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Dawson Type Heteropolyanions. 1. Multinuclear (^{31}P, ^{51}V, ^{183}W) NMR Structural Investigations of Octadeca(molybdotungstovanado)diphosphates α-1,2,3-$[P_2MM'_2W_{15}O_{62}]^{n-}$ (M, M′ = Mo, V, W): Syntheses of New Related Compounds[1]

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The mixed binary anions dimolybdopentadecatungstodiphosphate, 1,2-$[P_2Mo_2W_{15}O_{61}]^{10-}$, hexadecatungstodivanadodiphosphate, 1,2-$[P_2V_2W_{16}O_{62}]^{8-}$, and the ternary molybdotungstovanadophosphates 1,2-3-$[P_2Mo_2VW_{15}O_{62}]^{7-}$ and 1-2,3-$[P_2MoV_2W_{15}O_{62}]^{8-}$, derived from the Dawson anion α-$[P_2W_{18}O_{62}]^{6-}$ by formal substitution in one polar W_3O_{13} group, have been synthesized. The lacunary dimolybdo anion $P_2Mo_2W_{15}$, obtained by selective W elimination and then partial Mo addition, is the precursor for the saturated $P_2Mo_2W_{16}$ and $P_2Mo_2VW_{15}$. The divanado anions $P_2V_2W_{16}$ and $P_2MoV_2W_{15}$ were obtained by V substitution from P_2W_{18} and $P_2Mo_3W_{15}$, respectively. All the octadeca(molybdotungstovanado)diphosphates α-(1,2,3)-$[P_2MM'_2W_{15}O_{62}]^{n-}$ (M, M′ = Mo, V, W) were characterized by electrochemistry and multinuclear (^{31}P, ^{51}V, ^{183}W) solution NMR techniques. An empirical incremental formula was established to calculate the ^{31}P chemical shift of the P(1) phosphorus atom in the half-anion PMM'_2W_6 substituted in the polar position. Moreover, a simple additive model allows one to predict the ^{31}P chemical shifts of Dawson polyanions substituted in the equatorial position. The reactivity of 4-P_2MW_{17} toward alkaline degradation to get P_2MW_{14} is discussed on this basis: vanadium(V) in the 4-location directs the departure of the W_3O_{13} in the other half-anion (16-18-locations) whereas molybdenum(VI) has no directing effect. The ^{183}W chemical shifts are discussed also in relation with the nature and the location of the substituting atoms; although considerably remote from the polar substituted site, the tungsten atoms in the opposite polar group are generally as well affected (shielded) as those directly bound (μ-oxo junction in the same polar group) to the substituted atom (deshielded), even in the case of the isocharge W → Mo replacement.

Introduction

The heteropolyanions are of continuing interest as heterogeneous and homogeneous catalysts.[2,3] Among them the tungstovanadophosphates and molybdovanadophosphates have been long used, and several new species have been described in recent years.[4] With a view to obtaining more stable molybdovanadic species, we have attempted to prepare numerous octadodeca(molybdotungstovanado)diphosphates with Dawson structure[5] (α isomer) (Figure 1). This work concerns all the 1,2,3-$[P_2MM'_2W_{15}O_{62}]^{n-}$ (abbreviated as $P_2MM'_2W_{15}$ (M, M′ = Mo, V, W)) anions.[6] Until now all the known species, i.e. the 1,2,3-$P_2V_nW_{18-n}$ (n = 1–3) tungstovanadophosphates isolated by Harmalker, Leparulo, and Pope[7a] and the 1-P_2MoW_{17} and 1,2,3-$P_2Mo_3W_{15}$ molybdotungstophosphates, have been prepared by addition of vanadyl or acidified molybdate to the lacunar (1)-$P_2\square W_{17}$ (trivial name α_2)[8] and (1,2,3)-$P_2\square_3W_{15}$[9] tungstophosphates. We propose herein new routes to obtain $P_2M_2W_{16}$[10] and $P_2MM'_2W_{15}$ (M, M′ = Mo, V) compounds, which were characterized by ^{31}P NMR spectroscopy; their structures have been confirmed by ^{183}W NMR spectroscopy.

Experimental Section

Preparations. Potassium salts of α-P_2W_{18},[11] (1)-$P_2\square W_{17}$ (α_2),[11] (4)-$P_2\square W_{17}$(α_1),[11] 1,2,3-$P_2Mo_3W_{15}$,[9] 1- and 4-P_2MoW_{17},[8] and 1,2,3-$P_2V_3W_{15}$[12] and the sodium salt of (1,2,3)-$P_2\square_3W_{15}$[11] were prepared by published methods.

1,2-$K_{10}P_2Mo_2W_{15}O_{61}\cdot 18H_2O$.[13] A solution of 45 g (10 mmol) of $Na_{12}P_2W_{15}O_{56}$(aq.) in 500 ml of 1M LiCl and 10 mL of 1M HCl was simultaneously treated with 20 mL (20 mmol) of 1 M Li_2MoO_4 and 50 mL of 1M HCl. The pH was at about 4.5. Then 200 mL of saturated potassium chloride solution were added. The white crystalline precipitate was filtered off and recrystallized from the minimum of hot water. Anal. Calcd. for $K_{10}P_2Mo_2W_{15}O_{61}\cdot 18H_2O$: K, 8.31; P, 1.32; Mo, 4.08; W 58.6; H_2O, 6.86. Found: K, 8.23; P, 1.34; Mo, 3.9; W, 58.6; H_2O, 6.97. The ^{31}P NMR spectrum exhibits two equal peaks at -5.09 and -13.92 ppm. The crude yield was higher than 80%, which is similar for all compounds obtained from the addition of molybdate or vanadate.

For the following compounds the polarographic data are given in Table I and the ^{31}P and ^{51}V NMR data in Tables II and III.

1,2-$K_6P_2Mo_2W_{16}O_{62}\cdot xH_2O$ (Purity 75%). A solution of 9.5 g (2 mmol) of $K_{10}P_2Mo_2W_{15}O_{61}\cdot 18H_2O$ in a mixture of 160 mL of 1 M LiCl and 40 mL of molar acetic acid–lithium acetate buffer was treated with 2 mL (2 mmol) of 1 M Li_2WO_4 and 100 mL of 1 M HCl. While the mixture was vigorously stirred, 50 g of solid KCl was added. The yellow precipitate was filtered off and recrystallized from the minimum amount of water. Anal. Calcd for $K_6P_2Mo_2W_{16}O_{62}\cdot 15H_2O$: K, 5.00; P, 1.32; Mo, 4.09, W, 62.7; H_2O, 5.75. Found: K, 4.86; P, 1.34; Mo, 4.0; W, 63.1; H_2O, 5.64. Although the analysis agrees with the above proposed formula, ^{31}P and ^{183}W NMR spectroscopies show that this salt contains no more than 75% of $P_2Mo_2W_{16}$; the impurities were identified as P_2W_{18}, 1-P_2MoW_{17}, and 1,2,3-$P_2Mo_3W_{15}$ (see below). Attempts to obtain pure $P_2Mo_2W_{16}$ by selective precipitation or by recrystallization failed, all these anions being isocharged. Moreover, the aqueous solution evolves by disproportionation of $P_2Mo_2W_{16}$ into 1-P_2MoW_{17} and 1,2,3-$P_2Mo_3W_{15}$.

1,2-3-$K_7P_2Mo_2VW_{15}O_{62}\cdot 19H_2O$.[13] A sample of 47 g (10 mmol) of $K_{10}P_2Mo_2W_{15}O_{61}\cdot 18H_2O$ was added to a solution of 20 mL (10 mmol) of 0.5 M $NaVO_3$, 40 mL of 1 M HCl, and 250 mL of water. After dissolution 25 g of solid potassium chloride was added. The yellow

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(6) The tungsten atoms in α-P_2W_{18} (Figure 1) are numbered according to the IUPAC recommendations (Jeannin, Y.; Fournier, M. *Pure Appl. Chem.* **1987**, *59*, 1529). In order to make easily understandable the comparison between molybdenum- and vanadium-substituted anions, we adopted the following rules: (i) whatever its nature, the substituting atom in primarily substituted compounds (i.e. obtained directly from P_2W_{18}) is given the lowest index; (ii) this index is maintained in the subsequent modifications of the anion (partial hydrolysis or substitution); (iii) in the lacunary species, the vacancies (missing W atoms) are numbered too and symbolized as $\square$ in the formula of the anion. For example, P_2W_{15} will be written as (1,2,3)-$P_2\square_3W_{15}$.

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(9) Ciabrini, J. P.; Contant, R.; Fruchart, J. M. *Polyhedron* **1983**, *2*, 1229.

(10) Harmalker et al.[7a] have prepared $P_2V_2W_{16}$ from "P_2W_{16}" that should be present in a very small amount in solid P_2W_{15}. Indeed P_2W_{16} is an unstable intermediary observed during the spontaneous transformation of P_2W_{15} into (1)-$P_2\square W_{17}$ (Contant, R.; Thouvenot, R. Unpublished work).

