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NMR Studies of Heteropolyanion $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ Complexes with Metal Cations

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We have used multinuclear NMR and IR spectroscopy to study the interaction of a number of metal cations with monovacant heteropolyanion $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ ($\mathbf{P_2W_{20}}$) in aqueous solutions starting from its K salt. We have also prepared and studied $\mathbf{P_2W_{20}}$ in an Na-only medium. The observed differences in the NMR spectra of Na$\mathbf{P_2W_{20}}$ and K$\mathbf{P_2W_{20}}$ solutions and the importance of K^+ and Na^+ for the formation of $\mathbf{P_2W_{20}}$ suggest that this polyanion exists only as a complex with the alkaline cations. When both cations were simultaneously present in solution, we observed the broadening of the NMR signals of $\mathbf{P_2W_{20}}$ due to the Na−K exchange. Li^+ does not replace K^+ or Na^+ in such complexes, and in an Li-only medium $\mathbf{P_2W_{20}}$ does not form. Of all the M^{n+} cations studied (Pd^{2+}, Bi^{3+}, Sn^{4+}, Zr^{4+}, Ce^{4+}, Ti^{4+}, V^{5+}, and Mo^{6+}) only Bi^{3+}, Sn^{4+}, and Ce^{4+} form complexes with $\mathbf{P_2W_{20}}$ in strongly acidic solutions. The ^{183}W and ^{119}Sn NMR data suggest that Sn^{4+} forms in solution two mutually interconvertable $\mathbf{P_2W_{20}}$Sn complexes of the composition $P_2W_{20}O_{70}(H_2O)_3SnOH^{7-}$ and $(P_2W_{20}O_{70}(H_2O)_3Sn)_2O^{14-}$ while Bi^{3+} forms one complex of the proposed composition $P_2W_{20}O_{70}(H_2O)_2Bi.^{7-}$ We obtained complexes with Bi and Sn as free heteropoly acids and studied their thermostability in the solid state.

Introduction

Polyoxometalates including heteropolyacids (HPA) are an important class of compounds formed mainly by tungsten and molybdenum in aqueous solutions. They are used in acid and oxidation catalysis, analytical chemistry, materials science, medicine, and other fields.[1−3] HPA with one or several W or Mo atoms substituted by another transition metal such as V, Ti, Ru, etc. have attracted a lot of attention as selective oxidation catalysts.[2] The polyoxometalate skeleton stabilizes the unusual oxidation states of the heterometal, thus creating conditions for unique reactivity of these catalysts.

The complex structures of polyoxometalates present a challenge to investigators. Although X-ray analysis remains the main direct method for HPA basic structure determination, for HPA polyanions (pa) retaining their structure in solution, NMR spectroscopy provides valuable structural details including the location of heterometal substituents. Multinuclear NMR studies of pa often afford a complete structural picture, which is of special value when species cannot be isolated from solution.

Among numerous phosphorus- and tungsten-based pa, three structural types with different P/W ratios are best known: $PW_{12}O_{40}{}^{3-}$ ($\mathbf{PW_{12}}$), $P_2W_{18}O_{62}{}^{6-}$ ($\mathbf{P_2W_{18}}$), and $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ ($\mathbf{P_2W_{21}}$).[1,4] All of them can form lacunary derivatives by losing one or more W═O fragments. Lacunary pa $\mathbf{PW_{11}}$ is derived from $\mathbf{PW_{12}}$, and its complexes with many metals are well-known.[1] The pa $\mathbf{P_2W_{21}}$ gives two lacunary forms $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ ($\mathbf{P_2W_{20}}$) and $[P_2W_{19}O_{69}\ H_2O]^{14-}$ ($\mathbf{P_2W_{19}}$) by losing one or two W═O groups from the equatorial belt.[4−6] The $\mathbf{P_2W_{20}}$ pa, isolated as a potassium salt, was first identified by solution ^{183}W NMR studies.[4−6] It was concluded to be structurally between $\mathbf{P_2W_{21}}$ and $\mathbf{P_2W_{19}}$, containing two α-A-$\mathbf{PW_9}$ halves linked via two W_6 atoms in the equatorial plane (Figure 1a). According to an additional crystallographic study, the vacancy of the pa in the K$\mathbf{P_2W_{20}}$ salt is filled with a K^+ cation unlike the vacancies in the $\mathbf{P_2W_{19}}$ structure, which are filled with water molecules.[5,7] The preparation and NMR and IR spectra of $\mathbf{P_2W_{20}}$ were also described independently by our group,[8] but we mistakenly identified it as Fuchs' pa $[P_2W_{20}O_{72}]^{14-}$.[9] From ^{183}W NMR data and the synthesis pH range, it is now evident that $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ pa was obtained in all cases[4−8] while Fuchs' pa was isolated from less acidic solutions[9] and its NMR spectra have not yet been described.

Numerous substituted derivatives of $\mathbf{P_2W_{21}}$ with two and three M^{n+} cations in the belt have been described in the literature,[5,6] while data on $\mathbf{P_2W_{20}}$ complexes with multivalent cations are

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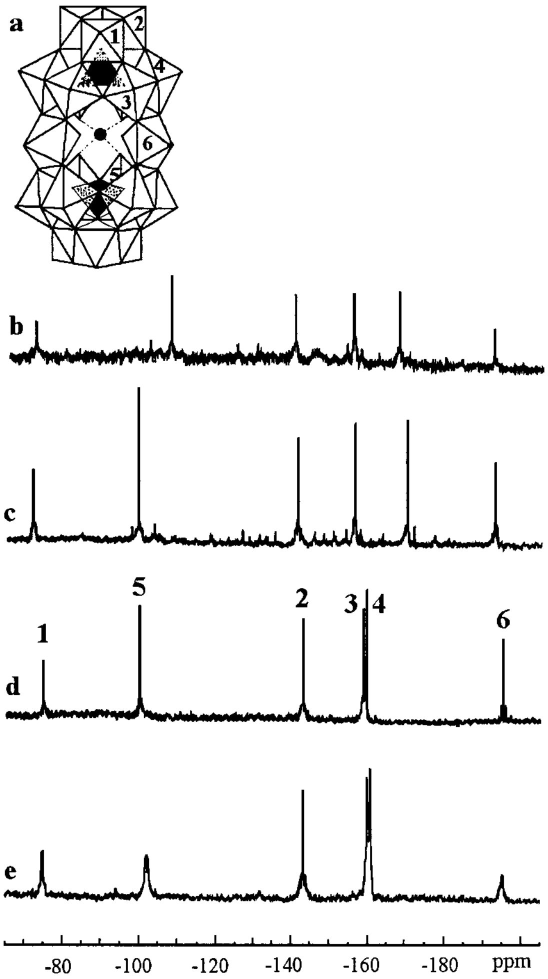

