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^{183}W INADEQUATE 2D NMR Spectroscopy of Hetero Arsenato−Phosphato−Tungstate P^{V}/As^{V} Substitution in Dawson-Type α-$[As_xP_{2-x}W_{18}O_{62}]^{6-}$ ($x = 0$−2) and α-$[H_4As_yP_{1-y}W_{18}O_{62}]^{7-}$ ($y = 0, 1$)

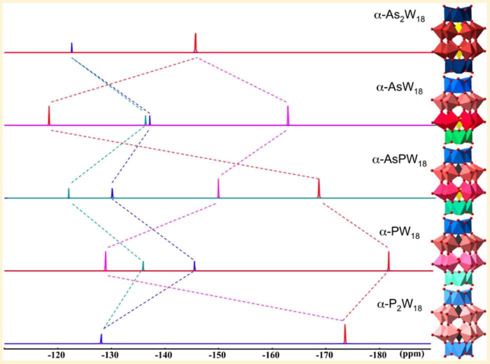
Mohamed Haouas,*,[†] Israël-Martyr Mbomekallé,*,[‡,§] Neus Vila,[‡] Pedro de Oliveira,[§] and Francis Taulelle[†]

[†]Tectospin, Institut Lavoisier de Versailles, 78035 Versailles Cedex, France

[‡]Groupe Solides Moléculaires, Institut Lavoisier de Versailles, 78035 Versailles Cedex, France

[§]Laboratoire de Chimie Physique, UMR 8000, CNRS, Equipe d'Electrochimie et de Photo-électrochimie, Université Paris-Sud Bâtiment 350, 91405 Orsay Cedex, France

S *Supporting Information*



ABSTRACT: The Dawson-type arsenato−phosphato−tungstate α-$[AsPW_{18}O_{62}]^{6-}$ has been prepared and unambiguously identified for the first time. A comparative study including the four other already known compounds, the symmetric α-$[X_2W_{18}O_{62}]^{6-}$ and unsymmetric α-$[H_4XW_{18}O_{62}]^{7-}$ for X = P^{V}, As^{V}, has been performed by spectroscopic ^{183}W and ^{31}P NMR. 2-D ^{183}W INADEQUATE experiments were systematically employed to unequivocally verify structures, assign all resonances, and determine precisely $^{2}J_{W-O-W}$ scalar couplings. The effects of P/As substitutions, generating unsymmetric structures, on the NMR observables $\delta_{W\text{-}183}$, $\delta_{P\text{-}31}$, $^{2}J_{W-O-W}$, and $^{2}J_{W-O-P}$ are discussed in relation to their bond length and bond angle alteration. General trends with respect to NMR parameter variations have been found when filling central cavities with P or As atoms, with less pronounced effects for As than for P. In addition, NMR characterization of three other isomers, i.e., β-$[X_2W_{18}O_{62}]^{6-}$ and γ-$[As_2W_{18}O_{62}]^{6-}$, were also provided for comparison. The present NMR results could serve as representative reference data for understanding the relationship between structure and NMR observables in polyoxotungstates.

■ INTRODUCTION

Wells−Dawson-type polyoxotungstates are of interest in polyoxometalate (POM) science because of their robustness, in solution and in the solid state, and the richness of their chemistry.[1−4] Furthermore, these molecules display a multitude of properties on the basis of their highly tunable compositions, alterable sizes, shapes, charge densities, and reversible redox chemistry. As a consequence of this diversity of properties, possible applications span a wide range of domains, including catalysis, electrocatalysis, medicine, materials science, photochemistry, analytical chemistry, and magnetochemistry.[5−10] Therefore, considerable endeavors have been made to improve their synthesis or to design novel species with targeted properties.[11−20]

Among these Wells−Dawson compounds, phosphorus- and arsenic-based polyoxotungstates are the most studied compounds and can be divided into two families: (1) the symmetric $[X_2W_{18}O_{62}]^{6-}$ containing the same heteroatom X (X = As^{V}, P^{V}) in both ends and (2) the unsymmetric $[H_4XW_{18}O_{62}]^{7-}$ containing the heteroatom X (X = As^{III}, As^{V}, P^{V}) in one end and three or four hydrogen atoms in the other end. The rational synthesis of compounds containing both heteroatoms As and P together remains a challenge due to the lack of control of the substitution process, which leads to statistically disordered structures difficult to characterize;[21] however, Cronin et al. have had some success using mass spectrometry for Dawson compounds with guests.[22,23]

Along with single-crystal X-ray diffraction, NMR spectroscopy is a suitable tool for the structural characterization of POM compounds, and both techniques have contributed to the discovery of numerous novel structures during the last few decades. Several attractive NMR-active nuclei, such as spin $^{1}/_{2}$ ^{183}W, ^{31}P, ^{29}Si, etc.[24−26] and also quadrupolar nuclei such as ^{6,7}Li and ^{17}O, have been found to be useful probes of the state of POMs in solution.[27,28] NMR observables, i.e., chemical shifts, line widths, relative signal intensities, and homonuclear and heteronuclear coupling constants provide the basis for identifying the anionic structure. One of the major advantages of NMR lies in the multiplicity and the flexibility of available experiments: from one-dimensional (1-D) for various nuclei to two-dimensional (2-D) experiments, in which one can select the interactions to be separated and/or the nuclei to be correlated to each other.