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(12) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947.

(13) One reviewer let us know about the following patent: Vasilevskis, J.; De Deken, J. C.; Saxton, R. J.; Wentrcek, P. R.; Fellmann, J. D.; Kipnis, L. S. Olefin oxidation catalyst system. PCT Int. Appl. WO 87 01,615, 1987. In it are described the syntheses of compounds formulated $K_{10}P_2W_{15}Mo_2O_{61}$ and $K_7P_2W_{15}Mo_2VO_{62}$ without any characterization.

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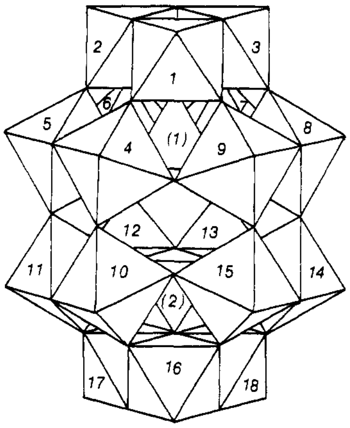

Figure 1. Idealized structure for α-$[P_2W_{18}O_{62}]^{6-}$ and its substitution derivatives.

crystalline precipitate was filtered off and then air-dried Anal. Calcd for $K_7P_2Mo_2VW_{15}O_{62}\cdot19H_2O$: K, 5.86; P, 1.33; Mo, 4.11; V, 1.09; W, 59.05; H_2O, 7.32. Found: K, 6.30; P, 1.35; Mo, 4.1; V, 1.1; W, 59.4; H_2O, 7.37.

1-2,3-$K_8P_2MoV_2W_{15}O_{62}\cdot18H_2O$. A solution of 35 g (7.5 mmol) of $K_6P_2Mo_3W_{15}O_{62}\cdot14H_2O$ in 375 mL of water was treated with a mixture of 30 mL of 0.5 M $NaVO_3$ (15 mmol) and 20 mL of 1 M NaOH (20 mmol). The solution was refluxed for 30 min and then cooled to room temperature, and 125 mL of saturated KCl solution was added. The yellow orange precipitate was filtered off and recrystallized at 5 °C from the minimum amount of acidified water (pH = 2). Anal. Calcd for $K_8P_2MoV_2W_{15}O_{62}\cdot18H_2O$: K, 6.71; P, 1.33; Mo, 2.06; V, 2.19; W, 59.1; H_2O, 7.33. Found: K, 6.52; P, 1.36; Mo, 2.2; V, 2.25; W, 58.5; H_2O, 7.47.

Concerning the following three products, Harmalker et al.[7a] have prepared and isolated the corresponding V(IV) compounds as solid salts. $P_2V_2W_{16}$ was only obtained in a very small amount as a byproduct of $P_2V_3W_{15}$.[10] The V(V) derivatives were obtained from oxidation of the V(IV) aqueous solutions; they were characterized in solution but not isolated as solid salts.

1,2-$K_8P_2V_2W_{16}O_{62}\cdot18H_2O$. A solution of 50 g (10 mmol) of α_2-$K_{10}P_2W_{17}O_{61}\cdot20H_2O$ in 250 mL of hot water was treated with 45 mL of 0.5 M $NaVO_3$ (22.5 mmol). The solution was refluxed for 1 h and then cooled to room temperature. A yellow precipitate (mainly P_2VW_{17}) appeared. It was filtered off after 2-3 h, and the filtrate was treated with 100 mL of saturated KCl solution. The precipitate was filtered off after about 1 h and then recrystallized from the minimum amount of water (yield 20 g). Anal. Calcd for $K_8P_2V_2W_{16}\cdot18H_2O$: K, 6.60; P, 1.31; V, 2.15; W, 62.1; H_2O, 6.84. Found: K, 6.58; P, 1.31; V, 2.2; W, 61.4; H_2O, 6.91.

1-$K_7P_2VW_{17}O_{62}\cdot18H_2O$ (α_2). To 140 mL of 0.5 M HCl were added 10 mL of 0.5 M $NaVO_3$ (5 mmol) and then 25 g (5 mmol) of α_2-$K_{10}P_2W_{17}O_{61}\cdot20H_2O$. After dissolution 22 g of KCl was added. The precipitate was filtered off and recrystallized from 30 mL of 0.1 M HCl. Anal. Calcd for $K_7P_2VW_{17}O_{62}\cdot18H_2O$: K, 5.67; V, 1.06; W, 64.7; H_2O, 6.71. Found: K, 5.80; V, 1.1; W, 63.3; H_2O, 6.52.

4-$K_7P_2VW_{17}O_{62}\cdot17H_2O$ (α_1). To 160 mL of 0.5 M HCl were added 10 mL of 0.5 M $NaVO_3$ (5 mmol) and then 25 g (5 mmol) of α_1-$K_9LiP_2W_{17}\cdot20H_2O$. On some occasions the solution was not quite clear so that it was filtered on filter paper. Then 25 g of KCl was added to the filtrate. The precipitate was filtered off and then recrystallized from the minimum amount of 0.1 M HCl. Anal. Calcd for $K_7P_2VW_{17}O_{62}\cdot17H_2O$: K, 5.69; V, 1.06; W, 65.0; H_2O, 6.36. Found: K, 5.67; V, 1.1; W, 64.7; H_2O, 6.26.

The following three compounds $Na_{12}P_2MoW_{14}O_{56}$, $K_8HP_2MoV_3W_{14}O_{62}$, and $K_6P_2Mo_4W_{14}O_{62}$ are mixtures of two isomers (see below).

4-$Na_{12}P_2MoW_{14}O_{56}\cdot24H_2O$. A suspension of 40 g (8 mmol) of 4-$K_6P_2MoW_{17}O_{62}\cdot14H_2O$ (α_1) in 80 mL of water was treated with 30 g of $NaClO_4\cdot H_2O$. The mixture was cooled by using an ice bath, and the $KClO_4$ was filtered off. The filtrate was treated with 120 mL of 1 M Na_2CO_3. The precipitate was decanted and then filtered out on a large sintered glass frit and sucked dry, washed with 20 mL of 1 M NaCl solution, washed twice with 25 mL of ethanol, and air-dried (yield 22 g). Anal. Calcd for $Na_{12}P_2MoW_{14}O_{56}\cdot24H_2O$: Na, 6.36; P, 1.43; Mo, 2.21; W, 59.4; H_2O, 9.96. Found: Na, 6.19; P, 1.41; Mo, 2.1; W, 60.7; H_2O, 9.83.

4-1,2,3- (or 4-16,17,18-) $K_8HP_2MoV_3W_{14}O_{62}\cdot18H_2O$. A solution of 100 mL of 1 M HCl and 28 mL (14 mmol) of 0.5 M $NaVO_3$ in 200 mL of water was treated with 20 g (4.6 mmol) of $Na_{12}P_2MoW_{14}O_{56}\cdot24H_2O$. After the solid had dissolved 100 mL of saturated KCl solution was added. The orange precipitate was filtered off and then air-dried. Anal. Calcd for $K_8HP_2MoV_3W_{14}O_{62}\cdot18H_2O$: K, 6.93; P, 1.37; Mo, 2.12; V, 3.39; W, 57.0; H_2O, 7.17. Found: K, 7.64; P, 1.34; Mo, 2.1; V, 3.15; W, 57.1; H_2O, 6.99.

1,2,3,4- (or 4,16,17,18-) $K_6P_2Mo_4W_{14}O_{62}\cdot16H_2O$. A solution of 12 mL (12 mmol) of 1 M Li_2MoO_4 in 200 mL of 0.5 M HCl was treated with 17 g (3.9 mmol) of $Na_{12}P_2MoW_{14}O_{56}\cdot24H_2O$. After the solid had dissolved 30 g of solid KCl was added. The yellowish precipitate was filtered off and air-dried. Anal. Calcd for $K_6P_2Mo_4W_{14}O_{62}\cdot16H_2O$: K, 5.17; P, 1.37; Mo, 8.46; W, 56.8; H_2O, 6.35. Found: K, 4.95; P, 1.37; Mo, 8.23; W, 57.0; H_2O, 6.20.

4-$Na_{13}P_2VW_{14}O_{56}\cdot xH_2O$. To a suspension of 20 g (4 mmol) of 4-$K_7P_2VW_{17}O_{62}\cdot17H_2O$ in 65 mL of water was added 20 g of $NaClO_4\cdot H_2O$. The potassium perchlorate was eliminated by filtration, and the filtrate was treated with 60 mL (60 mmol) of 1 M Na_2CO_3. After 1 h the precipitate was filtered off, washed with methanol, and air-dried (yield 3.2 g). Anal. Calcd for $Na_{13}P_2VW_{14}O_{56}\cdot25H_2O$: V, 1.18; W, 59.4. Found: V, 1.1; W, 59.0.