Figure 1. Polyhedral representation (a) of heteropolyanion $\mathbf{P_2W_{20}}$. Two α-A-$PW_9O_{34}^{9-}$ fragments are linked via two $WO_5(H_2O)$ octahedra. ^{183}W NMR spectra of $\mathbf{P_2W_{20}}$ in solutions are shown with different counterions: Li^+ (with Na impurity) (b); Na^+ (c); K^+ (d); K^+ with added sodium, K/Na = 10 (e).

rather scarce.[7,10] We could expect, by anology with the $\mathbf{PW_{12}}$ series, that the stability region of the monosubstituted $\mathbf{P_2W_{21}}$ complexes shifts to higher acidities. Therefore, in the search of modified HPA catalytic systems that are stable as free acids, we have prepared a number of new complexes of this type and characterized them by multinuclear NMR spectroscopy. We present our results in this contribution.

Experimental Section

Materials. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Starting compounds of M^{n+} were $ZrOCl_2{\cdot}8H_2O$, K_2PdCl_4, $SnCl_2 + H_2O_2$, $NaVO_3{\cdot}2H_2O$, $Na_2MoO_4{\cdot}2H_2O$, $(NH_4)_2Ce(NO_3)_6$, $Bi(NO_3)_3{\cdot}5H_2O$, and an aqueous solution of $TiCl_4$ (0.1 M in 15% HCl). Salt $K_{10}[P_2W_{20}O_{70}]{\cdot}23H_2O$ was prepared according to the literature procedure,[4b] and its identity was confirmed by ^{183}W and ^{31}P NMR spectroscopy (see Table 1). Preparation of HPA $\mathbf{P_2W_{21}}$ and the Na and Li salts of $\mathbf{P_2W_{20}}$ is described below.

Preparation of $\mathbf{P_2W_{21}}$ HPA. An aqueous solution containing Na_2WO_4 and H_3PO_4 in a molar ratio W/P = 11 was acidified and decationized using the electrodialysis technique as described in the literature.[11] Solid $Na_2WO_4{\cdot}2H_2O$ (21.8 g, 66 mmol) was dissolved in 50 mL of water with stirring, and H_3PO_4 (1 M, 6 mL) was added. The resulting solution was placed in the anode compartment of an electrodialyzer to conduct the electrochemical substitution of Na^+ by H^+. The solution composition was monitored by ^{31}P NMR spectroscopy. When the solution reached pH = 5, pa $\mathbf{PW_{11}}$ formed quantitively. Upon further removal of Na^+ from the solution until its residual concentration did not exceed 0.01 M, an equimolar mixture of $\mathbf{P_2W_{21}}$ and $\mathbf{PW_{12}}$ was obtained. HPA $\mathbf{PW_{12}}$ crystallized as large cubes upon solution evaporation under ambient conditions and was easily removed from the mixture by filtration. According to ^{31}P and ^{183}W NMR spectra, the resulting filtrate contained only HPA $\mathbf{P_2W_{21}}$, which could be used for further synthesis as is or crystallized into a solid of composition $H_6P_2W_{21}O_{71}{\cdot}30H_2O$. The yield was around 10 g.

IR (KBr disk, 1200−400, cm^{-1}): 1090, 1080,1026, 962, 930, 880, 790−700, 516. ^{31}P NMR: δ −13.7.

Preparation of $\mathbf{NaP_2W_{20}}$ and $\mathbf{LiP_2W_{20}}$. Aqueous NaOH or LiOH (1 M, 4.5 mL) was added dropwise to a stirring aqueous solution of HPA $\mathbf{P_2W_{21}}$ (0.1 M, 6 mL) at 20 °C. According to our ^{31}P NMR and literature[4b] data, upon interaction with bases, $\mathbf{P_2W_{21}}$ disproportionates according to reaction $\mathbf{P_2W_{21}} \rightarrow 0.5\mathbf{P_2W_{20}} + \mathbf{PW_{11}}$. The reaction is incomplete at pH = 3, and residual $\mathbf{P_2W_{21}}$ reacting with $\mathbf{PW_{11}}$ is gradually converted into a number of PW pa.[12] After the resulting solution was stored at room temperature for 1 week, according to ^{31}P NMR peak intensities, the $\mathbf{P_2W_{20}}$ content was around 60% (spectrum 7 of Figure 2). Therefore, these solutions were suitable for NMR studies of this pa without further isolating its highly soluble Na or Li salts.

The solid sodium salt of $\mathbf{P_2W_{20}}$ was obtained by electrochemical acidification (to pH ≈ 2) of a 1 M solution of Na_2WO_4 and H_3PO_4 taken in a molar ratio of (6−9):1 followed by aging for 2−4 months. Upon slow evaporation of the aged solution at ambient conditions, colorless crystals of $P_2W_{20}Na$ salt formed in 50% yield. For ^{31}P and ^{183}W NMR results, see Table 1.

Preparation of $\mathbf{P_2W_{20}}$ Complexes with Multivalent Metal Cations. To obtain $\mathbf{P_2W_{20}}$M complexes, 0.05 M aqueous solution of the potassium salt of $\mathbf{P_2W_{20}}$ was mixed with an M^{n+} compound taken in a stoichiometric amount. To obtain the corresponding HPA, the resulting solutions were treated with a cationic exchange resin KU-2-8 in its protonated form, yielding pH < 0. According to ^{31}P and ^{183}W NMR data (Table 2), only M = Sn^{4+} and Bi^{3+} gave complexes with $\mathbf{P_2W_{20}}$ that are stable as free HPA, which were obtained in solutions in practically quantitative yields and which retained their composition for many months.

Preparation of $\mathbf{P_2W_{20}}$Sn HPA. The potassium salt of $\mathbf{P_2W_{20}}$ (11.4 g, 2 mmol) was dissolved in water (35 mL). Solid $SnCl_2{\cdot}2H_2O$ (0.45 g, 2 mmol) was added to the resulting solution. Upon dissolution of $SnCl_2$ the solution turned brown. Decationization on the resin resulted in further darkening of the solution. Then, 1% H_2O_2 was added dropwise until the solution decolorized. To obtain chloride-free HPA $\mathbf{P_2W_{20}Sn}$, the solution was evaporated to dryness and the resulting solid was heated at 120 °C for 1 h. Then, it was redissolved in cold water and a small amount of white, thin precipitate was removed by centrifugation. Recrystallization followed by drying in air gave about 10 g (>90% yield) of a yellowish material, completely soluble in water.