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Of particular interest, 2D ^{183}W NMR including COSY[29−32] and INADEQUATE[18,20,29] spectroscopy has been employed successfully and can be used for many purposes, such as to distinguish new synthetic species, to examine product purity, to differentiate isomers, and to establish new structures in solution as well as to monitor the progress of reaction. In principle, any ^{183}W atom can have up to four different adjacent ^{183}W atoms. In more complex coupling problems the similarity of $^{2}J_{\mathrm{W-O-W}}$ values may produce ambiguity in the determination of connectivity from a 1-D spectrum only. Furthermore, the lower intensity of satellite lines makes them difficult to differentiate from major lines of slight impurities, and the line broadening caused by displacement of the quadrupolar nucleus or by the presence of vacancies leads even to the disappearance of some resonances.[27,29] These problems prompted Brevard et al.[11] and Domaille et al.[16] to introduce 2-D NMR techniques for establishing connectivity between tungsten atoms. Moreover, the INADEQUATE sequence allows us to accurately measure the $^{2}J_{\mathrm{W-O-W}}$ values, which could provide additional useful information about the structural features.[15,21]

Dawson polyanions are constituted of two A-type half-ions A-$X^{V}W_9O_{34}$ (X = P, As).[33,34] Formally, six isomers exist, denoted α, β, γ, α*, β*, and γ* (Figure 1), but only three for the P analogue (α, β, and γ) and four for the As analogue (α, β, γ, and γ*) have been isolated and characterized.[15] The stability of the isomers varies as follows from more to less stable: $\alpha > \beta > \gamma > \gamma^* > \beta^* > \alpha^*$.[35] Unsymmetrical compounds with only one central heteroatom are also known for both P and As atoms but only in the α-isomer form.[19,21] A compound with mixed heteroatoms containing both P and As atoms has also been reported nearly 50 years ago.[36] No structural characterization was described in the original paper, and only UV−vis spectroscopy was used for its identification. In this contribution we provide firm evidence of the structure of the Dawson arsenato−phosphato−tungstate from a full NMR characterization. These new NMR data in comparison to those of known compounds with only one heteroatom type (P or As) allowed us to study the effect of As/P substitution on the tungstate environments and to understand more the NMR parameters with respect to structural features. NMR results on other isomers (β and γ*) have also been obtained, and direct comparison allowed us to conclude that the arsenato−phosphato−tungstate should be, as expected, in the most stable α conformation.

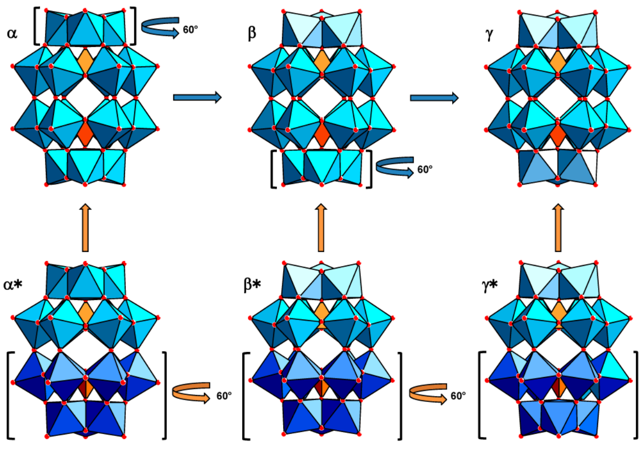

Figure 1. Representations of α, β, γ, α*, β*, and γ* Dawson isomers and their structural relationships.

■ EXPERIMENTAL SECTION

Samples of the six known polyanions α-$[H_4AsW_{18}O_{62}]^{7-}$, α-$[As_2W_{18}O_{62}]^{6-}$, α-$[H_4PW_{18}O_{62}]^{7-}$, α-$[P_2W_{18}O_{62}]^{6-}$, β-$[As_2W_{18}O_{62}]^{6-}$, and β-$[P_2W_{18}O_{62}]^{6-}$ were obtained by published procedures, and the purity was confirmed by IR and cyclic voltammetry.[12,14,18,19] All attempts to isolate a pure sample of $[AsPW_{18}O_{62}]^{6-}$ failed. The procedures used were adapted from the seminal work of Vandalen and Mellon published in 1964.[36]