4,16,17,18-$K_8H_2P_2V_4W_{14}O_{56}\cdot19H_2O$. To a solution of 30 mL (15 mmol) of 0.5 M $NaVO_3$ and 500 mL of 0.5 M HCl was added 21.5 g (5 mmol) of $Na_{13}P_2VW_{14}O_{56}$(aq). After the solid had dissolved 80 g of solid KCl was added. The orange precipitate was filtered off and air-dried. Anal. Calcd for $K_8H_2P_2V_4W_{14}O_{62}\cdot19H_2O$: K, 7.07; W, 57.8; V, 4.58; H_2O, 7.69. Found: K, 7.37; W, 57.5; V, 4.45; H_2O, 7.59.

16,17,18-4-$K_7P_2Mo_3VW_{14}O_{62}\cdot18H_2O$. A solution of 60 mL of 1 M HCl and 6 mL (6 mmol) of 1 M Li_2MoO_4 diluted with 40 mL of water was treated with 8 g (1.84 mmol) of $Na_{13}P_2VW_{14}O_{56}$(aq). After the solid had dissolved 25 g of KCl was added. The precipitate was filtered off and air-dried. Anal. Calcd for $K_7P_2Mo_3VW_{14}O_{62}\cdot18H_2O$: K, 6.04; P, 1.36; W, 56.4; Mo, 6.30; V, 1.12; H_2O, 7.08. Found: K, 6.37; P, 1.34; W, 56.9; Mo, 6.15; V, 1.05; H_2O, 7.11.

Analyses. Tungsten molybdenum, and vanadium were determined by polarography in an acetate buffer[8] of their respective pyrocatechol complexes. Potassium was determined by gravimetry of the tetraphenylborate salt, sodium by atomic absorption spectrophotometry, and phosphorus by spectrometry of the molybdovanadophosphate.[14] Water content was determined by thermogravimetric analysis.

NMR Measurements. The solutions for ^{183}W NMR measurements were obtained by dissolving the potassium salts in aqueous saturated $LiClO_4$ solution, filtering off the $KClO_4$ precipitate, and adding 10% heavy water for field frequency lock. ^{183}W NMR spectra were recorded in 10-mm o.d. tubes on a Bruker WM 250 or Bruker AM 500 apparatus operating at 10.4 or 20.8 MHz, respectively. The spectral width was generally restricted to 1000-1500 Hz (about 100-150 ppm) at 10.4 MHz, allowing a digitalization better than 0.2 Hz/pt after a 16K points Fourier transformation, but at higher frequency (20.8 MHz) the larger spectral width (2000-3000 Hz) leads to poorer digital resolution and consequently to a lower precision of the coupling constant values. Acquisiton time was in the range 1.5-2.5 s, which, according to the required number of scans (between 1000 and 20 000, depending on the number of lines and on the purity; see below), allowed us to get good quality spectra in a few hours, sometimes even in less than 0.5 h. Chemical shifts were measured with reference to an external 2 M Na_2WO_4 solution in alkaline D_2O by using saturated dodecatungstosilicate acid ($H_4SiW_{12}O_{40}$) in D_2O solution as a secondary standard (δ = -103.8 ppm[15a]).

^{31}P and ^{51}V NMR spectra were recorded in 10-mm o.d. tubes on a Bruker WM 250 apparatus operating at 101.2 and 65.7 MHz, respectively, in both cases in the Fourier transform mode. The ^{31}P chemical shifts were measured on 0.02 M solutions of the polyanions in aqueous 1 M LiCl (10% D_2O) and were referenced to external 85% H_3PO_4 by the substitution method. The ^{51}V chemical shifts and line widths were measured on the concentrated (and viscous) solutions already used for the ^{183}W NMR spectra and were externally referenced to neat $VOCl_3$ by using VO_4^{3-} solution in alkaline D_2O as a secondary standard (δ = -536 ppm[16a]).

Results

The pathways connecting the species investigated in this work are summarized in Schemes I and II. All the $[P_2MM'_2W_{15}O_{62}]^{n-}$

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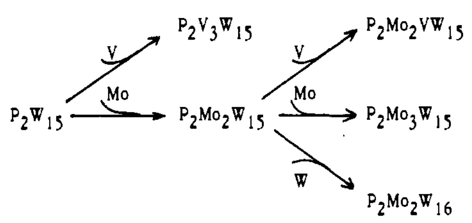
Scheme I



Scheme II

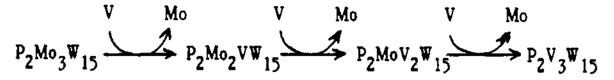


Table I. Polarographic Data[a] for α-Octadeca(molybdotungstovanado) diphosphates at pH 1.0 (0.1 M HCl; 0.9 M NaCl)

anion	$E_{1/2}$, V vs SCE		
α-P_2W_{18}	+0.04 (1)[b]	−0.14 (1)	
4-P_2MoW_{17}	+0.39 (1)	−0.08 (1)	
1-P_2MoW_{17}	+0.25 (1)	−0.15 (1)	
1,2-$P_2Mo_2W_{16}$	+0.27 (1)	+0.10 (1)	
1,2,3-$P_2Mo_3W_{15}$	+0.28 (1)	+0.14 (1)	−0.13 (1)
1,2-3-$P_2Mo_2VW_{15}$	+0.46 (1)	+0.05 (2)	
1-2,3-$P_2MoV_2W_{15}$	+0.37 (2)		
1,2,3-$P_2V_3W_{15}$	+0.42 (1)	+0.28 (2)	
1,2-$P_2V_2W_{16}$	+0.36 (2)		
1-P_2VW_{17}	+0.41 (1)	+0.15 (1)	
4-P_2VW_{17}	+0.49 (1)	+0.20 (1)	

[a] Rotating platinum electrode; uncertainty ±0.03 V. [b] Number of electrons confirmed by controlled potential coulometry for the first waves.

anions have been characterized by polarography (Table I), by ^{31}P and ^{51}V NMR spectroscopy (Table II), and by ^{183}W NMR spectroscopy (Tables IV and V). The ^{31}P NMR results for $[P_2MM'_3W_{14}O_{62}]^{n-}$ species are presented in Table III. These will be introduced at appropriate place in the section that follows.

Discussion

Characterization. For all the $K_xP_2MM'_2W_{15}O_{62}$ species the IR spectra are very similar[7a] and do not allow one to unambiguously identify a given compound. The Dawson type molybdotungstophosphates[17] and tungstovanadophosphates[7a] have been already characterized by polarography or cyclic voltammetry on a glassy-carbon electrode. With the molybdotungstovanadophosphates the potentials of the first waves, assigned to the V(V)/V(IV) couple, are little changed by the presence of molybdenum (Table I). Finally, ^{31}P NMR spectroscopy provides the best identification because of the existence of two lines of equal intensities and a large chemical shift range (ca. 7 ppm between extreme values).[18] It easily allows one to check the purity and to identify the impurities.

^{31}P NMR Spectroscopy of the 1,2,3-$[P_2MM'_2W_{15}O_{62}]^{n-}$ Anion (M, M′ = Mo, V, W). The gradual progression of the chemical shifts as the number of molybdenum atoms[18] or of vanadium atoms[7a] increases is well established. The same trend is observed in the progressive substitution of vanadium for molybdenum (Table II; Figure 2). The high-field peak has been assigned[7a,18] to the P(2) phosphorus atom in the unsubstituted half-anion. The low-field chemical shift corresponding to P(1) does not vary linearly as the number of substituted atoms. But the variation of the P(1) chemical shift when one atom M′ is substituted for M to give the triad $M_{3-n}M'_n$ can be expressed by the following empirical formula:

$$\Delta\delta = \delta_n - \delta_{n-1} = A + (n-1)B \qquad n = 1\text{–}3 \tag{1}$$

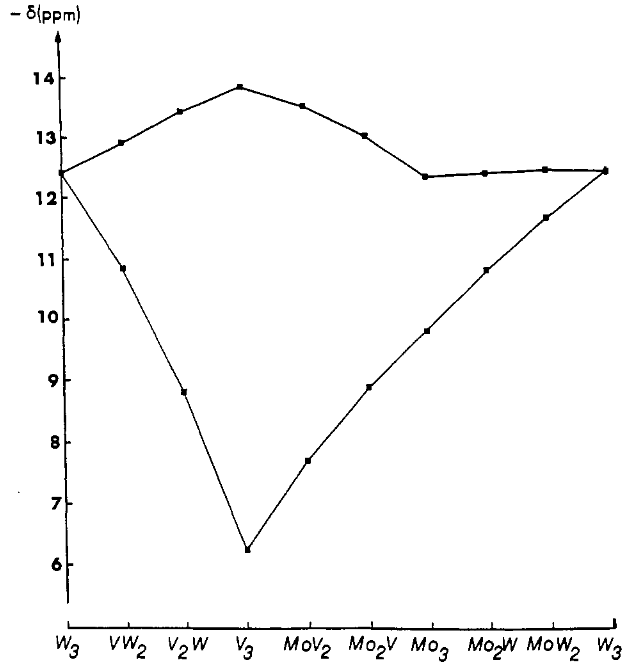


Figure 2. Variation of the ^{31}P chemical shifts in substituted Dawson anions with the number of molybdenum and vanadium atoms.