Anal. Calcd for $H_7[P_2W_{20}O_{70}SnOH]{\cdot}25H_2O$: P, 1.13; W, 67.22; Sn, 2.2; H_2O, 8.25. Found: P, 1.0; W, 63.3; Sn, 2.27; H_2O, 7.5. IR (KBr disk, 1200−400, cm^{-1}): 1090, 1082, 1025, 963, 928, 870(sh), 765, 620, 520. For ^{31}P, ^{119}Sn, and ^{183}W NMR results, see Table 1.

Preparation of $\mathbf{P_2W_{20}}$Bi HPA. The starting aqueous solution of 2 mmol of K$\mathbf{P_2W_{20}}$ was prepared as described above. Solid $Bi(NO_3)_3{\cdot}5H_2O$ (0.970 g, 2 mmol) was dissolved in 5 mL of water, acidified with acetic acid to pH = 3, and added dropwise to the K$\mathbf{P_2W_{20}}$ solution with stirring. Then, the solution was treated with the resin and evaporated to dryness at 20 °C. The resulting white solid was recrystallized from cold water, giving about 80% yield.

Anal. Calcd for $H_7[P_2W_{20}O_{70}Bi]{\cdot}25H_2O$: P, 1.1; W, 66.5; Bi, 3.78; H_2O, 8.1. Found: P, 1.1; W, 63.4; Bi, 3.75; H_2O, 7.8. IR (cm^{-1}): 1090, 1080, 1025, 960, 930, 850(sh), 760, 670, 520. For ^{31}P and ^{183}W NMR results, see Table 1.

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Table 1. ^{183}W, ^{31}P, and ^{119}Sn NMR Chemical Shifts (ppm) of P_2W_{20} Complexes with Different Cations[a]

cation	$2W_1$	$4W_2$	$4W_3$	$4W_4$	$4W_5$	$2W_6$	^{31}P	^{119}Sn	ref
Li(K)[b]	−74.6	−142.4	−159.2	−159.6	−103.6	−195.9	−12.3		6
Li(K)[b]	−75.6	−142.9	−164.3	−166.3	−116.1	−201.1			4
K	−74.2	−142.5	−159.1	−159.1	−100	−195.3	−12.8		8
K	−74.6	−142.6	−158.6	−159.3	−100.1	−195.3	−12.8		
Na	−71.6	−140.8	−156	−169.6	−99.3	−192.8	−14.1		
Li(Na)	−72	−139.9	−155.6	−167.3	−107.3	−192.2	−14.1		
Bi $^{3+}$ (**I**)	−82.7	−132.1	−152.7	−137.1	−70.5	−187.5	−14.9		
^2J (±0.5), Hz:	$2W_2$ 7 $2W_3$ 21	W_1 7 W_4 18 W_5 18	W_4 8 W_1 19 W_6 20	W_3 8 W_2 18 W_5 25 W_6 21	W_2 18 W_4 25	W_3 20 W_4 21			
Sn^{4+}(**II**)	−87.6	−132.5	−139.3	−136.5	−197.5	−252.9	−14.13	−632	
2*J* (±0.5), Hz:	$2W_2$ 9 $2W_3$ 21	W_1 9 W_4 21 W_5 21	W_4 7 W_1 21 W_6 18	W_3 7 W_2 21 W_5 25 W_6 18	W_2 21 W_4 25 ^{117,119}Sn 165	$2W_3$ 18 $2W_4$ 18		$4W_5$ 172	
Sn^{4+} (**III**)	−86.7	−134.1	−141.4	−137.3	−201.2	−243	−14.15	−601.6	
^2J, Hz:					^{117,119}Sn 155			$4W_5$ 163	

[a] The numbering of tungsten atoms corresponds to that in Figure 1. [b] Prepared from potassium salt by resin exchange.

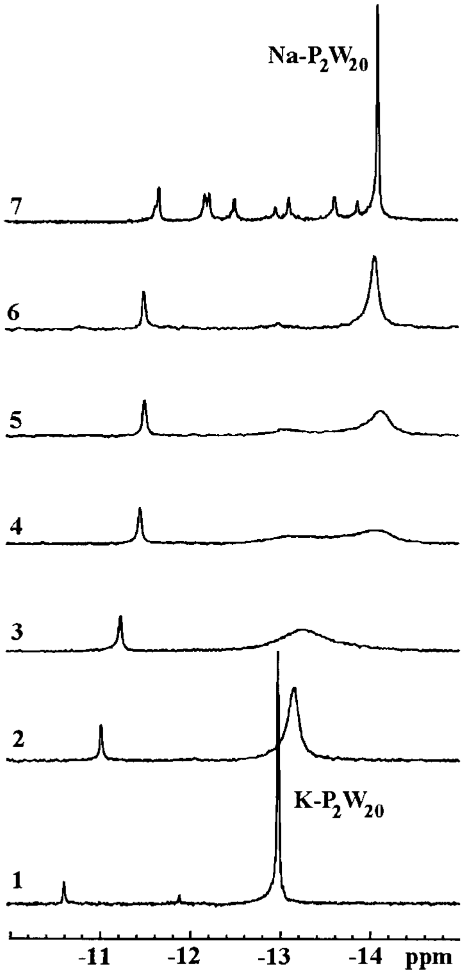

Figure 2. ^{31}P NMR spectra of $K_{10}P_2W_{20}O_{70}(H_2O)_2$ solutions (~0.1 M) measured during stepwise addition of $NaClO_4$ (1−6) and of solution [$\mathbf{P_2W_{21}}$ + 7.5NaOH] (7), containing Na$\mathbf{P_2W_{20}}$ and some other pa impurities. The molar ratio of the introduced amount of Na to the initial amount of K for spectra 1−6 is equal to 0, 0.2, 0.5, 0.75, 1, and 1.5. The ^{183}W NMR corresponding to spectrum 7 is given in Figure 1c.