All NMR measurements were recorded at 24−25 °C using a 10 mm sample tube in D_2O/H_2O perchloric acid solution with a typical concentration range of ca. 0.1 mol L^{-1}. The ^{31}P NMR spectra were obtained by using a Bruker AVANCE 400 MHz spectrometer, referenced to 85% H_3PO_4 as an external standard. Free induction decays (FIDs) were accumulated with pulse lengths of 12 μs (45° pulse), a recycle time of 65 s ($T_1 \approx 190$ s), and a total number of FIDs of 64. Time-averaged ^{183}W FT NMR spectra were recorded on Bruker AVANCE 400 MHz (16.7 MHz) and 500 MHz (20.8 MHz) spectrometers equipped with a specific low-γ BBO LR X-H-D probehead. Chemical shifts were referenced to the ^{183}W resonance of an external 2 M Na_2WO_4 solution in alkaline D_2O (pD 9) and to dodecatungstosilicic acid as a secondary standard (δ −103.8 ppm). For 1-D experiments, FIDs were accumulated with 45° pulses, a recycle time of 2 s, and a total number of FIDs ranging from 3072 to 8192. Typically, phase-sensitive 2-D INADEQUATE[37] acquisition of 3072 transients and 128 experiments along t_1 required a total of 66 h. The delay time Δ between pulses (90°−Δ−180°−Δ−90°−t_1−90°−acquire) was fixed to 11 ms to match as closely as possible an average $1/(4^{2}J_{\mathrm{W-O-W}})$. The 90° ^{183}W pulse width was 28 μs, the acquisition time 0.5 s, the recycle time 0.1 s, the number of data points 2048, and the spectral width 2000 Hz.

■ RESULTS

Contant and Thouvenot in 1993 provided a complete ^{31}P and ^{183}W NMR characterization of all known symmetric Dawson-type polyoxotungstate isomers with phosphate (α, β, and γ) and arsenate (α, β, γ, and γ*) as heteroatoms.[15] NMR data of the asymmetric monophosphate[21] and monoarsenate[19] compounds were reported some years later. Here we report, for the first time, NMR results of the mixed heteroatom arsenato−phosphate together with the two asymmetric and the four α- and β-form symmetric Dawson phosphato− and arsenato−tungstates for comparison.

^{183}W NMR. The ^{183}W NMR spectra of the seven D_2O solutions are shown in Figure 2. The spectra of the six known compounds β-P_2W_{18}, α-P_2W_{18}, α-PW_{18}, α-AsW_{18}, α-As_2W_{18}, and β-As_2W_{18} (Figure 2a−c,e−g, respectively) are in agreement with the literature data and reveal that all compounds are pure (>99%) except for β-As_2W_{18}, which is a 50/50 mixture with the γ*-As_2W_{18} isomer. The spectrum of β-P_2W_{18} (Figure 2a) consists of four resonances at −194, −173, −133, and −114 ppm in a 2:2:1:1 intensity ratio, consistent with the C_{3v} symmetry of the isomer constituted of two different caps (2 × 3 W) and two different belts (2 × 6 W). The four resonances are actually doublets due to heteronuclear $^{2}J_{\mathrm{W-O-P}}$ couplings with ^{31}P. The 2-D INADEQUATE spectrum (shown in the Supporting Information, Figure S1) confirms the assignment of Contant and Thouvenot on the basis of a comparison of $^{2}J_{\mathrm{W-O-W}}$ couplings:[15] the −194 and −114 ppm resonances correspond to a PW_9 half-ion and the −173 and −133 ppm signals to the second PW_9 half-ion. The spectrum of α-P_2W_{18} (Figure 2b) exhibits the expected characteristic two doublets ($^{2}J_{\mathrm{W-O-P}}$) at −174 ppm accounting for the 12 W of the belts

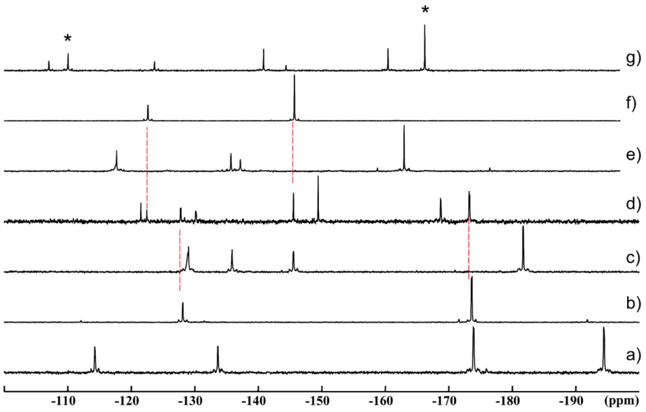

Figure 2. ^{183}W NMR spectra of Dawson tungstates: (a) β-P_2W_{18}; (b) α-P_2W_{18}; (c) α-PW_{18}; (d) α-$AsPW_{18}$; (e) α-AsW_{18}; (f) α-As_2W_{18}; (g) β-As_2W_{18}. Spectrum d contains resonances of α-P_2W_{18} and α-As_2W_{18}. Asterisks in spectrum g denote resonances of the γ^*-As_2W_{18} isomer.

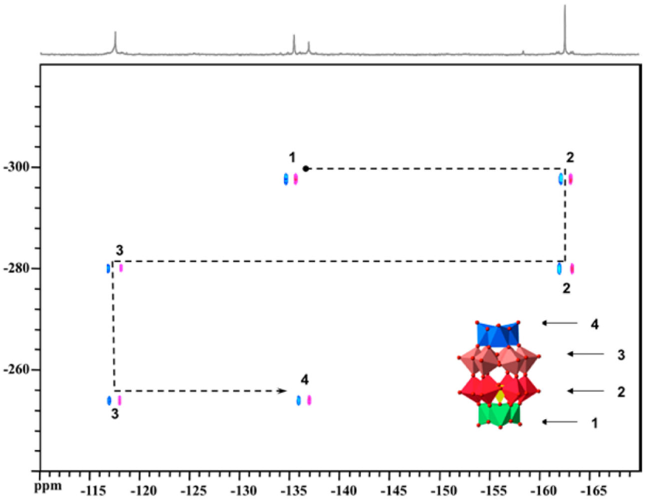

Figure 3. 2-D INADEQUATE ^{183}W NMR spectrum of α-AsW_{18}. The 1-D NMR spectrum is presented at the top of the 2-D map.