Table II. ^{31}P and ^{51}V NMR Data for Dawson Type Molybdotunstovanadophosphates

anion	$-\delta(P(1))$	$-\delta(P(2))$	$-\delta(^{51}V)$	$\Delta\nu_{1/2}$
α-$[P_2W_{18}O_{62}]^{6-}$	12.44	12.44		
	12.7[a]			
1-$[P_2VW_{17}O_{62}]^{7-}$	10.84 (10.84)[b]	12.92	553.8	90
	11.4[c]	13.5[c]	554.7[c]	33[c]
1,2-$[P_2V_2W_{16}O_{62}]^{8-}$	8.82 (8.78)[b]	13.44	527.5	180
	9.3[c]	13.9[c]	528[c]	70[c]
1,2,3-$[P_2V_3W_{15}O_{62}]^{9-}$	6.25 (6.26)[b]	13.90	501.3	350
	6.8[c]	14.4[c]	503[c]	130[c]
1-2,3-$[P_2MoV_2W_{15}O_{62}]^{8-}$	7.70 (7.70)[b]	13.57	524.5	250
1,2-3-$[P_2Mo_2VW_{15}O_{62}]^{7-}$	8.89 (8.88)[b]	13.04	549.1	100
1,2,3-$[P_2Mo_3W_{15}O_{62}]^{6-}$	9.81 (9.80)[b]	12.34		
	10.2[a,d]	12.7[a,d]		
1,2-$[P_2Mo_2W_{16}O_{62}]^{6-}$	10.80 (10.81)[b]	12.41		
1-$[P_2MoW_{17}O_{62}]^{6-}$	11.69 (11.69)[b]	12.45		
	11.9[a]	12.6[a]		
4-$[P_2VW_{17}O_{62}]^{7-}$	11.83	12.90		
	12.3[c]	13.4[c]	570[c]	180[c]
4-$[P_2MoW_{17}O_{62}]^{6-}$	11.60	12.51		

[a] Reference 18. The differences between our values and those reported in refs 18 and 7, all without bulk magnetic susceptibility correction,[16] arise mainly from the kind of spectrometer used: permanent[18] or electromagnet[7a] with horizontal field instead of our superconducting magnet with vertical field. [b] The values in parentheses were calculated with eq 1 given in the text. [c] Reference 7a. The line widths reported in these reference for ^{51}V are systematically about 3 times smaller in accordance with the fact that our concentrated solutions are more viscous and the quadrupolar relaxation of the vanadium solution is more rapid in our case. [d] These values were given for the compound erroneously formulated $P_2Mo_2W_{16}$.

where *A* and *B* are constants that depend on both M and M′. The empirical values of *A* and *B* are respectively (i) +1.60 and +0.46 when vanadium is substituted for tungsten, (ii) +0.75 and +0.13 when molybdenum is substituted for tungsten, and (iii) +0.92 and +0.16 when vanadium is substituted for molybdenum.

Experimental and calculated (according to eq 1) ^{31}P chemical shifts are reported in Table II. In the formula (1) the coefficient *A* expresses the intrinsic effect of the M → M′ substitution and the coefficient *B* expresses the influence of neighboring substituted M′ atoms.

^{31}P NMR Spectroscopy of the 1,2,3-4- (or 4-16,17,18-) $[P_2MM'_3W_{14}O_{62}]^{n-}$ Anion (M, M′ = Mo, V). These species are obtained from 4-P_2VW_{17} or 4-P_2MoW_{17} by the same process as

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(17) Contant, R.; Ciabrini, J. P. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1525.

(18) Massart, R.; Contant, R.; Fruchart, J. M.; Ciabrini, J. P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916.

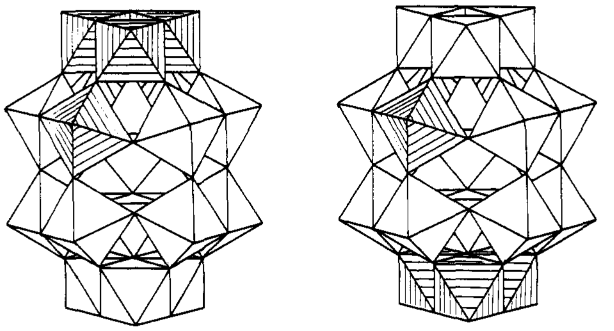

Figure 3. Idealized structures for both 1,2,3,4- and 4,16,17,18-$P_2M_4W_{14}$ isomers. Hatched octahedra correspond to the M (Mo, V) atoms.

that for $P_2M_3W_{15}$ from P_2W_{18}. The hydrolysis by sodium carbonate leads to the departure of a polar W_3O_{13} group to give a trivacant compound $P_2\square_3W_{15}$, $P_2\square_3VW_{14}$, or $P_2\square_3MoW_{14}$ whose lacuna can be refilled by a Mo_3O_{13} or V_3O_{13} group. Because in P_2W_{18} (symmetry D_{3h}) the two polar W_3O_{13} groups are equivalent, there is only one $P_2\square_3W_{15}$ and only one $P_2M_3W_{15}$. On the contrary, in 4-P_2MW_{17} (symmetry C_1) the two polar W_3O_{13} groups are inequivalent and therefore two $P_2\square_3MW_{14}$ and two $P_2MM'_3W_{14}$ compounds can be expected (Figure 3). The problem is then to determine if Mo or V in an equatorial site influences the departure of tungsten atoms from polar sites. In the case of M = Mo, we obtained a mixture of two $P_2Mo_4W_{14}$ (and a mixture of two $P_2MoV_3W_{14}$), as shown by its ^{31}P NMR spectrum, which presents four lines of the same height. On the contrary, in the case of M = V, only one $P_2V_4W_{14}$ (and one $P_2Mo_3VW_{14}$) isomer is obtained (two-line ^{31}P NMR spectrum). In order to determine the nature of this isomer, we assumed that the ^{31}P chemical shifts in $P_2MM'_3W_{14}$ can be calculated by using a simple additive model: the difference of chemical shifts from P_2W_{18} will be considered as the sum of their respective values for 1,2,3-$P_2M_3W_{15}$ and 4-$P_2M'W_{17}$. This hypothesis does not take into account the mutual influence of neighboring polar–equatorial substitutions. In order to check the validity of this model, we calculated the chemical shifts of both $P_2MoV_3W_{14}$ isomers. For the 4-1,2,3-$P_2MoV_3W_{14}$ isomer, (i) the equatorial molybdenum atom (4-position) involves as in 4-P_2MoW_{17} a downfield shift (−11.60 + 12.44 = +0.84 ppm) for the phosphorus atom P(1) in the same half-anion and a small shift (−12.51 + 12.44 = −0.07 ppm) for the phosphorus atom P(2) in the opposite half-anion, (ii) the three polar vanadium atoms V(1,2,3) involve as in 1,2,3-$P_2V_3W_{15}$ a downfield shift of −6.25 + 12.44 = +6.19 ppm for P(1) in the same half-anion and an upfield shift of −13.90 + 12.44 = −1.46 ppm for P(2). So for 4-1,2,3-$P_2MoV_3W_{14}$, the low-field line would appear at −12.44 + 6.19 + 0.84 = −5.41 ppm and the upfield line would appear at −12.44 − 1.46 − 0.07 = −13.97 ppm. For the 4–16,17,18-$P_2MoV_3W_{14}$ isomer, the low-field line would appear at −12.44 + 6.19 − 0.07 = −6.32 ppm and will be assigned to the phosphorus atom P(2) in the same half-anion as the V_3O_{13} group. The high-field line should be observed at −12.44 − 1.46 + 0.84 = −13.06 ppm and will be assigned to the phosphorus atom P(1) in the $PMoW_8$ half-anion. Comparison with the experimental spectra (Table III) shows a good agreement between observed and calculated values (maximal deviation less than 0.1 ppm). Such a good agreement is also obtained for both $P_2Mo_4W_{14}$ isomers. These results allow us to conclude that, though very simple, this model could predict the ^{31}P chemical shifts of the other mixed Dawson anions reported in this paper. When applied to $P_2V_4W_{14}$, this model gives the following predicted values: −5.64 and −14.36 ppm for the 1,2,3,4-isomer and −6.71 and −13.29 ppm for the 4,16,17,18-isomer. The observed chemical shifts of the unique isomer (−6.71 and −13.20 ppm, Table III) agree only with the latter one. In the same way the $P_2Mo_3VW_{14}$ compound was identified to be the 16,17,18-4-isomer. In conclusion it appears that vanadium located in the equatorial 4-position directs the departure of the W_3O_{13} group in the opposite half-anion, contrary to the molybdenum atom, which has no directive effect. This behavior could be related to a localization of the supplementary negative charge due to the vanadium atom in the P_2VW_8 half-anion, which protects it from basic hydrolytic cleavage. Another explanation would be the instability of the (1,2,3-4)-$P_2\square_3VW_{14}$ isomer owing to a vanadium atom bound to two unshared oxygen atoms. This would agree with the low yield obtained when P_2VW_{14} is prepared (about 15% against 60% for P_2MoW_{14}).