Instrumentation and Methods. ^{183}W NMR spectra were measured on an MSL-400 Bruker NMR spectrometer at an operating frequency of 16.67 MHz, with a 5 kHz sweep width, 50 μs pulse width, and 10 s interpulse delay, using 1 M Na_2WO_4 as an external reference. The corresponding parameters for ^{119}Sn were 149.1 MHz, 10 kHz, 12 μs, 10 s, and $SnMe_4$ as a reference; for ^{31}P they were 161.98 MHz, 5 kHz, 10 μs, and 30 s, relative to 85% H_3PO_4. In some cases we used HPA $\mathbf{PW_{12}}$ as an internal standard to determine ^{31}P NMR chemical shifts (δ) of the closely located peaks more precisely. The $\mathbf{PW_{12}}$ chemical shift was taken as $\delta = -15.05 \pm 0.03$ ppm relative to 85% H_3PO_4. This value was found by taking into account the correction for the solutions magnetic susceptibility difference ($\Delta\delta$)[13] and was confirmed independently through measurements in spherical ampuls and through a comparison of the δ values obtained in superconducting (−14.5 ppm) and iron-core (−15.23 ppm) magnets, which have different sample orientations relative to the external magnetic field.[14] Infrared spectra of 0.5−1 wt % samples in KBr pellets were measured on a Specord 75 IR spectrometer. Elemental analyses were conducted by the Analytical Laboratory of the Boreskov Institute of Catalysis. The P, W, Sn, and Bi content was found by X-ray fluorescence spectral analysis on analyzer VRA-20 using an external standard method with a relative error of ±10%. The residual sodium in solutions was determined by

Table 2. ^{31}P NMR Data for the Decationized Solutions (pH < 0) Containing $\mathbf{P_2W_{20}}$ (0.05 M) and Cations M^{n+} in a Molar Ratio of 1:1

cation	δ ^{31}P, ppm	content, ±3%	assignment
Pd^{2+}	−13,7	100	$\mathbf{P_2W_{21}}$ [11,12]
Bi^{3+}	−14,9	100	$\mathbf{P_2W_{20}}$Bi (**I**)
Sn^{4+}	−14,1	100	$\mathbf{P_2W_{20}}$Sn (**II, III**)
Zr^{4+}	−13,6	90	$\mathbf{PW_{11}}$Zr [17]
	−13,7	10	$\mathbf{P_2W_{21}}$
Ce^{4+}	−13,9	75	~$\mathbf{P_2W_{20}}$Ce
	−13,4	20	?
	−13,1	<5	$\mathbf{PW_{11}}$Ce [17]
Ti^{4+}	−13,6	95[a]	$\mathbf{PW_{11}}$Ti [b,18]
V^{5+}	−14,0	55	~$\mathbf{P_2W_{20}}$V
	−14,4	20	?
	−14,9	25	~$\mathbf{PW_{11}}$V
Mo^{6+}	−14,0	65[a]	~$\mathbf{P_2W_{20}}$Mo
	−15,1	20	$\mathbf{PW_{12}}$

[a] There are also several peaks of low intensity. [b] The assignment is confirmed by the ^{183}W NMR spectrum.

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(14) From measurement in spherical ampuls, $\Delta\delta$ is equal to zero. For cylindrical ampouls $\Delta\delta = (^4/_3)\pi\Delta\chi$ for orientation along the magnetic field, as in the superconducting magnets, and $\Delta\delta = -(^2/_3)\pi\Delta\chi$ for the perpendicular orientation, as in the iron-core magnets. $\Delta\chi$ is the magnetic susceptibility difference.

atomic absorption spectroscopy. The amount of water was found from the weight loss after heating the samples at 500 °C for 3 h.

Results and Discussion

Preparation of Heteropolyanions. In the earlier NMR studies of **P_2W_{20}**, its potassium salt, easily obtainable in the crystalline form, was used.[4−6] The solubility of this salt was increased by means of K−Li exchange in solution, using an Li-exchange resin or a $LiClO_4$ treatment followed by $KClO_4$ precipitate removal. The sodium salt solution studied by Tourné et al.[5] was obtained by cationic exchange from the potassium salt, and the authors noticed the dependence of the NMR spectra on the countercation and the pH. Since it is impossible to completely remove one of the alkaline cations from the mixed solutions in this way and, as will be demonstrated further, this may influence the appearance of the NMR spectra, we took special care to prepare **P_2W_{20}** solutions containing only one of the cations (see Experimental Section). Only in our earlier report[8] and in this work, spectra were measured on solutions of pure K and Na salts of **P_2W_{20}**, which gave noticeable differences with the literature results. It should also be noticed that while the solutions with sodium or lithium also contained some PW pa impurities, the individual content of the latter was low enough (≤5% of total P) compared to that of **P_2W_{20}** (>50%) so that their ^{183}W NMR signals were hardly noticeable in the solution spectrum (Figure 1c, spectra 2−7). This allowed us to identify the **P_2W_{20}**Na complex under in situ conditions.

Interaction of P_2W_{20} with Alkaline Cations. ^{183}W NMR spectra of the aqueous solutions of **P_2W_{20}** alkaline salts consist of six signals (Table 1) and their coupling satellites, which were assigned[6] to the corresponding W atoms (Figure 1) on the basis of the intensity ratio (1:2:2:2:2:1) and values of the ^{183}W−O−^{183}W coupling constants. According to the spectra, each half of the pa contains four different tungsten pairs and a unique tungsten atom in the polar cap (W_1), with two equivalent belt tungstens (W_6) connecting the pa halves. As a result, **P_2W_{20}** pa was concluded to be a precursor of **P_2W_{21}** pa, which was later confirmed by the study of the pa structure in the solid salt.[7]

P_2W_{20} in pure K and Na salt solutions gives sets of six very narrow ^{183}W NMR peaks with similar chemical shift values, except for the peak corresponding to W_4 atoms (Figure 1, Table 1), while in the ^{31}P NMR spectra, the signals corresponding to **P_2W_{20}** with K and Na are observed at distinctly different chemical shifts: −12.8 and −14.1 ppm, respectively (Figure 2, Table 1). Upon stepwise addition of $NaClO_4$ to the potassium salt solution, the ^{183}W NMR peaks of the pa broaden without shifting, and at Na/K molar ratio of ∼1 only two broad peaks corresponding to W_2 and W_4 atoms are visible in the spectrum. At the same time, in the ^{31}P NMR spectra, the peak corresponding to **P_2W_{20}** in the presence of potassium broadens significantly and shifts slightly upfield, in the direction of the Na salt signal (Figure 2). These data indicate that **P_2W_{20}** exists in solutions in the form of complexes with K or Na and that there is a chemical exchange between them. Addition of $NaClO_4$ removes potassium from the solution as $KClO_4$ precipitate. However, the broadening of the peak corresponding to the **P_2W_{20}**Na complex, even in the presence of excess $NaClO_4$ (spectrum 6 of Figure 2, Na/K= 1.5), suggests that a small amount of K still remains in solution and participates in the complexation with **P_2W_{20}**. From the solubility of $KClO_4$, we estimate that the amount of K present in the latter case corresponds to about one K per pa. A similar situation is likely taking place in the case of the Na salt solution obtained by Tourné et al.[5] using resin exchange with K. Their ^{183}W spectrum is similar to the one of our pure sodium salt in terms of the peak positions; however, the signals are noticeably broader, suggesting the presence of a potassium impurity.