and −128 ppm for the 6 W of the caps, consistent with a D_{3h} symmetry.[15] The spectrum of the asymmetric α-PW_{18} (Figure 2c) shows four resonances: two doublets at −182 and −146 ppm and two singlets at −136 and −129 ppm in relative proportions 2:1:1:2, respectively. Assignments are easy thanks to the presence of $^2J_{W-O-P}$ couplings, allowing us to differentiate the resonances of the empty half-$\square W_9$ moiety (singlets) ($\square$ represents a vacant central site) from those of the half-filled PW_9 moiety (doublets). It should be noted that the high-field resonance (−129 ppm) undergoes an unusual line broadening in comparison to the spectrum published previously,[21] which could originate from dynamic hopping of some protons located in the vacant cavity. Such a phenomenon has been observed in other systems, leading to severe line broadening of ^{183}W resonances up to signal extinction.[26] In order to check the concordance of the NMR spectrum with the expected structure, a 2-D INADEQUATE experiment was performed (Supporting Information, Figure S2), allowing us to definitively confirm the assignments. The spectrum of the asymmetric α-AsW_{18} (Figure 2e) exhibits four singlets at −163, −137, −136, and −118 ppm with an intensity ratio of 2:1:1:2, respectively, very close to the spectrum published in 2003 by Mbomekallé et al.[19] The authors gave assignments on the basis of comparison with the spectrum of the phosphorus analogue structure. Because of the lack of resolution in their spectrum due to partially overlapped resonances, assignments from the 1-D spectrum using $^2J_{W-O-W}$ couplings were not possible. From our 2-D INADEQUATE experiment (Figure 3) the correct assignments are therefore provided. The relative positions of the resonances of the 3 W of the caps are inverted by comparison to those of the phosphorus analogue compound: the resonance of the empty $\square W_9$ moiety (−137 ppm) appears at higher field with respect to that of the filled AsW_9 moiety (−136 ppm). The spectrum of α-As_2W_{18} (Figure 2f), indicating two singlets at −146 and −123 ppm in the relative proportion 2:1, is in agreement with previously published data.[15] The spectrum shown in Figure 2g corresponds to a mixture of two isomers, β-As_2W_{18} (C_{3v} symmetry), with four resonances at −160 (6 W), −141 (6 W), −124 (3 W), and −107 ppm (3 W) and γ^*-As_2W_{18} (C_{3d} symmetry) with only two resonances at −166 (12 W) and −110 ppm (6 W). These assignments are supported by the data from the literature[15] and confirmed by the 2-D INADEQUATE spectrum shown in Figure S3 (Supporting Information).

The spectrum of the mixed heteroatom arsenato−phosphato−tungstate (Figure 2d) consists of eight resonances, the positions of some of which coincide with chemical shifts of known compounds. Thus, the two doublets ($^2J_{W-O-P}$) of α-P_2W_{18} and the two singlets of α-As_2W_{18} (red dashed lines in Figure 2) can be easily recognized, suggesting that both isomers are present in the solution. The remaining four resonances at −169, −150, −130, and −121 ppm in a 2:2:1:1 intensity ratio had never been observed before for Dawson type phosphato− or arsenato−tungstates and thus should correspond to the monoarsenato−monophosphato-tungstate compound most probably belonging to the most stable α-isomer form with C_{3v} group symmetry. Furthermore, two of the resonances (−169 and −130 ppm) exhibit $^2J_{W-O-P}$ coupling patterns (Figure 4) consistent with the presence of a single central phosphorus. Therefore, −169 and −130 ppm resonances are assigned to the half-anion PW_9, whereas the signals at −150 and −121 ppm correspond to the other half-anion AsW_9. The 2-D INADEQUATE spectrum (Figure 5) confirms unequivocally not only the consistency of the assignment with the structure of α-$AsPW_{18}$, but also the presence of the two additional phases α-P_2W_{18} and α-As_2W_{18}. Indeed, two isolated correlations sit next to three coupled correlations due to two

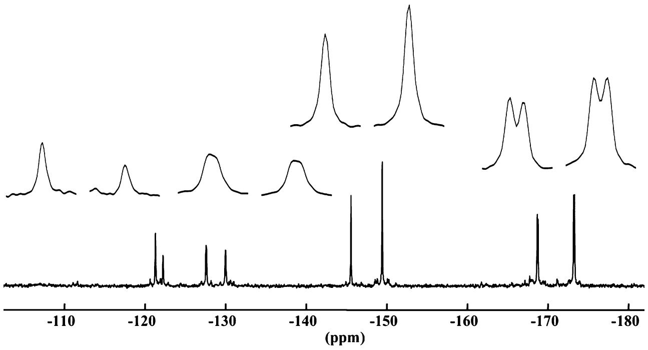

Figure 4. ^{183}W NMR spectrum of a Dawson tungstate α-$AsPW_{18}$ solution containing α-P_2W_{18} and α-As_2W_{18} isomers. Insets show expansion around each individual signal.

