

An NMR study of nanostructured ammonium 12-tungstophosphate*

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The structure of ammonium 12-tungstophosphate hydrate, $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, was examined by ^1H , ^2H , ^{31}P , and ^{15}N MAS NMR spectroscopy. The morphology of nanostructured ammonium 12-tungstophosphate was determined from the NMR spectra showing a clear distinction between "bulk" and "surface" ammonium cations in its crystallites. The constants of couplings between the nitrogen (^{14}N , ^{15}N) and hydrogen nuclei (^1H) in the crystalline phase were measured for the first time.

Key words: heteropoly oxometalates, ammonium, 12-tungstophosphate, MAS NMR spectroscopy, coupling constants, isotope exchange.

Heteropoly oxometalates (POM) is a large class of stable, highly organized inorganic compounds exhibiting various properties.¹ Although studied for over 150 years, these compounds still remain of current interest because of an exceptional variety of their structures and properties. Heteropoly oxometalates have a number of unique properties (chemical and thermal stability, high ionic conductivity, and highly developed surface) and are actively used in many scientific and engineering applications.^{1–3}

Insoluble POM are of greatest interest; having large specific surface areas and high acidity, they are employed in catalysis and as ion conductors.^{2–7} However, single crystals of insoluble POM are very difficult to obtain, which makes it problematic to study their cation–anion interactions and systematize the variety of their supramolecular organization in the solid state. In turn, X-ray powder diffraction studies of their polycrystalline samples should involve initial models and do not provide additional information on the crystallite texture, especially for highly porous systems.

Nevertheless, attempts have been made^{8a} to examine the crystal structure of ammonium 12-tungstophosphate by refining powder diffraction patterns under the assumption that this salt is isostructural to phosphotungstic acid hexahydrate. A successful single-crystal X-ray diffraction study has been also reported.^{8a} However, the lack of atomic coordinates in both the paper itself and structural databases casts doubt on the conclusions made therein. The only irrefutable fact emerging from the literature data is localization of the ammonium cation in the cavity between

symmetrically arranged Keggin anions that make up the cubic lattice of the salt itself.

The study of proton dynamics in hydrogen-containing POM is important for both acid catalysis and the design of proton conductors and commonly involves NMR spectroscopy (see, e.g., Refs 3, 5, and 9). Specifically, for trisubstituted salts of phosphotungstic acid, which show high conductivity (from 10^{-4} to $10^{-2} \text{ } \Omega^{-1} \text{ cm}^{-1}$) in the absence of free hydrogen or onium ions (H_3O^+ , H_5O_2^+) in their molecular formulas, electric conductivity and NMR relaxation have been measured.⁵ A curve of the relaxation time T_2 obtained for ammonium 12-tungstophosphate shows two minima, one of which being attributed⁵ to rotation of the ammonium cation with an activation energy of $\sim 0.1 \text{ eV}$.

Likewise, Ishimaru *et al.*¹⁰ have examined the dynamics of the crystallization water in sodium 12-molybdophosphate hydrates and demonstrated that the number of water molecules is crucial for translational diffusion of protons in the case of the nonacosahydrate; the energy of activation of this diffusion is 12.4 kJ mol^{-1} (0.13 eV).¹⁰ For the hexahydrate, limited proton motion even at 120 K has been noted.

The formation of the so-called "quaternary structure" of insoluble salts of heteropoly acids with the Keggin anion has been studied;¹¹ these salts have large specific surface areas and show microporosity. These facts suggest that the molecular groups identical in the crystalline salt will differ in a nanostructured state. Since NMR spectroscopy is the most sensitive method of distinguishing between structurally different molecular groups, here we used ^1H , ^2H , ^{31}P , and ^{15}N MAS NMR spectroscopy to study the structure of ammonium 12-tungstophosphate.

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Experimental

Ammonium salts were prepared by a metathesis reaction between $1 \cdot 10^{-4}$ M NH_4Cl (special purity grade 8-5, REAKHIM) and $1 \cdot 10^{-4}$ M 12-tungstophosphoric acid (reagent grade, REAKHIM, purified before use according to the etherate procedure) in a ratio of 3.2 : 1.0 (mol/mol). The reaction mixture was stirred at room temperature for 20–30 min. The precipitate that formed was centrifuged, washed five to six times with distilled water, and dried in air at room temperature for ~48 h.