The observed line broadening for the two complexes (Figure 2) corresponds to a slow exchange on the NMR time scale. This allows us to use the following approximated equation[15] to estimate the rate of Na−K exchange from the ^{31}P NMR peak widths:

$$\tau_2^{\ -1} = T_2^{\ -1} + \tau^{\ -1} \qquad (1)$$

where τ is the lifetime of K or Na in the complex with the pa, T_2 is the cross-relaxation time related to the inherent line width $\Delta f_{1/2}$ of the signals in Hz: $(\pi T_2^{-1}) = \Delta f_{1/2}$, and τ_2 is in the same manner related to the observed line width $(\pi\tau_2^{-1}) = \Delta f_{1/2}$. The mean lifetime of **P_2W_{20}** complexes with K and Na was estimated as $(3.7 \pm 1) \times 10^{-3}$ s. We have also estimated the second-order rate constant k for the exchange process from the equation $\tau^{\ -1} = kC_o$[16] as equal to $(3 \pm 0.8) \times 10^3$ M^{-1} s^{-1}. The main sources of errors are the uncertainties in the determination of the line widths and the complex concentrations.

The addition of lithium to a solution of **P_2W_{20}**K has a different effect. The ^{31}P NMR peak shifts only slightly upfield (by 0.2 ppm) without broadening. No ^{183}W peak broadening is observed either, but the chemical shifts change, especially those of W_5 atoms surrounding the vacancy. The resulting ^{183}W NMR spectrum is different from that of the "Li" salt of **P_2W_{20}**, obtained from **P_2W_{21}** and LiOH as described in the Experimental Section (Table 1, Figure 1).

Our attempts to prepare **P_2W_{20}** directly from lithium tungstate and phosphate were unsuccessful. The complex of **PW_{11}** with Li [12] was formed instead. All **P_2W_{20}** solutions with Li reported in the literature were prepared from the K salt of this pa[4−6] by ion exchange or $LiClO_4$ treatment and contained residual K. Similarly, our "Li salt" solution generated by adding LiOH to the solution of **P_2W_{21}**, which was prepared by electrodialysis from Na tungstate and phosphoric acid, could contain a sodium impurity. As is evident from a comparison of the data in Table 1, lithium does not completely replace potassium or sodium in their complexes with **P_2W_{20}** and K and Na still determine the NMR spectra of the resulting solutions. On the basis of the literature data and our observations, we can conclude that **P_2W_{20}** does not form without the alkaline cations, with the dimension of a cation being of importance. Evidently these cations can occupy the vacancy of **P_2W_{20}** as in a solid K salt[7] and also interact with the pa in solution in the same manner as in the potassium salt of divacant **P_2W_{19}**,[5] where K cations strongly coordinate from the outside to the oxygens of the pa equatorial region with the K−O distances typical for the potassium kryptates. Such interaction must promote retention of the alkaline cations in solutions and strengthen the linkage of the pa halves. Apparently, in this role Na and K are mutually replacable, which is suggested by the chemical exchange between their complexes with **P_2W_{20}**. It appears that the Li cation cannot stabilize the pa without K or Na, but its influence on the ^{183}W NMR spectra shows that, nevertheless, it interacts with the pa in some other manner. It is likely that Li may occupy the vacancy between four W_5 atoms, whose signal shifts most strongly in the presence of this cation. In addition, the variation

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[15] Emsley, J. W.; Feeney, J.; Sutcliffe, I. H. *High-Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: Oxford, 1965; Vol. 1, Chapter 9.

[16] The peak widths are (100 ± 20) Hz. The inherent peak width is less than 2 Hz. Calculated for $C = [K{-}HPAn] = [Na{-}HPAn] = 0.09$ M.

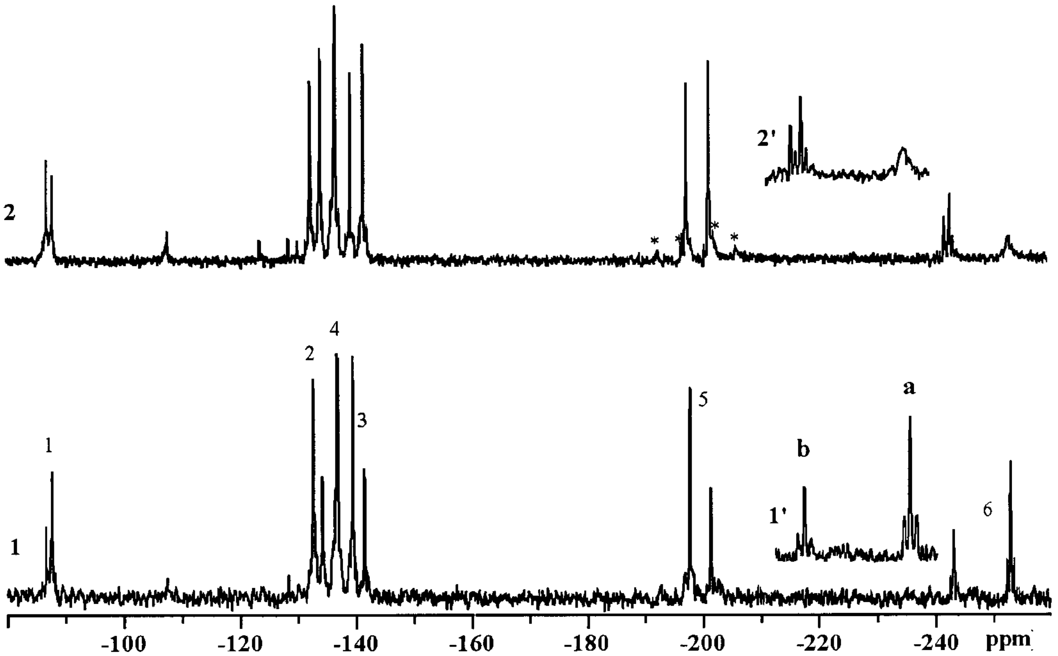

Figure 3. ^{183}W NMR spectra of $\mathbf{P_2W_{20}}$Sn complexes **II** (a) and **III** (b) in H_2O (spectrum 1) and in H_2O-D_2O, 2:1 (spectrum 2). Spectra 1′ and 2′ are expanded W_6 multiplets. The HPA concentration is about 0.04 mol/L for spectrum 1 and 0.06 mol/L for spectrum 2. The numbering of the ^{183}W peaks corresponds to Figure 1. The satellites in the W_5 resonances due to ^{183}W−O−^{117,119}Sn coupling are labeled with asterisks.

of the ^{183}W chemical shifts, depending on the degree of K/Li replacement (Table 1), and the narrow peaks suggest a fast Li exchange between the pa and solution.