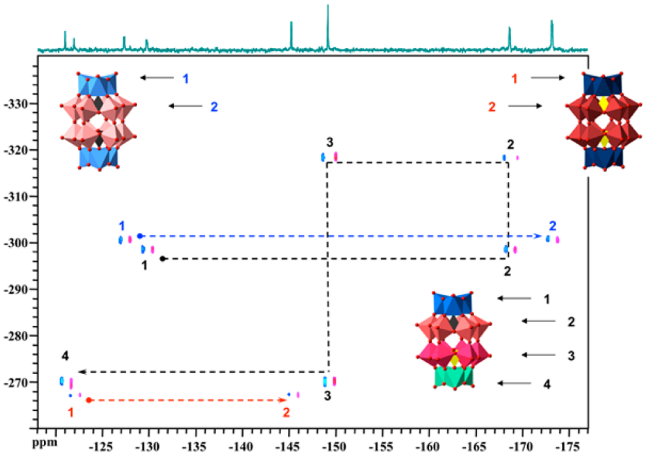

Figure 5. 2-D INADEQUATE ^{183}W NMR spectrum of α-$AsPW_{18}$ solution containing α-P_2W_{18} and α-As_2W_{18} isomers. The 1-D NMR spectrum is presented at the top of the 2-D map.

cap–belt W–W couplings and one belt–belt W–W coupling of the α-$AsPW_{18}$ structure. Quantitative analysis of the spectrum indicates the composition of the mixture to be α-$AsPW_{18}$:α-P_2W_{18}:α-As_2W_{18} = 54:31:15. Attempts to improve the purity failed.

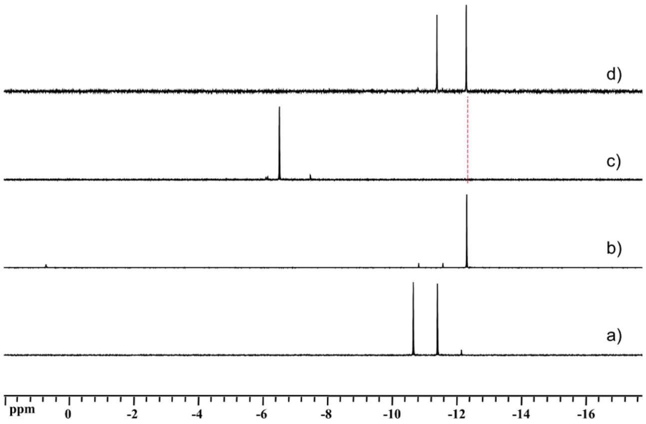

Figure 6. ^{31}P NMR spectra of Dawson tungstates: (a) β-P_2W_{18}; (b) α-P_2W_{18}; (c) α-PW_{18}; (d) α-$AsPW_{18}$. Spectrum d contains a resonance of α-P_2W_{18}.

^{31}P NMR. Figure 6 shows the ^{31}P NMR spectra of the phosphorus derivatives β-P_2W_{18}, α-P_2W_{18}, α-PW_{18}, and α-$AsPW_{18}$. The β-P_2W_{18} compound (Figure 6a) exhibits two signals at −10.7 and −11.4 ppm of equal intensity,[38] in agreement with the C_{3v} ($3m$) symmetry. The spectrum of α-P_2W_{18} (Figure 6b) showed, as expected, a unique resonance at −12.3 ppm characteristic of the α isomer, confirming that the two phosphorus atoms are equivalent in this form.[39] The resonance of the phosphorus in the asymmetric α-PW_{18} undergoes significant deshielding and appears at −6.5 ppm, in agreement with the published value.[40] The spectrum of compound α-$AsPW_{18}$, which also contains α-As_2W_{18} and α-P_2W_{18}, consists of two resonances at −11.4 and −12.3 ppm. This latter signal obviously corresponds to α-P_2W_{18}, and consequently the signal at −11.4 ppm should correspond to the mixed heteroatom As and P tungstate α-$AsPW_{18}$. The relative proportion of their signal areas (53:47, respectively) is in accordance with the solution composition of α-$AsPW_{18}$:α-P_2W_{18}:α-As_2W_{18} = 54:31:15 determined by ^{183}W NMR. Indeed, α-As_2W_{18} is silent with respect to ^{31}P NMR; only α-$AsPW_{18}$ and α-P_2W_{18} are detected in ^{31}P NMR with 54% and 31% fractions, respectively.

■ DISCUSSION

Table 1 summarizes all NMR data recorded in the current study, where they are compared to the literature data. Globally, both the values of chemical shifts and ^2J couplings found consistently agree with the reported results. Systematic differences in chemical shifts are observed in some cases that could arise from some shifting of chemical shift scaling. As Table 1 shows, some new data are derived from the present study: namely, those of compounds α-$AsPW_{18}$ ($\delta_{W\text{-}183}$, $^2J_{W-O-W}$, $^2J_{W-O-P}$, and $\delta_{P\text{-}31}$) and α-AsW_{18} ($^2J_{W-O-W}$). The lack of resolution due to both superimposed signals and dynamic line broadening did not allow us to determine accurately the $^2J_{W-O-W}$ couplings in the compound α-AsW_{18} from 1-D spectra, but they are now easily achieved with the help of a 2-D INADEQUATE experiment.

