atoms.[9] Moreover, a vacant site leads to a strong deshielding of the phosphorus atoms in the same half-anion (P1). We have tried to determine if this model can be applied to the mixed V−Mo−W anions derived from the hexavacant [H$_2$P$_2$W$_{12}$O$_{48}$]$^{12-}$ anion **1**. The ^{31}P NMR chemical shifts of the reference compounds are indicated in Table 2, as well as the variations $\Delta\delta(P1)$ and $\Delta\delta(P2)$ of these chemical shifts relative to the value observed with [P$_2$W$_{18}$O$_{62}$]$^{6-}$. It appears clearly that the variations of the chemical shifts of the phosphorus atoms are dominated by the contributions of vacant sites and trivanadic polar groups.

Let us consider two examples to illustrate the model. The first example is 4,9,10,15,16-1-[P$_2$Mo$_5$VW$_{12}$O$_{62}$]$^{7-}$ **8**. To calculate the chemical shift of P1, according to the above-defined rules, we have to take into account the effect of one polar atom V1 (pv, see Table 2) and two equatorial Mo (4 and 9), in the same half-anion (em), and of one polar Mo (16) (pm′) and two equatorial Mo (10 and 15) (em′), in the second half-anion: $\Delta\delta(P1) = (pv + 2\,em) + (pm′ + 2\,em′)$

$= (+1.6 + 2 \times 0.92) + (-0.01 + 2 \times 0.01) = +3.45$ ppm, and $\delta(P1) = -12.44 + 3.45 = -8.99$ ppm (see Table 2 for the definition of pv, em, pm′, and em′). To calculate the increment for P2 we simply have to substitute pv′ for pv, em′ for em, and so one in the above formula., i.e., $\Delta\delta(P2) = (pv′ + 2\,em′) + (pm + 2\,em) = (-0.48 + 2 \times 0.01) + (0.75 + 2 \times 0.92) = +2.13$ ppm, and $\delta(P2) = -12.44 + 2.13 = -10.31$ ppm. These values are in rather good agreement with the experimental ones, $\delta(P1) = -8.88$ and $\delta(P2) = -9.86$ ppm.

The second example is the compound **15** (4,9,10,15-1,2,3-[P$_2$Mo$_4$V$_3$W$_{11}$O$_{62}$]$^{9-}$). $\Delta\delta(P1) = (pv3 + 2\,em) + (2\,em′) = (+6.19 + 2 \times 0.92) + (2 \times 0.01) = +8.05$ ppm and $\Delta\delta(P2) = (pv3′ + 2\,em′) + (2\,em) = (-1.45 + 2 \times 0.01) + (2 \times 0.92) = +0.41$ ppm. The calculated values $\delta(P1) = -4.39$ and $\delta(P2) = -12.03$ ppm are in good agreement with the experimental ones, -4.57 and -11.75 ppm, respectively.

The calculated and observed chemical shifts of the phosphorus atoms of several mixed W−Mo−V Dawson heteropolyanions prepared according to the Figure 2 are listed in Table 1. For unsymmetrical species, we have also considered the difference $\Delta\delta = \delta(P1) - \delta(P2)$, which might be preferred to separate $\delta(P1)$ and $\delta(P2)$, values for the characterization of these compounds. From Table 1, we observe that the larger deviations between calculated and experimental $\Delta\delta$ values (ca. 1 ppm) occur for the monova-
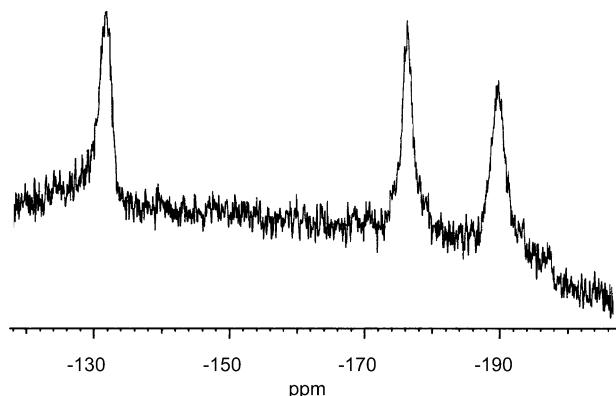
Figure 8. 20.8 MHz ^{183}W NMR spectrum of a ca. 0.3 M aqueous solution of $[H_3P_2V_6W_{13}O_{62}]^{12-}$, **18**. Total spectrometer time 12 h.

cant species. Smaller discrepancies (ca. 0.5 ppm or less) are present for some vanadium-containing compounds.

Actually, this additive model is unable to take into account some "second order" effects resulting from the neighboring of perturbations (except for trivanadium groups for which pv3 is different from 3.pv). Nevertheless, it can be seen that the additive model of the influence of Mo and V groups on the chemical shifts of the two phosphorus atoms of the Dawson structure applies fairly well.

Stability of $[H_3P_2V_6W_{12}O_{62}]^{9-}$ in Solution. The ^{31}P NMR spectrum of $[H_3P_2V_6W_{12}O_{62}]^{9-}$ exhibits one signal at -10.57 ppm, in good agreement with the calculated value -10.67 ppm if we assume that the tungstic framework is the same as in the hexavacant precursor (Table 1). The ^{183}W NMR spectrum of the concentrated solution (0.3 mol·L^{-1}) exhibits three broad signals of equal intensities (Figure 8) at -131.5 ppm ($\Delta\nu = 50$ Hz), -176.3 ppm ($\Delta\nu = 35$ Hz), and -190.2 ppm ($\Delta\nu = 55$ Hz).

The hexavanadium species is however not indefinitely stable in aqueous solution. The initial ^{31}P NMR line at natural

pH in 1 mol·L^{-1} LiCl aqueous solution splits slowly with time into two signals in the intensity ratio 1:1 at slightly different chemical shifts, -10.41 and -10.72 ppm. For its completion, this reaction requires more than 1 week at room temperature and ca. 15 h at boiling. In order to interpret this behavior, we can observe that there is a very asymmetric distribution of charges in the 1,4,9,10,15,16-$[H_3P_2V_6W_{12}O_{62}]^{9-}$ anion, with an accumulation of the negative charge on the face containing the six neighboring vanadium atoms. This asymmetry could destabilize the anion, and a migration of the vanadium atoms away from each other should occur in the framework in order to spread out the negative charge. A possibility would be the migration of equatorial vanadium atoms to other equatorial positions in such a way that the symmetry is lowered. According to the model developed before, the chemical shift variations are expected to be low (observed values $+0.16$ and -0.15 ppm) since the number of equatorial and polar vanadium atoms is not modified.

In acid solution (pH 3), a progressive replacement of the signal at -10.57 ppm by a signal at -9.07 ppm occurs. According to our model, this could correspond to the migration of two equivalent vanadium atoms of the two half-anions (for example 4 and 10) from an equatorial to a polar position with conservation of the symmetry of the polyanion. We can forecast for such an acidified species one signal with a variation of the chemical shift of $+1.32$ ppm close to the observed value $+1.50$ ppm.

Note that the ^{51}V NMR spectra of all these vanadium-rich compounds are very complex and cannot afford any structural information.

Supporting Information Available: A table giving the ^{183}W NMR data for the saturated Dawson species. This material is available free of charge via the Internet at http://pubs.acs.org.

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