Interaction of P_2W_{20} with Bi^{3+}, Sn^{4+}, and Other Multivalent Cations. According to our NMR data (Tables 1 and 2), of all multivalent metals studied only Bi^{3+} and Sn^{4+} quantitatively formed complexes with $\mathbf{P_2W_{20}}$ that were stable in the form of free HPA. Solutions of these HPA could be concentrated up to 0.1 M without precipitate formation or any change in their ^{31}P NMR spectra. It is likely that in dilute solutions HPA $\mathbf{P_2W_{20}Ce}$ and $\mathbf{P_2W_{20}Mo}$ also exist, but upon concentration these HPA partially decompose into other species, forming precipitates. Incorporation of Bi^{3+} and Sn^{4+} into the pa resulted in the upfield shift of the ^{31}P NMR signal compared to the starting K$\mathbf{P_2W_{20}}$.

According to ^{31}P NMR spectra, the interaction of K$\mathbf{P_2W_{20}}$ with Bi^{3+} in a 1:1 ratio converts the starting pa ($\delta = -12.8$ ppm) completely into a new PW complex (**I**) ($\delta = -14.9$ ppm). Since the unbound Bi^{3+} precipitates from solutions, the absence of any precipitate as well as any other PW complexes suggests that all added Bi is bonded to $\mathbf{P_2W_{20}}$ in a new complex quantitatively, i.e., that complex **I** has composition $\mathbf{P_2W_{20}Bi}$. The upfield shift of the ^{31}P NMR signal also confirms the complexation of the pa with a cation more highly charged than K^+. The unchanged number and the intensity ratio of the ^{183}W NMR signals of **I**, which were assigned to certain W atoms on the basis of their relative intensities and ^{183}W−O−^{183}W coupling constants (Table 1) as described in the literature,[4,6] are consistent with the retention of the $\mathbf{P_2W_{20}}$ skeleton. At the same time, the positions of the signals change, especially those of W_5 atoms, confirming that the Bi cation enters the vacancy forming a monosubstituted pa on the basis of $\mathbf{P_2W_{21}}$ structure. After treatment of the solution of **I** with the exchange resin to remove alkaline cations,[17] the pH decreases from 3 to about −0.5 but the NMR spectra of $\mathbf{P_2W_{20}Bi}$ remain unchanged, which suggests that the pa stays unprotonated in the entire pH range up to strong acidity and that therefore the anion charge is not too high. From the latter observation we can suggest that Bi^{3+}, because of its lone pair electrons directed outside as in the case of Pb^{2+} and Sn^{2+} in some other polytungstates,[19,20] is not connected to terminal oxygen; i.e., the composition of **I** is evidently $P_2W_{20}O_{70}(H_2O)_2Bi^{7-}$. Two other known PWBi complexes are $\mathbf{PW_{11}Bi}$ forming at pH < 1 and stable as free HPA and $\mathbf{(PW_{11})_2Bi}$ forming at pH > 2.[17] Their ^{31}P NMR δ values are −12.2 and −12 ppm, respectively, and they have distinctly different ^{17}O and ^{183}W NMR spectra. These two complexes interconvert with pH variations, and overstoichiometric Bi precipitates and dissolves again upon their transformations. In this work we have found that when the solution of $\mathbf{(PW_{11})_2Bi}$ is acidified to pH < 0 through decationization, the mixture of **I**, $\mathbf{PW_{11}Bi}$, and $\mathbf{PW_{12}}$ forms. Similarly, formation of $\mathbf{P_2W_{20}}$-Cr(III) was observed upon acidification of a solution containing Cr(III) and $\mathbf{PW_{11}}$.[10]

Unexpectedly, in its ^{183}W NMR spectrum the solution containing $\mathbf{P_2W_{20}}$ and Sn^{4+} gave two similar sets of six signals with the W_4 peaks overlapping (Figure 3), which was consistent with the presence of two different $\mathbf{P_2W_{20}}$ complexes. The intensity ratio of the two sets of peaks varied from sample to sample. In the ^{31}P NMR spectra of such solutions, we observed two overlapping peaks with a chemical shift difference of less than 0.02 ppm. The ^{119}Sn NMR spectra (Figure 4) revealed the presence of two types of Sn-containing species with an intensity ratio identical to that of the two $\mathbf{P_2W_{20}}$ complexes in the corresponding ^{183}W NMR spectra. The ^{119}Sn resonance of each Sn species, similar to the individual ^{183}W resonances of the pa, consists of a main signal and coupling satellites arising because of the indirect spin−spin coupling[21] with the magnetic tungsten

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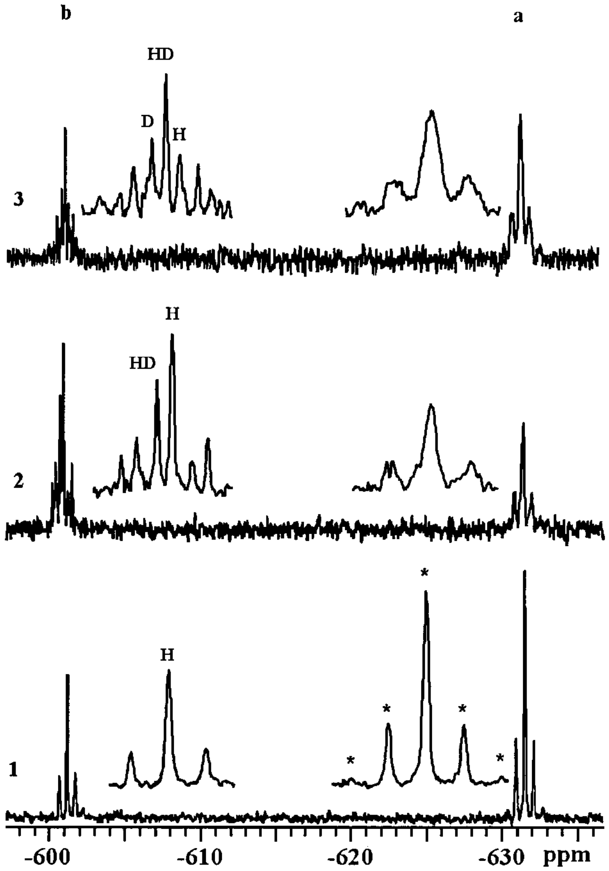