With new NMR data of the mixed arsenato–phosphato heteroatom derivative α-$AsPW_{18}$, a complete picture is now available about the evolution of the ^{183}W spectra when changing from α-P_2W_{18} to α-As_2W_{18}, passing through the asymmetric and mixed-heteroatom intermediates. This is schematically illustrated in Figure 7. Thanks to the 2-D INADEQUATE results, all assignments were performed unambiguously, which allow us now to trace the evolution of each resonance upon the progressive P substitution with As in the α isomer of the Dawson structure, passing through the vacant site intermediates. Interestingly, the lower symmetry of the intermediates leads to differentiation between the two subunits of each half anion, i.e., the cap trimers and the belt hexamers, and the evolution of their NMR signatures during the substitution process.

The removal of one central phosphorus in α-P_2W_{18} leads to a lowering of the symmetry of the α-isomer Dawson structure that initially contains two equivalent PW_9 subunits. Consequently, both ^{183}W resonances of the cap and of the belt W split into two resonances each, representing the two distinct subunits PW_9 and $\square W_9$ formed. The belt W resonance of the filled subunit PW_9 shifts to higher field, whereas that of the empty subunit $\square W_9$ undergoes a strong deshielding effect. Nevertheless, the cap W resonances of both subunits evolve similarly toward high field but that of the filled PW_9 subunit felt the effect much more. When the cavity is filled with an As atom, all the four resonances evolve toward the reverse direction with respect to their own first change: i.e., to lower field for the caps W and belt W of the PW_9 unit and to higher field for the belt W of the AsW_9 unit. Although the replacement of one P by one As tends to restore the original spectrum of α-P_2W_{18}, there is still net differentiation in chemical shifts of W between the two subunits PW_9 and AsW_9 that translates the difference of electronic effects of P and As on the W in the cluster. Globally, the As subunit gives ca. 20–10 ppm lower field resonances of W for the belt as well as for the cap in comparison to those of the P subunit. Similar effects were also observed on other structures such as P_8W_{48} with respect to As_8W_{48}[42,43] or $(AsW_9)_2(Mo_2O_2S_2)_3$ with respect to $(SbW_9)_2(Mo_2O_2S_2)_3$.[44,45] When the second P atom is removed, the same trends on the ^{183}W chemical shifts are observed in comparison to the first removal of P: i.e., high-field shifts for W of the two caps and

Table 1. NMR Parameters ($\delta_{W\text{-}183}$, $^2J_{W-O-W}$, $^2J_{W-O-P}$, and $\delta_{P\text{-}31}$) of the Dawson Tungstates Studied: β-P_2W_{18}, α-P_2W_{18}, α-PW_{18}, α-$AsPW_{18}$, α-AsW_{18}, α-As_2W_{18}, β-As_2W_{18}, and γ*-As_2W_{18}[a,b]

compound	$\delta_{W\text{-}183}$, ppm	$^2J_{W-O-W}$, Hz		$^2J_{W-O-P}$, Hz	$\delta_{P\text{-}31}$, ppm
β-P_2W_{18}	−194.2 (−191.2)	19.5 (19.2)	30.9 (31.0)	1.6 (1.6)	−11.4 (−12.2)
	−173.8 (−171.1)	20.5 (21.0)	30.9 (31.0)	1.7 (1.6)	−10.7 (−11.5)
	−133.4 (−131.1)	20.5 (21.0)		1.1 (1.1)	
	−114.0 (−111.6)	19.5 (19.2)		1.2 (1.2)	
α-P_2W_{18}	−173.6 (−173.8)	20.8 (21.1)		1.6 (1.6)	−12.3 (−12.4)
	−128.1 (−128.1)	20.8 (21.1)		1.1 (1.2)	
α-PW_{18}	−181.7 (−181.3)	20.0 (20.0)	26.7 (26.8)	1.5 (1.5)	−6.5 (−6.5)
	−145.6 (144.9)	20.0 (20.0)		1.2 (1.3)	
	−135.9 (−135.7)	21.8 (21.7)			
	−128.9 (−127.8)	21.8 (21.7)	26.7 (26.8)		
α-$AsPW_{18}$	**-168.8**	**21.1**	**28.7**	**1.6**	**-11.4**
	-149.5	**21.2**	**28.7**		
	-130.2	**21.1**		**1.3**	
	-121.5	**21.2**			
α-AsW_{18}	−162.9 (−161.3)	**20.2**	**26.7**		
	−136.8 (−134.6)	**21.7**			
	−135.5 (−134.1)	**20.2**			
	−117.7 (−112.4)	**21.7**	**26.7**		
α-As_2W_{18}	−145.7 (−142.9)	21.2 (21.4)			
	−122.6 (−120.1)	21.2 (21.4)			
β-As_2W_{18}	−160.4 (−160.1)	19.7 (19.5)	30.5 (30.3)		
	−140.9 (−140.6)	21.1 (21.4)	30.5 (30.3)		
	−123.7 (−123.4)	21.1 (21.4)			
	−107.1 (−106.6)	19.7 (19.5)			
γ*-As_2W_{18}	−166.2 (−166.0)	20.5 (20.7)			
	−110.1 (−110.0)	20.5 (20.7)			