In the synthesis of $(^{15}\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$, aqueous $(^{15}\text{NH}_4)_2\text{SO}_4$ (98% purity) served as a ^{15}N source. Isotope exchange of proton for deuterium was carried out in a closed vessel containing 95% D_2O ($p_{\text{D}_2\text{O}} = 17$ and 6 Torr). To obtain a particular ammonium 12-tungstophosphate hydrate, the salt was kept in a salt chamber with a required humidity to a constant weight.

X-ray powder diffraction studies of the salts obtained were carried out on a Bruker D8 Advance Vario instrument. The experimental data were processed with the Jana 2000 program. The stability and purity of the Keggin anions (>98%) in all experiments were checked by recording ^{31}P NMR spectra of powders of the compounds under study (the ^{31}P NMR spectrum of any Keggin anion is known¹² to contain a characteristic signal at $\delta -15$ relative to 85% H_3PO_4).

Earlier,⁶ it has been demonstrated that Fischer titration and thermogravimetric measurements of 12-tungstophosphate hydrates provide the same water content. In the present work, we determined the water content by thermogravimetry in an argon flow (heating to 350 °C at a rate of 10 °C min^{-1}) on a STA 409C Luxx analyzer coupled with a QMS 403 C Aeolos quadrupole mass spectrometer (NETZSCH).

Specific surface areas were determined from nitrogen sorption–desorption isotherms measured with a Quadrasorb SI instrument (USA). The morphology of the samples obtained was examined using a LEO SUPRA-25 scanning electron microscope (Zeiss).

^1H , ^2H , ^{31}P , and ^{15}N NMR spectra (400, 61, 162, and 41 MHz, respectively) were recorded on an AVANCE III 400 spectrometer (Bruker). High-resolution solid-state MAS spectra were recorded at a spinning rate of 15–20 kHz. Powdered samples were placed in a standard ceramic rotor (outer diameter 3.2 mm). The scale of chemical shifts for MAS NMR spectra was calibrated against adamantane (δ 1.87 (^1H), spinning rate 5 kHz). Note that the integration of the signal for water molecules in the ^1H NMR spectra gave the total number of the protons of the ammonium cations, which allowed one to follow the stoichiometry of ammonium 12-tungstophosphate.

Results and Discussion

The ammonium 12-tungstophosphate obtained is a white powder with a picnometric density of 5.6 g cm^{-3} ($\rho_{\text{crist}} = 6.102 \text{ g cm}^{-3}$). According to TGA data, the sample contains ten water molecules per salt molecule. Indexing of the diffraction pattern gave a lattice constant of 11.684(1) Å for the salt obtained (space group $Pn-3m$). The specific surface area is $90 \pm 5 \text{ m}^2 \text{ g}^{-1}$ (from the BET isotherm).

The SEM images (Fig. 1) show that the samples under study are completed "cubicosahedra" ($D = 300 \text{ nm}$) made up of smaller spherical crystallites ($d = 7-10 \text{ nm}$).

The ^1H MAS NMR spectrum of the polycrystalline salt $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$ is shown in Fig. 2. The spinning rate was 20 kHz, which provided good resolution of the spectrum, in contrast to that obtained for a spinning rate of 8 kHz.¹³ The spectrum contains a signal for water molecules (δ 4.4) and two signals for the protons of the ammonium cation. One of these signals (δ 5.2) is a triplet with the characteristic coupling constant $^1J_{\text{H}-^{14}\text{N}} = 57 \text{ Hz}$, while the other signal (δ -6) is a broadened singlet. The constant $^1J_{\text{H}-^{14}\text{N}}$ in the tetrahedral ammonium cation is known¹⁴ to be 52 Hz for the liquid phase. In our case, the constant $^1J_{\text{H}-^{14}\text{N}}$ is not 52 Hz characteristic of the liquid, which suggests a distortion of the tetrahedral (T_d) environment in the NH_4^+ cation. Nevertheless, the presence of the triplet is indicative of an averaged quadrupole interaction between the ^1H and ^{14}N atoms. This can result either from disordering of the positions of the ammonium cation or from its highly symmetric environment. Therefore, the ammonium cations (δ 5.2) can be located in several positions of the salt structure, and a rapid exchange between these positions gives rise to the triplet in the ^1H NMR spectra. It is also probable that the ammonium cations are symmetrically surrounded by the O...W atoms.^{8a}