Figure 4. ^{119}Sn NMR spectra of $\mathbf{P_2W_{20}}$Sn complexes **II** (a) and **III** (b) in H_2O (spectrum 1) and in H_2O-D_2O, 2:1 (spectrum 2) and 0.65:1 (spectrum 3). The HPA concentration is about 0.04 mol/L for spectra 1 and 3 and 0.06 mol/L for spectrum 2. The central peaks of multiplets from Sn linked to internal H_2O, HDO, and D_2O are labeled H, HD, and D, respectively. The multiplet components arising from $^{119}Sn-O-^{183}W$ coupling are labeled with asterisks.

isotope ^{183}W (natural abundance 14.3%), through Sn−O−W bonds. The Sn atoms, surrounded only by nonmagnetic tungstens, give the most intense central component, and those having one ^{183}W neighbor give a doublet with the same δ and a coupling constant proportional to the product of the magnetogyric ratios, g_n, of ^{119}Sn and ^{183}W. The Sn atoms adjacent to two ^{183}W atoms give a triplet with the same δ and coupling constant and an intensity ratio of 1:2:1. For an Sn atom surrounded by four chemically equivalent tungstens the probabilities of having none, one, or two magnetically active W neighbors are 0.54, 0.36, and 0.09,[22] respectively, with the probability of having more ^{183}W neighbors being negligible. The calculated component intensity ratio for the resulting spectrum would then be equal to 1:8:26:8:1, which is in a close agreement with the observed one. A similar splitting pattern is observed for the ^{183}W NMR signals of the bridging W_6 atoms (Figure 3) except that the two weakest peaks are not visible because of the lower sensitivity of ^{183}W NMR, but the triplet's central peak coinciding with the singlet influences the intensity ratio of the three visible peaks: 8:26:8 (0.3:1:0.3) instead of 8:24:8 (0.33:1:0.33). Since the values of $|g_n|$ for ^{119}Sn and ^{183}W are equal to 2.095 and 0.236, respectively, the $^{119}Sn-O-^{183}W$ coupling constant ^2J is about an order of magnitude higher than that for $^{183}W-O-^{183}W$ coupling (Table 1). Splittings similar to those found in the ^{119}Sn NMR spectra are expected in the ^{183}W NMR for the W atoms connected to Sn. In fact, such components are present for the resonance assigned to W_5 atoms on the basis of the $^{183}W-O-^{183}W$ couplings (Figure 3). However, they are not as clearly seen as for the resonances of W_6 and Sn atoms because they are less intense (the overall content of ^{119}Sn and ^{117}Sn, which is also magnetically active, is about 16%, and there is only one neighboring Sn atom) and broadened because of the different splittings by the two tin isotopes.

The above observations are consistent with the existence of two different $\mathbf{P_2W_{20}}$Sn HPA in the studied solutions, with the tin atom inserted into the cavity of the equatorial belt of the pa and connected to it through four $Sn-O-W_5$ bonds. The difference between the observed complexes might stem from the presence of different ligands in the fifth or sixth coordination positions of the tin atom. Careful reduction of excess of H_2O_2 by hydrogen or replacement of the starting tin compound $SnCl_2$ by $SnSO_4$ did not change the NMR spectra of the resulting Sn complexes with $\mathbf{P_2W_{20}}$, which suggested that Sn did not retain any ligands derived from the starting compounds upon entering the pa. Increasing the solution pH from −0.5 to about 1.5 resulted in almost complete disappearance of complex **III** (Table 1) while complex **II** became predominant. This may indicate that the two $\mathbf{P_2W_{20}}$Sn HPA differ by the degree of protonation; i.e., the different ligands attached to the Sn atom are H_2O, OH^-, or O^{2-}. Taking into account the electronic structure (d^0), the lower positive charge than for W^{6+}, the high acidity of the solutions, and typical coordination of Sn^{4+} cations in some polytungstates,[20] we believe that OH^- and H_2O are the most probable ligands that may be attached to Sn atom from inside or outside the pa. To determine if this is the case, we have measured the ^{119}Sn and ^{183}W NMR spectra of the $\mathbf{P_2W_{20}}$Sn HPA dissolved in a H_2O-D_2O mixture. Similar measurements were previously conducted for the parent $\mathbf{P_2W_{21}}$ HPA dissolved in the H_2O-D_2O mixture for which the presence of the internal water molecule coordinated to one of the three belt tungstens gave an additional splitting of their ^{183}W resonances due to the isotope presence.[4a] The observation of the nonaveraged spectra ("β effect") in that case was possible because of the slow H−D exchange of the internal water with solution. The same effect was observed for several $\mathbf{P_2W_{20}}$M complexes, although it was not specified for what M exactly.[16]

We have found that in our case this characteristic additional splitting is observed for both complexes in their ^{119}Sn (Figure 4) and ^{183}W NMR spectra for the W_6 resonances (Figure 3). This confirms the presence of the internally coordinated water molecule in both **II** and **III** complexes. However, there is a noticeable difference in the appearance of the NMR spectra of the two complexes: for complex **II** the multiplet lines in both ^{119}Sn and ^{183}W NMR spectra are broadened, and splitting is not as clearly seen as for **III** (Figures 3 and 4). It is evident that in complex **II** the proton exchange between the internal aqua ligand and solution proceeds considerably more quickly than in **III**. Furthermore, the equilibrium between the two complexes is dependent on the overall HPA concentration, with higher concentration favoring complex **III**. The above data are consistent with **III** being a dimer of **II**. In fact, condensation of M-substituted polytungstates of different structural types through M−O−M linkages to yield dimeric aggregates is not rare and

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(21) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance with Applications to Chemistry and Chemical Physics*; Harper and Row Publishers: New York, Evanston, London, 1967; Chapter 4.