Table III. Comparison between Observed and Calculated ^{31}P NMR Data for Tetra(molybdovanado)tetradecatungstodiphosphates

anion	obsd δ(^{31}P)		calcd[a] δ(^{31}P)	
			P(1)	P(2)
4,16,17,18-$P_2V_4W_{14}$	−6.71	−13.20	−13.29	−6.71
1,2,3,4-$P_2V_4W_{14}$	*b*	*b*	−5.64	−14.36
16,17,18-4-$P_2Mo_3VW_{14}$	−10.26	−11.83	−11.73	−10.27
1,2,3-4-$P_2Mo_3VW_{14}$	*b*	*b*	−9.20	−12.80
4-1,2,3-$P_2MoV_3W_{14}$	−5.46	−13.92	−5.41	−13.97
4-16,17,18-$P_2MoV_3W_{14}$	−6.29	−12.97	−13.06	−6.32
1,2,3,4-$P_2Mo_4W_{14}$	−8.86	−12.26	−8.97	−12.41
4,16,17,18-$P_2Mo_4W_{14}$	−9.73	−11.36	−11.50	−9.88

[a] See text. [b] Not observed.

^{51}V NMR Spectroscopy of 1,2,3-[$P_2VM_2W_{15}O_{62}$]$^{n-}$ (M = Mo, V, W). As already reported by Pope et al.,[7a] the ^{51}V chemical shifts vary nearly linearly with the number of vanadium nuclei (Table II); the resonance line shifts downfield by about 25 ppm by adding one V atom. The δ(^{51}V) values are less sensitive to tungsten–molybdenum replacement: substitution of one Mo for one W induces a minor low-field shift of only about 2.5 ppm. Although the resonance lines of the quadrupolar ^{51}V nucleus are relatively broad (Table II) with respect to the narrow lines of the spin-$^1/_2$ ^{31}P nucleus, the wider spread of ^{51}V chemical shifts allows nevertheless a synthetic mixture of vanadium-containing Dawson polyanions to be characterized by ^{51}V NMR spectroscopy. The line width of the ^{51}V resonance increases as the number of vanadium increases; this broadening, essentially due to favorable relaxation properties of adjacent vanadium atoms, has been already observed in numerous molybdo- and tungstovanadates by Pope et al., who correlated it with the ^{51}V chemical shifts variations.[7b]

^{183}W NMR Spectroscopy of 1,2,3-[$P_2VM_2W_{15}O_{62}$]$^{n-}$ (M = V, W). Before we discuss the ^{183}W NMR chemical shifts, it must be remembered that all tungsten resonances appear as more or less resolved doublets because of coupling with the phosphorus atom. The coupling constant $^2J_{P-W}$ is invariably significantly smaller (about 1 Hz or less) for the polar tungstens than for the equatorial ones (about 1.5 Hz or more);[15] this observation is very helpful for the assignment.

The ^{183}W NMR spectra of mono- and disubstituted vanadium compounds are represented in Figure 4 with those of α-P_2W_{18}[15] and 1,2,3-$P_2V_3W_{15}$[12] for comparison (Table IV).

Substitution of vanadium for tungsten in the polar group induces a loss of all symmetry elements of the initial Dawson anion except one vertical plane containing the unique polar atom, and we expect therefore a spectrum of nine lines for both P_2VW_{17}[19] and $P_2V_2W_{16}$ anions. The twelve equatorial tungsten atoms are responsible for six lines (two W each) in both anions; the polar atoms give three lines of relative intensities 1:2:2 in P_2VW_{17} and 1:1:2 in $P_2V_2W_{16}$. The line assignments for each group (polar or equatorial) were made on the basis of the tungsten–phosphorus coupling constants (see above).

A first general remark can be made: the resonances of all equatorial tungsten nuclei are always upfield, reasonably well displaced from the resonances of all polar nuclei. The spread of the polar resonances is about (lower than) 80 ppm around −120 ppm and that of the equatorial resonances is markedly smaller (about 50 ppm around −200 ppm).

Domaille[20] first noted that in Keggin-substituted polyanions,

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(19) It should be noted that our ^{183}W NMR spectrum of authentic 1-P_2VW_{17} is in complete disagreement with that published by Acerete et al.[15b] The compound prepared by following the synthetic principle reported by Acerete gives ^{183}W and ^{31}P NMR spectra very similar to those of the monovacant α$_2$-P_2W_{17} anion, and its ^{51}V NMR spectrum exhibits many broad resonance lines instead of one sharp line for the α$_2$-P_2VW_{17} anion.[7]

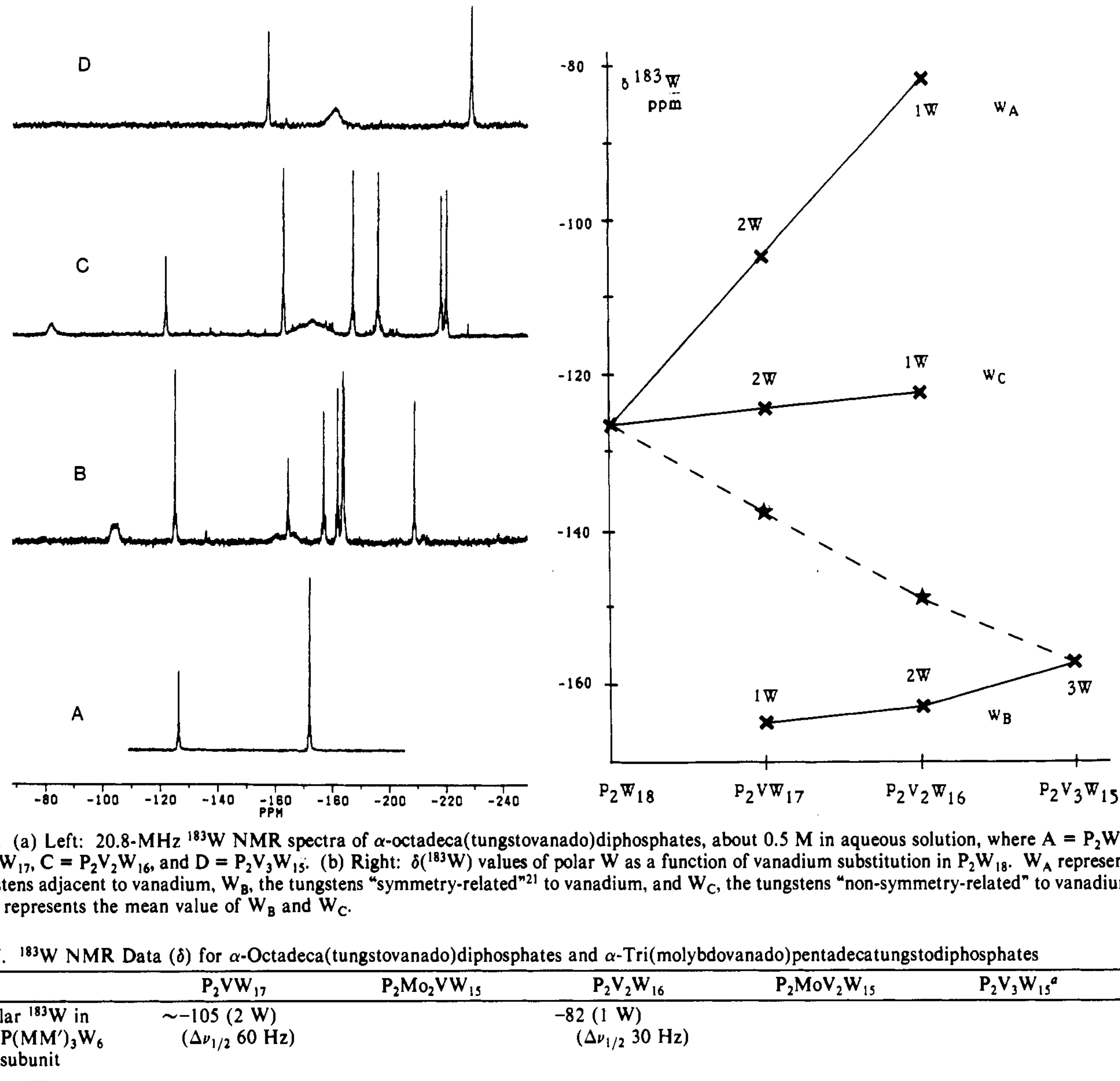

Figure 4. (a) Left: 20.8-MHz ^{183}W NMR spectra of α-octadeca(tungstovanado)diphosphates, about 0.5 M in aqueous solution, where A = P_2W_{18}, B = P_2VW_{17}, C = $P_2V_2W_{16}$, and D = $P_2V_3W_{15}$. (b) Right: δ(^{183}W) values of polar W as a function of vanadium substitution in P_2W_{18}. W_A represents the tungstens adjacent to vanadium, W_B, the tungstens "symmetry-related"[21] to vanadium, and W_C, the tungstens "non-symmetry-related" to vanadium. The star represents the mean value of W_B and W_C.