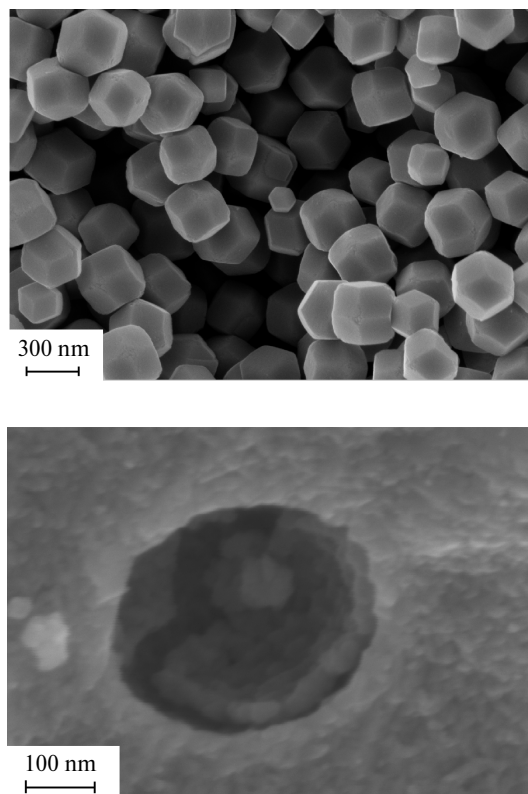


Fig. 1. SEM images of nanostructured $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$.

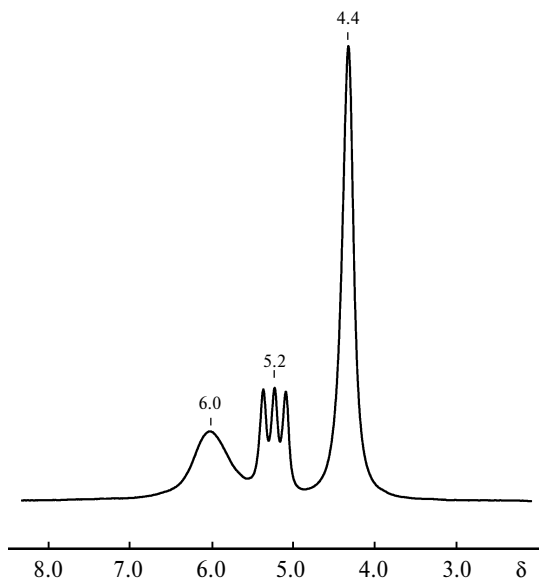


Fig. 2. ^1H MAS NMR spectrum (20 kHz) of $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$.

The symmetric environment of the disordered ammonium cation has also been noted^{8b} for $(\text{NH}_4)_{2.6}(\text{H}_3\text{O})_{0.4}\text{PW}_{12}\text{O}_{40}$.

As the number of water molecules in the salt hydrate decreases, the corresponding signal becomes less intense and shifted upfield. The broadened singlet for the ammonium cation is similarly shifted upfield, while the position of the triplet at δ 5.2 is independent of the water content of the salt (Fig. 3). In the case of ammonium 12-tungstophosphate monohydrate (see Fig. 3, *b*), the broadened "singlet" is transformed into a triplet with $^1J_{\text{H}-^{14}\text{N}} = 51$ Hz, which is close to 52 Hz characteristic of hydrat-

ed NH_4^+ (with the T_d symmetry). The difference between the constants $^1J_{\text{H}-^{14}\text{N}}$ for the different NH_4^+ cations manifested in the ^1H NMR spectrum at δ 5.2 and 5.6 suggests that the formally identical ammonium cations in the salt $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ differ in geometrical structure.

The presence of two types of signals for the ammonium cations in the ^1H NMR spectra suggests that these groups are not equivalent in the nanostructured salt. One type of the ammonium cations (the low-field signal, see Fig. 3) is linked by a network of hydrogen bonds, and is in proton exchange, with water molecules. The other type of the ammonium cations (the triplet at δ 5.2, see Fig. 3) is obviously linked with water molecules by appreciably weaker hydrogen bonds. One can thus assume that the former type refers to "surface" NH_4^+ cations (localized on the surface of smaller spherical crystallites 7–10 nm in diameter) and that the latter type refers to "bulk" NH_4^+ cations. The signal intensity ratio for the protons of the ammonium cations (~ 0.7 from the NMR data, see Fig. 3, *b*) agrees with the ratio calculated from the particle size (7–9 nm). Based on the fact that the chemical shifts for the two types of ammonium cations become nearly equal ($\Delta\delta = 0.4$ ppm) in ammonium 12-tungstophosphate monohydrate, one can assume that the "surface" ammonium cations cause small crystallites of the salt to come closer to each other and thus have a similar environment of the O atoms of the Keggin anion.