[a] Data in boldface type are new from the present study. [b] Values in parentheses are from the literature for $\delta_{W\text{-}183}$, $^2J_{W-O-W}$, and $^2J_{W-O-P}$[15,19,21,24,41] and for $\delta_{P\text{-}31}$.[38−40]

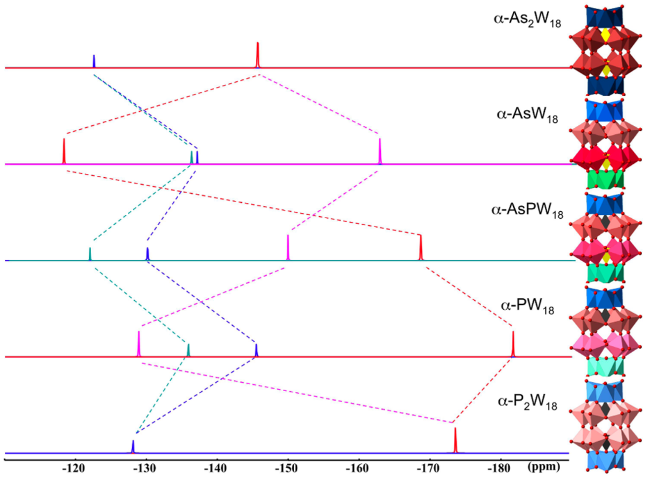

Figure 7. Schematic representation of the evolution of the ^{183}W NMR spectra of Dawson tungstates when progressively substituting P by As from α-P_2W_{18}, to α-$AsPW_{18}$, and then to α-As_2W_{18}, passing through the asymmetric intermediates α-PW_{18} and α-AsW_{18}.

belt W of the AsW_9 subunit and, on the other hand, a strong low-field shift for the belt W of the empty AsW_9 subunit. Finally, incorporation of an As atom into the vacant cavity restores the original symmetry of the Dawson α isomer and allows resonances of the belts and those of the caps to merge into one single resonance for each. As noted previously, the resonances appeared significantly deshielded in comparison to those observed in the phosphorus analogue, reflecting the softer character of the larger As atom in comparison to the P atom. The consistency of the trends observed on the ^{183}W spectra with a change of the central heteroatoms confirms that these spectral features are directly linked to the structural alteration provoked by the substitution effects of the heteroatom. In the absence of crystallographic data, fine analysis of the NMR-observable parameters would provide some structural information by comparing the trends observed when removing or adding the central heteroatom. Indeed, with the set of NMR data now available for intermediate structures between α-P_2W_{18} and α-As_2W_{18}, one can follow the change of the NMR parameters. Thus, Tables 2 and 3 summarize the effects of P and As, respectively, on the observed NMR parameters when these atoms are added to a given compound.

From Table 2, one can see that the presence of phosphorus induces ca. 10 and 15 ppm low-field shifts for the belt and cap ^{183}W resonances of the neighbor XW_9 (X = P, As) and a ca. 50 ppm high-field shift and 7 ppm low-field shift for the belt and cap ^{183}W resonances of the involved PW_9 unit, respectively. This implies that all W atoms undergo some deshielding effect, except those of the belt where the phosphorus is located, which feel a considerable shielding. The W−O distances should consequently be lengthened everywhere in the cluster except those involved in bonding with the added heterotaom P, which become much shorter. The vacancy of the central heteroatom in the Dawson structure then leads to contraction of terminal W−O bonds pointed toward the outside, but to inner extension of the W−O bonds pointed toward the empty cavity. There are

Table 2. Effect of Phosphorus on the NMR Parameters ($\delta_{W\text{-}183}$, $^2J_{W-O-W}$, $^2J_{W-O-P}$, and $\delta_{P\text{-}31}$) of the Dawson Tungstates α-P_2W_{18} and α-$AsPW_{18}$

effect of P	$\Delta\delta_{W\text{-}183}$, ppm	Δ^2J_{W-W}, Hz	Δ^2J_{W-P}, Hz	$\Delta\delta_{P\text{-}31}$, ppm
	α-PW_{18} → α-P_2W_{18}			
				5.8
belt (indirect)	−8		−0.1	
belt (direct)	45			
cap (indirect)	−17		0.1	
cap (direct)	−8			
belt−cap (indirect)		−0.8		
belt−cap (direct)		1.0		
belt−belt				
	α-AsW_{18} → α-$AsPW_{18}$			
belt (indirect)	−13			
belt (direct)	51			
cap (indirect)	−14			
cap (direct)	−7			
belt−cap (indirect)		−1.1		
belt−cap (direct)		0.6		
belt−belt		−2.0		
	Average			
				5.8
belt (indirect)	−11		−0.1	
belt (direct)	48			
cap (indirect)	−16		0.1	
cap (direct)	−7			
belt−cap (indirect)		−0.9		
belt−cap (direct)		0.8		
belt−belt		−2.0		