Table IV. ^{183}W NMR Data (δ) for α-Octadeca(tungstovanado)diphosphates and α-Tri(molybdovanado)pentadecatungstodiphosphates

	P_2VW_{17}	$P_2Mo_2VW_{15}$	$P_2V_2W_{16}$	$P_2MoV_2W_{15}$	$P_2V_3W_{15}$[a]
polar ^{183}W in $P(MM')_3W_6$ subunit	~−105 (2 W)		−82 (1 W)		
	($\Delta\nu_{1/2}$ 60 Hz)		($\Delta\nu_{1/2}$ 30 Hz)		
polar ^{183}W in PW_9 subunit	−125.6 (2 W)		−121.9 (1 W)		
		−135.5 (2 W)		−136.8 (1 W)	
		−150.8 (1 W)		−158.8 (2 W)	
	−164.8 (1 W)		−162.9 (2 W)		−157.3 (3 W)
δ mean value	−139	−144	−150	−151.8	
Δδ amplitude	39.2	15.3	41	22	
equatorial ^{183}W	~−164 (2 W)	~−158 (2 W)			
	($\Delta\nu_{1/2}$ 180 Hz)	($\Delta\nu_{1/2}$ 150 Hz)			
			−173 (4 W)	−174 (4 W)	
			($\Delta\nu_{1/2}$ 150 Hz)	($\Delta\nu_{1/2}$ 150 Hz)	
all $^2J_{W-P}$ about 1.7 Hz	−177.2 (2 W)	−181.2 (2 W)			−180.6 (6 W)
	−182.0 (2 W)	−184.5 (2 W)	−187.1 (2 W)	−190.9 (2 W)	($\Delta\nu_{1/2}$ 45 Hz)
	−184.0 (2 W)	−190.8 (2 W)	−195.9 (2 W)	−206.0 (2 W)	
	−184.4 (2 W)	−191.5 (2 W)			
	−208.8 (2 W)	−202.6 (2 W)			
			−218.0 (2 W)	−218.2 (2 W)	
					−228.5 (6 W)
			−220.0 (2 W)	−219.0 (2 W)	
δ mean value	−183.4	−184.8	−194.5	−197	−204.5
Δδ amplitude	44.8	44.6	47	45	47.9

[a] δ reported at −158, −179, and −226.7 ppm by Domaille et al.[12]

the tungsten atoms in the same triad as the substituent are always the more deshielded nuclei and that tungsten atoms corner coupled to the substituent are generally the more shielded of all W's. It may then be surprising that, in these Dawson substituted polyanions, W atoms adjacent to the vanadium are in all cases at the low-field part of the corresponding absorption region (see Figure 4). Let us recall that the assignment of the lines of W adjacent to vanadium is very easy: these lines are relatively broad with respect to the other ^{183}W NMR lines. This broadening due

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(20) (a) Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677. (b) Domaille, P. J.; Knoth, W. H. *Inorg. Chem.* **1983**, *22*, 818.

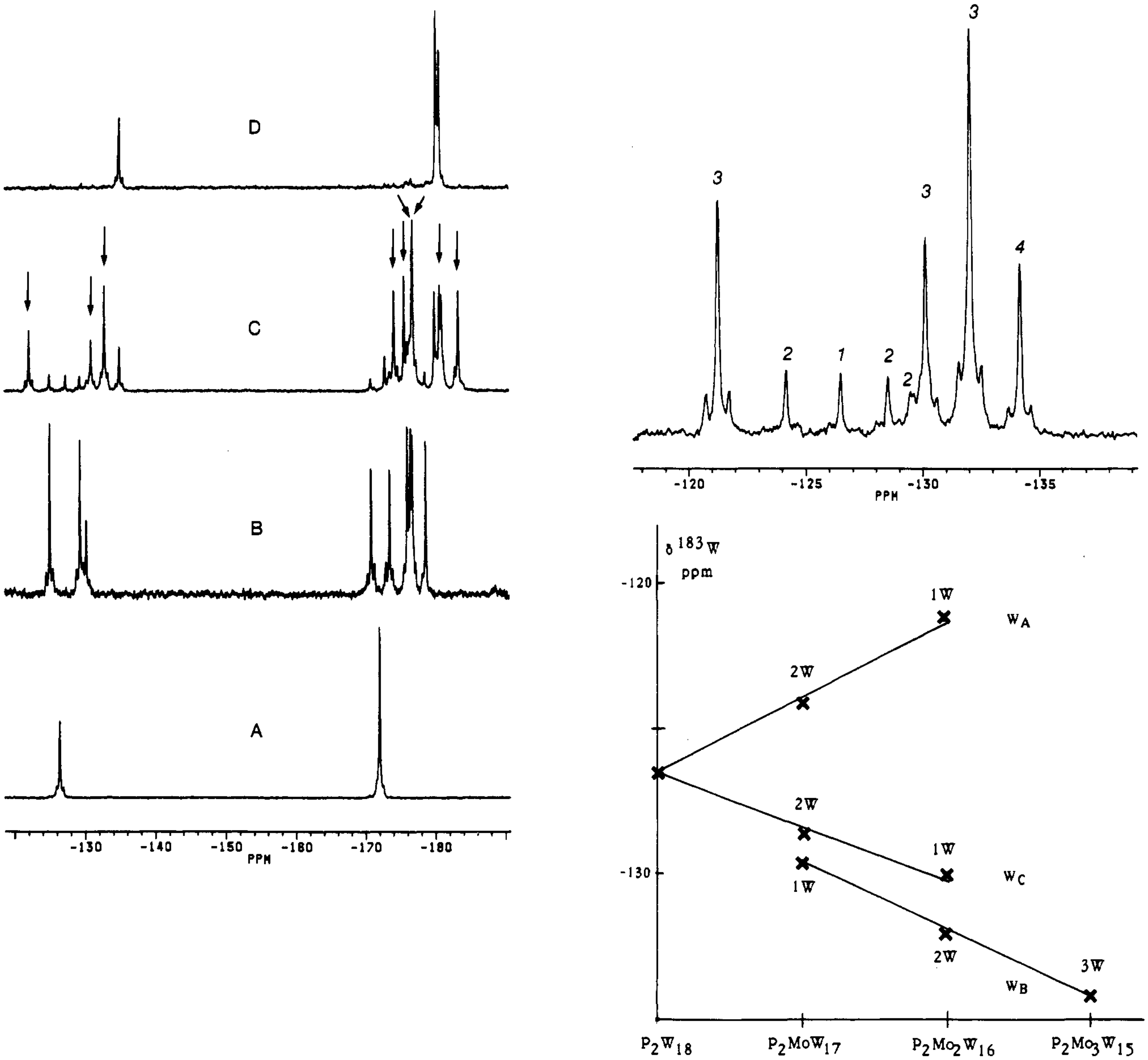

Figure 5. (a) Left: 20.8-MHz ^{183}W NMR spectra of α-octadeca(molybdotungsto)diphosphates, about 0.5 M in aqueous solution, where A = P_2W_{18}, B = P_2MoW_{17}, C = solution containing about (composition determined by the integration of the NMR lines) 70% $P_2Mo_2W_{16}$, 20% $P_2Mo_3W_{15}$, 8% P_2MoW_{17}, and 2% P_2W_{18} (arrows indicate the $P_2Mo_2W_{16}$ lines), and D = $P_2Mo_3W_{15}$. In C, note the easy observation of the low abundance highly symmetric P_2W_{18} anion. (b) Top Right: Expansion of the high-frequency part (polar tungsten resonances) of spectrum C. The resonance lines of individual anions are marked by 1 for P_2W_{18}, 2 for P_2MoW_{17}, 3 for $P_2Mo_2W_{16}$, and 4 for $P_2Mo_3W_{15}$. (c) Bottom Right: $\delta(^{183}W)$ values of polar W as a function of molybdenum substitution in P_2W_{18}. W_A represents the tungstens adjacent to molybdenum, W_B, the tungstens symmetry-related[21] to molybdenum, and W_C, the tungstens non-symmetry-related to molybdenum.

to partial coalescence of the vanadium–tungsten octuplet has been experimentally and theoretically thoroughly investigated by Domaille.[20a]

Chemical Shifts of the Polar Tungsten Atoms. The three lines of the mono- and divanadium anions are easily assigned on the following basis: (i) the resonance of W in the substituted PV_xW_{9-x} half-anion appears as a broad line; (ii) the remaining two lines (doublets) are assigned according to their intensities (one and two W in the PW_9 half-anion).