To confirm the presence of "surface" ammonium cations involved in proton exchange with adsorbed water, we carried out isotope exchange of protons for deuterium atoms in the vapor of deuterated water and recorded ^1H and ^2H NMR spectra in different time intervals (Figs 4, 5).

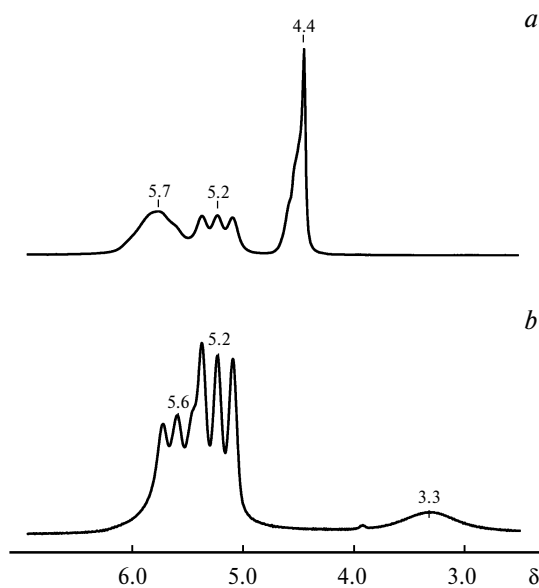


Fig. 3. ^1H MAS NMR spectra (20 kHz) of $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$: $n = 4$ (*a*) and 1 (*b*).

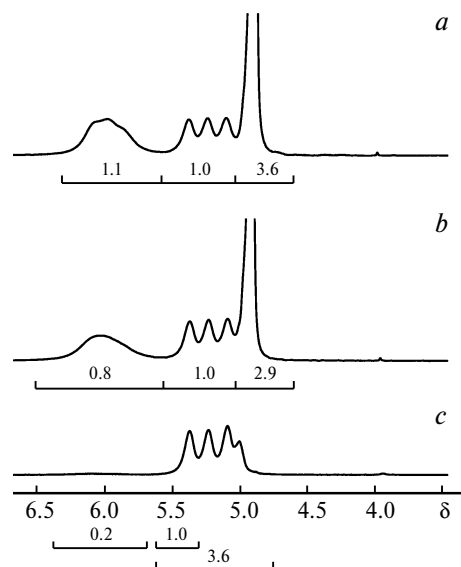


Fig. 4. ^1H MAS NMR spectra (15 kHz) of $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$ prior to deuterium exchange (*a*) and after the exposure to the D_2O vapor for 6 (*b*) and 96 h (*c*).

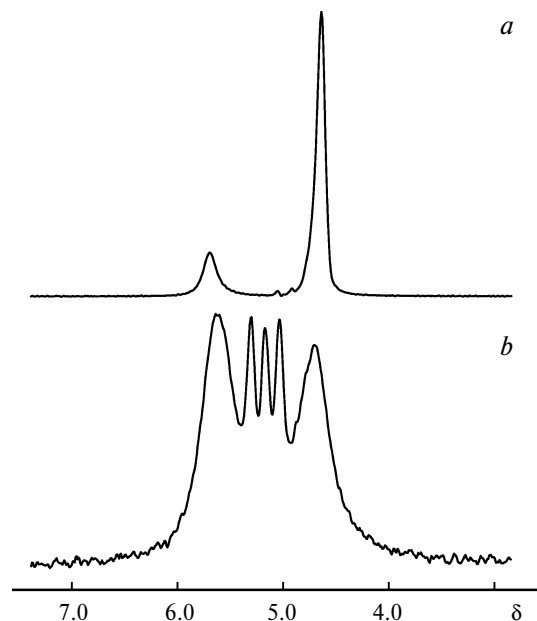


Fig. 5. ^2H MAS NMR spectra (15 kHz) of $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ exposed to the D_2O vapor for 96 h (a) and a month (b).