Table 3. Effect of Arsenic on the NMR Parameters ($\delta_{W\text{-}183}$, $^2J_{W-O-W}$, $^2J_{W-O-P}$, and $\delta_{P\text{-}31}$) of the Dawson Tungstates α-As_2W_{18} and α-$AsPW_{18}$

effect of As	$\Delta\delta_{W\text{-}183}$, ppm	Δ^2J_{W-W}, Hz	Δ^2J_{W-P}, Hz	$\Delta\delta_{P\text{-}31}$, ppm
	α-AsW_{18}→ α-As_2W_{18}			
belt (indirect)	−17			
belt (direct)	28			
cap (indirect)	−13			
cap (direct)	−14			
belt−cap (indirect)		−1.1		
belt−cap (direct)		0.5		
belt−belt				
	α-PW_{18} → α-$AsPW_{18}$			
				4.9
belt (indirect)	−13		−0.1	
belt (direct)	21			
cap (indirect)	−15		−0.1	
cap (direct)	−14			
belt−cap (indirect)		−1.2		
belt−cap (direct)		0.7		
belt−belt		−2.0		
	Average			
				4.9
belt (indirect)	−15		−0.1	
belt (direct)	24			
cap (indirect)	−14		−0.1	
cap (direct)	−14			
belt−cap (indirect)		−1.1		
belt−cap (direct)		0.6		
belt−belt		−2.0		

also remarkable trends in the $^2J_{W-O-W}$ coupling constants. One can note that the presence of phosphorus makes $^2J_{W-O-W}$ ca. 1 Hz smaller between resonances of belt and cap W atoms of the neighboring XW_9 (X = P, As), but $^2J_{W-O-W}$ ca. 1 Hz larger between resonances of belt and cap W atoms of the involved PW_9 unit. The $^2J_{W-O-W}$ value between resonances of the belts decreases noticeably by 2 Hz when the heteroatom P is introduced in the vacant cavity. This may indicate changes in the W−O−W angles occurring when the phosphorus is present in the central position. Larger values of $^2J_{W-O-W}$ would reflect wider angular W−O−W opening.[15] Thus, one can conclude, in line with the above W−O bond changes, that incorporation of P into the central position in the Dawson structure induces a wider angular junction between the cap and belt units of the half-anion PW_9 where the phosphorus resides, but smaller angles within the second half-anion. This is consistent with the previous conclusion about the bond contractions in the half-anion with a vacant site $\square W_9$. Moreover, the bridge angles between the two subunits experience some contraction. The accuracy of the variation in $^2J_{W-O-P}$ could not allow us to establish a clear correlation between these parameters, although globally a general tendency of a decrease in the $^2J_{W-O-P}$ coupling constants with an increase in the bridge angles is observed. The high-field shift (ca. 6 ppm) of the ^{31}P NMR signal when the vacancy is filled with P in α-PW_{18} is indicative of more shielding on P and thus shorter P−O distances. This is fully consistent with the previous ^{183}W observation about the deshielding of tungsten atoms of the neighboring subunit that should experience longer W−O bonds.

The same trends are observed for arsenic as the incorporating heteroatom (Table 3). However, some differences mainly in the extent of these effects are noticed in comparison to those for phosphorus. Of particular interest, the ^{183}W chemical shifts of W atoms directly involved in interaction with the incorporated heteroatom show higher sensitivity for belt W with P and for cap W with As. Indeed, a high-field shift of belt W resonance of ca. 50 ppm is observed for the P effect, whereas it is only ca. 25 ppm for the As effect. On the other hand, the cap W resonances are shifted to lower field by ca. 7 ppm as a P effect and by 14 ppm as an As effect. These differences certainly arise from the difference in the electronic densities around the heteroatom considered and should be obviously linked to the molecular orbital filling. As the general tendency is that the shielding effect is more pronounced with P than with As (and conversely the deshielding effect is stronger with As than with P), the electron density transfer to the W 5d orbital from molecular orbital overlapping involving the P ligand is thus expected to be more effective than those involving As.

■ CONCLUSIONS

^{183}W and ^{31}P NMR were used to monitor fine structural characterization of Dawson isomers of arsenato− and phosphato−tungstates as well as the mixed arsenato−phosphato−tungstate. Of particular interest, 2D-INADEQUATE correlation experiments were systematically used to unambiguously assign all observed resonances, to accurately determine $^2J_{W-O-W}$, and to identify the composition of mixtures. The NMR observables including chemical shifts and J scalar couplings were correlated to the small structural alteration induced by incorporation/removal of the central heteroatom P or As. The effects of these heteroatoms on the ^{183}W NMR parameters in the Dawson α-isomer structure were established for each of these heteroatoms, which could be generalized and used to predict NMR features of other isomers or even other polyoxotungstate structures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving 2-D INADEQUATE ^{183}W NMR spectra of β-P_2W_{18}, α-PW_{18}, and β-As_2W_{18}. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for M.H.: mohamed.haouas@uvsq.fr.
*E-mail for I.-M.M.: israel.mbomekalle@u-psud.fr.

Notes

The authors declare no competing financial interest.

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