The tungsten adjacent to the vanadium atom is significantly deshielded with respect to α-P_2W_{18} by about 20 ppm per vanadium atom (see Figure 4b). For the opposite polar group (PW_9 half-anion), the chemical shifts of the tungsten nuclei also only depend on their position relative to the vanadium atoms. The tungsten atoms "non-symmetry-related" to the vanadium atoms[21] are nearly unaffected and keep the same chemical shift as in α-P_2W_{18}, but the other tungsten atoms are considerably shielded by about 35 ppm with respect to α-P_2W_{18} (Figure 4). This observation is in someways disconcerting in that these W atoms are at the farthest (through space as well as through bond) location of the perturbing V atom. Consequently, the barycenter of ^{183}W chemical shifts of this polar group varies quasi linearly with the number of vanadium atoms in the opposite polar group (slope about −12 ppm; see Figure 4b).

Variation of the Chemical Shifts of the Equatorial Tungsten with the Number of Vanadium Atoms. The number of tungsten–tungsten satellites, their duplication by coupling with the phosphorus nuclei, and the degeneracy of some coupling constants do not allow a complete assignment of the resonance lines, which would require a correlation spectroscopy experiment. Therefore, we will not discuss individual line displacements but rather the barycenter of these lines. It appears that the mean value of the chemical shifts of the equatorial tungsten decreases by about 10 ppm per vanadium atom substitution, i.e. about -172 ppm for the unsubstituted α-P_2W_{18} anion[15] to about −204 ppm for the trisubstituted 1,2,3-$P_2V_3W_{15}$ compound.[12]

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[21] "Symmetry-related" nuclei are nuclei that occupy locations related through the horizontal symmetry plane of the initial Dawson anion (D_{3h}), for example positions 1 and 16, 2 and 17, and 3 and 18.

Table V. ^{183}W NMR Data for α-Octadeca(molybdotungsto)diphosphates[a]

	α-P_2W_{18}[b]	P_2MoW_{17}	$P_2Mo_2W_{16}$	$P_2Mo_3W_{15}$[c]
polar ^{183}W in PMo_xW_{9-x} subunit		−124.2 (2 W) (1 Hz)	−121.3 (1 W) (1 Hz)	
polar ^{183}W in PW_9 subunit	−126.5 (6 W) (1 Hz)	−128.5 (2 W) (1 Hz) −129.5 (1 W) (0.9 Hz)	−130.1 (1 W) (0.8 Hz) −132.0 (2 W) (0.8 Hz)	−134.2 (3 W) (0.6 Hz)
Δδ amplitude		5.3	10.7	
equatorial		−170.0 (2 W)		
^{183}W	−172.0 (12 W)			
		−172.8 (2 W)	173.4 (2 W)	
all			174.9 (2 W)	
$^2J_{W-P}$		−175.3 (2 W)		
about		−175.9 (2 W)	−176.0 (2 W)	
1.7 Hz		−176.1 (2 W)	−176.1 (2 W)	
		−177.8 (2 W)		
				−179.2 (6 W)
			−179.9 (2 W)	
				−180.2 (6 W)
			−182.6 (2 W)	
δ mean value		−174.6	−177.1	−179.7
Δδ amplitude		7.8	9.2	1

[a] From the solution of impure $P_2Mo_2W_{16}$ (except for P_2MoW_{17}) (coupling constant $^2J_{W-P}$ in parentheses; digital resolution 0.122 Hz/pt). [b] δ reported at −128.1 and −173.8 ppm by Acerete et al.[15c] [c] δ reported at −134.1, −179.3, and −180.1 ppm by Acerete et al.[15c]

Surprisingly, this shielding (upfield displacement) of the equatorial tungsten is not due to the W nuclei near the perturbation (i.e. adjacent to the vanadium atoms), which appear little affected by the substitution.

^{183}W NMR Spectroscopy of 1,2,3-[$P_2MoM'_2W_{15}O_{62}$]$^{6-}$ (M′ = Mo, W). The ^{183}W NMR spectra of mono- and disubstituted molybdenum compounds are represented on Figure 5a with those of α-P_2W_{18} and 1,2,3-$P_2Mo_3W_{15}$[15] for comparison.

Because of the great similarity between tungsten and molybdenum, Mo–W substitution induces only limited changes of the ^{183}W chemical shifts (Table V). As the ^{183}W are also sensitive to small external perturbations, the variation of chemical shifts induced by molybdenum–tungsten substitution will be extracted from a spectrum of a mixture containing all species, i.e. a solution of the 1,2-$P_2Mo_2W_{16}$ anion. The individual lines of each species were previously identified from the pure compounds (except of course $P_2Mo_2W_{16}$).

Polar Tungsten Resonances (Figure 5b). The three lines of the mono- and dimolybdenum anions are assigned on the following basis: the two lines (one W and two W) of the PW_9 half-anion correspond to tungsten atoms, which are mutually coupled. Although the coupling constant ($^2J_{W-O-W}$ ~ 10 Hz) is relatively small, the very weak chemical shift difference between their ^{183}W resonances induce AB patterns for the tungsten satellites on both lines. Moreover, the resonance line of the W in the substituted PMo_xW_{9-x} half-anion appears only with tungsten satellites bearing large (about 20 Hz) coupling; the tungsten atoms that are able to exchange a small coupling are replaced by molybdenum. The two magnetically active isotopes of molybdenum, i.e. ^{95}Mo ($I = {}^5/_2$; 15.7%) and ^{97}Mo ($I = {}^5/_2$; 9.5%), do not affect the ^{183}W spectrum because their very quick relaxation leads to an effective self-decoupling of the expected sextuplets.

As for the vanadium compounds, the tungstens adjacent to the molybdenum atoms in the same trimetallic group are deshielded with respect to α-P_2W_{18} (by about 2.5 ppm per Mo atom) and the tungstens in the opposite polar group are relatively shielded. But in that case, the tungstens symmetry-related to the molybdenum atom[21] are shielded by about −2.6 ppm per Mo atom and the remaining tungsten nucleus in the opposite polar group is only shielded by about −1.8 ppm per molybdenum atom with respect to α-P_2W_{18} (Figure 5c).

As noted above, these chemical shift variations are very subtle as compared with the total chemical shift scale of the ^{183}W nucleus, but it is noticeable that δ variations are of the same order for tungsten nuclei directly bound to the perturbing Mo atom and for tungsten nuclei the most remote from this perturbation. This is very remarkable for molybdenum-substituted polyoxotungstates, since in the isocharge W–Mo substitution no dramatic charge redistribution can be involved as it is likely the case in W–V substitution.

Equatorial Tungsten Resonances. The total chemical shift amplitude for one species does not exceed 10 ppm (for example 9.2 ppm for $P_2Mo_2W_{16}$) (Table V), and nearly all tungsten–tungsten couplings are degenerate; therefore, a precise assignment is impossible without a correlation spectroscopy experiment. Consequently, as for the vanadium-substituted anions, we will discuss only mean values of chemical shifts. In this case also, the center of gravity of equatorial resonances shifts regularly to high field with increasing tungsten–molybdenum substitution, but the increment per Mo atom is only −2.5 ppm instead of −10 ppm for vanadium substitution.

^{183}W NMR Spectroscopy of Ternary 1-2,3-[$P_2MoV_2W_{15}O_{62}$]$^{8-}$ and 1,2-3-[$P_2Mo_2VW_{15}O_{62}$]$^{7-}$. These anions can be considered as deriving from 1,2,3-$P_2Mo_3W_{15}$ by progressive substitution of vanadium for molybdenum in the trimolybdic polar group (Figure 6).

Polar Tungsten Atoms (Table IV). As for the tungsten–vanadium substitution in P_2W_{18}, tungsten atoms symmetry-related[21] to the vanadium-substituting atoms are strongly shielded with respect to $P_2Mo_3W_{15}$ (δ = −134.2 ppm), but in that case this shielding is markedly stronger for the divanadium compound (−158.8 ppm; Δδ − −24.6 ppm) than for the monovanadium one (−150.8 ppm; Δδ = −16.6 ppm). Nevertheless, this shielding induced by the polar molybdenum–vanadium substitution in $P_2Mo_3W_{15}$ appears significantly less important than the constant shielding (Δδ = −33 ppm) induced by the polar tungsten–vanadium substitution in P_2W_{18}. The other tungsten atoms in the polar group (i.e. those symmetry-related[21] to the molybdenum atoms) are only slightly shielded (by about −1.2 ppm per vanadium atom) as they are in the substitution derivatives of P_2W_{18}.

As a result of both effects, the ^{183}W interline separation in the polar group of $P_2Mo_{3-x}V_xW_{15}$ anions is about two times smaller than in the $P_2(V_xW_{3-x})W_{15}$ compounds (respectively 20 and 40 ppm; Table IV).