It can be seen in Fig. 4 that the intensities of the signals at δ 6 and 4.7 decrease with time, in contrast to the signal at δ 5.2. Clearly, the protons of adsorbed water and "surface" ammonium cations are exchanged for deuterium first, which is confirmed by the ^2H NMR spectrum (see Fig. 5, a). Note that "bulk" ammonium cations are also exchanged for deuterium upon longer exposure to the D_2O vapor (see Fig. 5, b). In this case, we determined the coupling constant $^1J_{^{14}\text{N}-^2\text{H}}$ from the ^2H NMR spectrum. Its value (8 Hz) agrees with the literature data.¹⁴

To immediately prove the presence of two nonequivalent ammonium cations, we recorded a ^{15}N MAS NMR spectrum of ^{15}N -enriched ammonium 12-tungstophosphate. The spectrum (Fig. 6, a) contains a quintet at δ 19.5 (with reference to aqueous NH_4^+ salt) with $^1J_{^{15}\text{N}-^1\text{H}} = 58$ Hz. The $^{15}\text{N}\{^1\text{H}\}$ NMR spectrum (with proton decoupling, Fig. 6, b) shows two distinct signals at δ 19.5 and 18.5, which can easily be assigned by analyzing the $^{15}\text{N}\{^1\text{H}\}$ NMR spectrum of the partially deuterated salt (Fig. 6, c).

Indeed, the low-field signal is slightly shifted compared to its position in the spectrum of the nondeuterated salt and broadened because of a spin-spin coupling of the ^{15}N and ^2H nuclei. Therefore, the signal at δ 18.5 corresponds to "bulk" ammonium cations and the signal at δ 19.5, to "surface" ammonium cations. Preliminary measurements of the spin-lattice relaxation times T_1 of the ^{15}N nuclei revealed that "bulk" ammonium cations are characterized by much higher T_1 values (tens minutes against a few minutes). By analyzing the ^2H NMR spectrum of deuterated ammonium 12-tungstophosphate con-

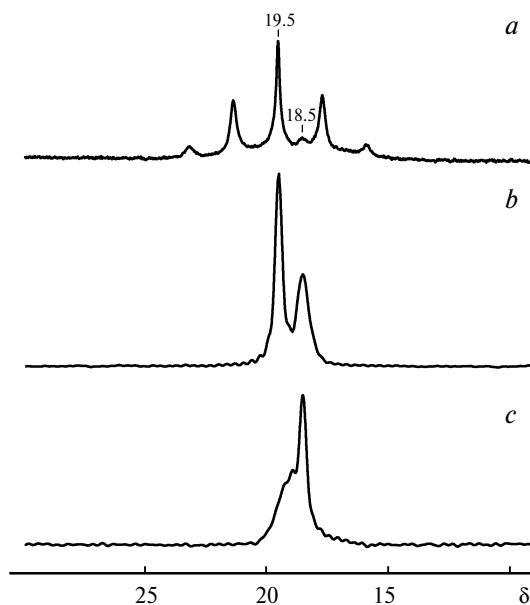


Fig. 6. ^{15}N MAS NMR spectra (15 kHz) of $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ without (a) and with proton decoupling (b) and the ^{15}N MAS NMR spectrum of the same salt exposed to the D_2O vapor (with proton decoupling) (c).

taining the ^{15}N isotope, we determined the constants $^1J_{^2\text{H}-^{15}\text{N}} = 12$ and 10 Hz for "bulk" and "surface" ammonium cations, respectively (Table 1).

Using ^1H and ^{15}N MAS NMR spectroscopy, we detected two types of ammonium cations in ammonium 12-tungstophosphate. Comparison of the ^1H NMR spectra of the salts $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ with different n values and the ^1H MAS NMR spectra of the partially deuterated salts reliably demonstrated that one type of ammonium cations is in the bulk of crystallites, while the other type is on their surface. We also were the first to measure the coupling constants for the solid-state ammonium cation.

To sum up, our comprehensive study of ammonium 12-tungstophosphate revealed a relationship between the morphology of nanoparticles of the crystalline salt and the hydrogen atom isotopes. The data obtained can be used to examine 12-tungstophosphate salts applied to, e.g., silicon and titanium oxides, carbon, etc.

Table 1. Indirect coupling constants ($^1J_{\text{H-N}}/\text{Hz}$) for the ammonium cation in different isotopomers

Isotope of N	"Bulk" ammonium cation		"Surface" ammonium cation	
	^1H	^2H	^1H	^2H
^{14}N	57	8	51	—
^{15}N	78	12	75	10

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