(22) Hoel, P. G.; Port, S. C.; Stone, C. J. *Introduction to Probability Theory*; Houghton Mifflin Co.: Boston, 1971.

has been described in the literature.[23,24] Therefore, we assign compositions $P_2W_{20}O_{70}(H_2O)_3Sn(OH)^{7-}$ and $(P_2W_{20}O_{70}(H_2O)_3Sn)_2O^{14-}$ to **II** and **III**, respectively. As is evident, **II** has practically the same structure and the same location of the three equatorial water molecules as the parent $\mathbf{P_2W_{21}}$ except that the external O atom bonded to Sn^{4+} is protonated because of its higher negative charge. Protonation of the pa in strongly acidic solutions is the first step of its acid hydrolysis and leads to further condensation with formation of dimers: $2\mathbf{II} \rightarrow \mathbf{III} + H_2O$. This reaction is favored by the increase in the pa concentration and solution acidity, which is consistent with all our observations.

Proposed formulas for **II** and **III** easily explain different rates of the proton exchange of the internal ligands in these pa's with solution. For monomeric **II** the proton exchange of the internal water must be facilitated by the presence of the external OH^- attached to the same Sn atom while in the dimer, as well as in $\mathbf{P_2W_{21}}$, in which the proton exchange proceeds slowly, external protonated oxoligands capable of the exchange with solution are coordinated to the W_6 atoms and therefore are farther away from the Sn atom. It seems that upon crystallization the equilibrim shifts completely to complex **III** and the solid HPA evidently consists of the dimeric units. This may be confirmed by the IR spectrum of solid $\mathbf{P_2W_{20}}$Sn HPA, which is very similar to that of $\mathbf{P_2W_{21}}$ except for a band at 620 cm^{-1} observed in the former. The region of 600−700 cm^{-1} is considered characteristic for M−O−M bonds[23,24] so that the band at 620 cm^{-1} could be assigned to the Sn−O−Sn bridges connecting two monomeric $\mathbf{P_2W_{20}}$Sn units.

It should be noted that a similar band (670 cm^{-1}) is observed in the IR spectra of solid HPA $\mathbf{P_2W_{20}}$Bi (**I**). However, the formation of Bi−O−Bi bonds for Bi^{3+} with its lone pair electrons is fairly unlikely. In this case the band at 670 cm^{-1} evidently belongs to the Bi−O−W bonds as similar bands of HPA $\mathbf{PW_{11}}$M.[25] Furthermore, in the ^{183}W NMR spectra of the D_2O-H_2O solution of **I** we did not observe the β effect for W_6 atoms as we did for the $\mathbf{P_2W_{20}}$Sn solutions, which evidently suggests the absence of the internal water in the case of **I** (or its fast proton exchange with solution). This may be explained by the large ionic radius of Bi^{3+} (1.2 Å) and large Bi−O bond lengths typical for its oxocompounds,[26] which are in the range of 2.1−2.23 for the three nearest oxygens and 2.6−3.2 Å for the remaining three to four oxygens. As a result, Bi may shift from the plane of oxygens, binding it with W_5 atoms outside or inside the pa. In the latter case it may coordinate directly to two internal oxygens of W_6 atoms. On the other hand, if H_2O does internally coordinate to the Bi atom, its proton exchange with solution is expected to be fast because of the lone-pair electrons, which may explain the absence of the β effect. It should be noted that in the case of another known $\mathbf{P_2W_{20}}$ complex with a trivalent cation, $\mathbf{P_2W_{20}}$Cr(III), which in contrast to Bi(III) does not possess lone pair electrons, the equilibrium between a monomer and a dimer does appear to occur.[10] In the latter case already at pH of around 2 the 11-component ^{183}W NMR spectrum is observed, which must be arising from a monomer and a dimer, similar to $\mathbf{P_2W_{20}}$Sn case.

The similarity of the ^{183}W NMR spectra of complexes **II** and **III** shows that upon $\mathbf{P_2W_{20}}$Sn dimerization the structure of a separate unit changes insignificantly. The fact that the coupling constant $^2J_{Sn-O-W5}$ in **III** (163 Hz) is smaller than that in **II** (172 Hz) evidently indicates the lengthening of the W_5−Sn bonds in the dimer, which in its turn causes the corresponding changes of the W−O bonds and inversion of the order of W_5 signals for **II** and **III** compared to their W_6 signals (Figure 3, Table 1).

Evaporation of a 0.1 M aqueous solution of $\mathbf{P_2W_{20}}$Sn under ambient conditions resulted in a yellowish compound completely soluble in water. Evaporation of a 0.1 M solution of $\mathbf{P_2W_{20}}$Bi under these conditions gave a white powder that could be redissolved in water upon heating. The ^{31}P NMR spectra of the redissolved compounds confirmed that after drying at room temperature the Bi^{3+}- and Sn^{4+}-containing HPA retained their composition.

When 0.05 M $\mathbf{P_2W_{20}}$Sn and $\mathbf{P_2W_{20}}$Bi HPA solutions were heated to 100 °C to remove water, the resulting solids were only partially soluble in water. The soluble part of the solids further decreased upon their heating to 150 °C. The ^{31}P NMR spectra of the soluble fraction showed the presence of the initial metal-containing HPA, while the insoluble part could not be identified. Thus, the thermostability of $\mathbf{P_2W_{20}}$Sn and $\mathbf{P_2W_{20}}$Bi HPA is similar to that of the parent HPA $\mathbf{P_2W_{21}}$,[11] but unlike the parent they do not form soluble $H_3PW_{12}O_{40}$ during thermolysis.

Conclusions

In this work we have found that the monovacant pa $\mathbf{P_2W_{20}}$ forms more or less stable $\mathbf{P_2W_{20}}$M complexes with a number of M^{n+} cations. Compared to the double- and triple-substituted HPA of the 2:21 series, the range of the existence of $\mathbf{P_2W_{20}}$M shifts to higher acidities and a higher valence state of M, just like for the 1:12 series. The stability in strongly acidic solutions allowed some of these complexes to be isolated in the form of free HPA. Infrared spectra of such HPA in the solid state confirm the similarity of their structures to that of $H_6P_2W_{21}O_{71}$. Some of $\mathbf{P_2W_{20}}$M form dimers through M−O−M bridges.

The incorporation of M^{n+} into the vacancy shifts the ^{31}P NMR peak of the HPA upfield (Table 1).

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