These experimental results can be discussed also by focusing onto the isocharge tungsten–molybdenum substitution, i.e. on comparing the Δδ in the $P_2V_2W_{16} \rightarrow P_2MoV_2W_{15}$ substitution with their values in the $P_2W_{18} \rightarrow P_2MoW_{17}$ substitution. Although in the second case the replacement of one W by one Mo induces minor high-field shifts on both types of ^{183}W in the opposite polar group (see above; Table V), in the first case the tungsten atom symmetry-related[21] to Mo is shielded by 15 ppm whereas the other two tungsten atoms are deshielded by 4 ppm (with respect to $P_2V_2W_{16}$). The same difference of behavior in the tungsten–molybdenum substitution is also to be noted for the $P_2VW_{17} \rightarrow P_2Mo_2VW_{15}$ path: in that case too the two tungsten atoms sym-

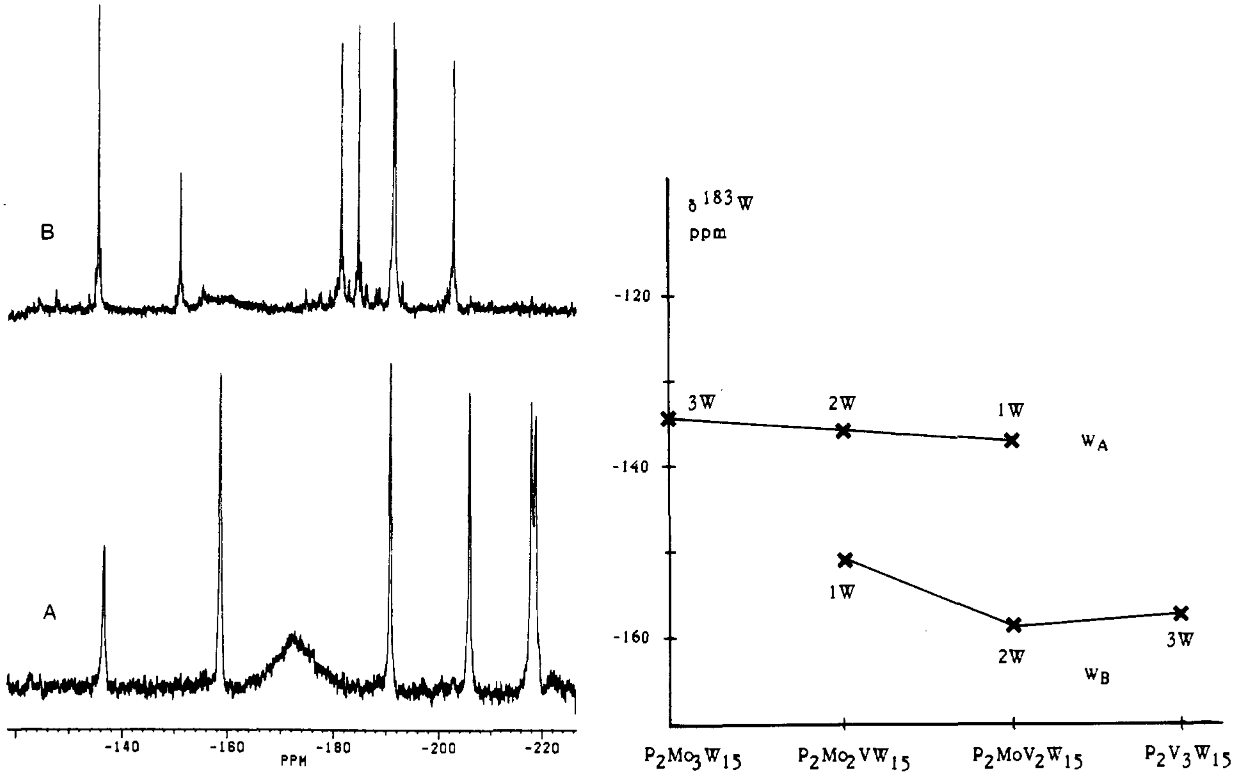

Figure 6. (a) Left: 20.8-MHz ^{183}W NMR spectra of α-tri(molybdovanado)pentadecatungstodiphosphates, about 0.5 M in aqueous solution, where A = $P_2MoV_2W_{15}$ and B = $P_2Mo_2VW_{15}$. (b) Right: $\delta(^{183}W)$ values of polar W as a function of vanadium substitution in $P_2Mo_3W_{15}$. W_A represents the tungstens symmetry-related[21] to molybdenum, and W_B, the tungstens symmetry-related to vanadium.

metry-related to molybdenum atoms are shielded (by 10 ppm), but the other tungsten atom is strongly deshielded by 14 ppm.

It appears then that the effect of tungsten–molybdenum substitution in a polar group on the ^{183}W chemical shifts in the opposite polar group strongly depends on the nature of the neighboring atoms of the substituting molybdenum atom.

Syntheses. Until now all the known 1,2,3-$P_2MM'_2W_{15}$ (M, M′ = Mo, V, W) complexes have been prepared by refilling the lacuna of a mono- or multivacant species. Like tungstate, molybdate can be added stepwise to multivacant species. So $P_2Mo_2W_{15}$ has been obtained from P_2W_{15} and has been used as a synthetic intermediary (Scheme I).

Unlike molybdate, the addition of vanadate to P_2W_{15} always leads to the "saturated" $P_2V_3W_{15}$ species. As P_2W_{16}[7,10] is not a stable intermediary, we have had to find a new route for preparing the compounds with two vanadium atoms. ^{31}P NMR spectra of a mixture of $P_2Mo_3W_{15}$ and vanadate show that it is easy to gradually substituate vanadium for molybdenum (Scheme II). All the steps are slow at ambient temperature, and the equilibria are reached only after several months. The final composition depends on the V/Mo ratio. For instance when 2 equiv of HVO_4^{2-} anion is added to a solution of $P_2Mo_3W_{15}$, the formation of $P_2MoV_2W_{15}$ is almost complete after 3 months (Figure 7).

The gradual addition of vanadate to a solution of P_2W_{18} gives the same sequence, all the substitutions occurring in only one W_3O_{13} group. Attempts for further substitutions in the other W_3O_{13} group were unsuccessful. It is the only case of specific substitution. It has been shown that the reaction of bivalent transition-metal ions with P_2W_{18} in acetate buffer leads to a mixture of α_1 and α_2 isomers of P_2MW_{17}.[22] In the same conditions the substitution of molybdenum for tungsten gives a mixture of numerous $P_2Mo_nW_{17-n}$ compounds.

The study of octadeca(molybdotungsto)diphosphates had shown that their acidobasic behavior is almost identical with that of P_2W_{18} and in particular that progressive alkalinization gives[17] monovacant and multivacant lacunar compounds that can be refilled by molybdate or tungstate and so give back new saturated species with different Mo/W ratios. On the contrary, vanadium increases the negative charge of the anion and so shifts the stability of the saturated species to higher pH. This effect being relatively weaker in lacunary species, their pH range of formation gets narrower or disappears. So monovacant species containing vanadium are unknown. Therefore, an important new route to synthesize octadeca(molybdotungstovanado)diphosphates is the gradual substitution of vanadium for tungsten or molybdenum.

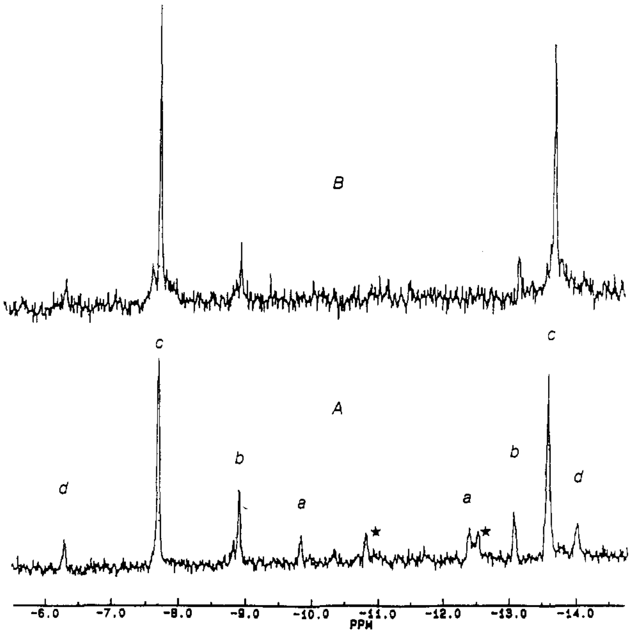

Figure 7. 101.2-MHz ^{31}P NMR spectra of an aqueous solution of pure α-(1,2,3)-$[P_2Mo_3W_{15}O_{62}]^{6-}$ (0.01 M) added to 2 equiv of HVO_4^{2-}: (A) after 5 h, (B) after 3 months. The resonance lines of the mixed anions are marked by "a" for $P_2Mo_3W_{15}$, "b" for $P_2Mo_2VW_{15}$, "c" for $P_2MoV_2W_{15}$, and "d" for $P_2V_3W_{15}$. The stars indicate $P_2Mo_2W_{16}$, which appears transiently.

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