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Abstract

Full Text

PHYSICAL CHEMISTRY

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INVESTIGATION OF THE "CONSTITUTIONAL WATER"OF CERTAIN HETEROPOLY COMPOUNDS BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE

Our earlier investigation by the NMR method ([1]) of phosphomolybdic acid with different contents of hydrate water showed, in particular, that a decrease in the water content in the heteropolyacid lattice leads to a substantial change in the line of proton resonance absorption observed at 80°K. Along with the broad line from the remaining water molecules, a narrow line appears; its contribution may be due to protons with a distance $r_{H-H} > 3$ Å. It was natural to suppose that this line characterizes the salt-forming hydrogen ions. Then the spectrum of proton resonance absorption for heteropolyacids completely freed of crystallohydrate water would be represented precisely by this line.

In a study ([2]) of the dehydration and thermal stability of heteropoly compounds, the existence was established of stable structures with a small content of "constitutional water," the removal of which leads to destruction of the heteropolyanion. Since questions connected with the nature and properties of this water remain unclear, we considered it essential to study proton magnetic resonance in samples of heteropoly compounds precisely on structures devoid of crystallohydrate water. For this purpose the heteropoly compounds listed in Table 1 were obtained and investigated.

Phosphotungstic (PTA) and phosphomolybdic (PMA) acids of analytical-reagent grade were purified by ether extraction followed by re-

Table 1

Composition of the compounds investigated

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Compound	MoO_3, WO_3	P_2O_5	SiO_2	Na_2O	BaO	H_2O	Formula
Phosphomolybdic acid	Found	81,51	3,29			15,37	$P_2O_5 \cdot 24{,}35\ MoO_3 \cdot 35{,}2\ H_2O$
Phosphomolybdic acid	Calculated	81,46	3,34			15,20	$P_2O_5 \cdot 24\ MoO_3 \cdot 35\ H_2O$
Phosphotungstic acid	Found	88,90	2,24			8,77	$P_2O_5 \cdot 24{,}22\ WO_3 \cdot 30{,}8\ H_2O$
Phosphotungstic acid	Calculated	89,01	2,27			8,72	$P_2O_5 \cdot 24\ WO_3 \cdot 30{,}8\ H_2O$
Silicotungstic acid	Found	84,65		1,84		13,50	$SiO_2 \cdot 12{,}01\ WO_3 \cdot 24{,}65\ H_2O$
Silicotungstic acid	Calculated	84,67		1,83		13,50	$SiO_2 \cdot 12\ WO_3 \cdot 24{,}65\ H_2O$
Disubstituted sodium phosphotungstate	Found *	95,67	2,49		2,13	9,25	$1{,}96\ Na_2O \cdot P_2O_5 \cdot 23{,}62 WO_3 \cdot 33{,}1\ H_2O$
Disubstituted sodium phosphotungstate	Calculated	95,44	2,43		2,13		$2Na_2O \cdot P_2O_5 \cdot 24 WO_3 \cdot 33{,}1 H_2O$

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Figure 1

Figure 1: Figure 1

Compound	MoO_3, WO_3	P_2O_5	SiO_2	Na_2O	BaO	H_2O	Formula
Disubstituted barium phosphotungstate Found	92,58	2,39			4,94	12,76	1,96 $BaO \cdot P_2O_5 \cdot$ 24,19 $WO_3 \cdot$ 49,2 H_2O
Disubstituted barium phosphotungstate Calculated	92,54	2,36			5,10		$2BaO \cdot P_2O_5 \cdot 24WO_3 \cdot$ 49,2 H_2O

* The analytical data for all salts are given recalculated to the anhydrous composition.

crystallization. The hydrates obtained were analyzed as follows: the water content in all preparations was determined by calcination at 650–700°C; P_2O_5 was determined by the pyrophosphate method; MoO_3 and WO_3 by quinoline precipitation from the filtrate after removal of phosphorus.

Silicotungstic acid (STA) was prepared by the method of ([3]). Silicon was determined by hydrochlorination of the dehydrated substance; the WO_3 content was calculated by difference.

Disodium phosphotungstate was synthesized according to ([4]) by the interaction of sodium dihydrogen phosphate and sodium tungstate in nitric-acid medium. For the analysis, the method of ([5]) was used. After precipitation of the heteropolyanion, the Na_2O content in the filtrate was determined by the uranyl acetate and sulfate methods. Dibarium phosphotungstate was obtained according to ([6]). The analysis was carried out by the quinoline method; after precipitation of the heteropolyanion, BaO was determined in the filtrate by the sulfate method. Average data from four analyses are summarized in Table 1.

Fig. 1. Experimental derivatives of proton absorption lines at 80°K in the compounds:
1 –$H_4SiW_{12}O_{40}$; 2 –$H_3PW_{12}O_{40}$; 3 –$Na_2HPW_{12}O_{40}$.

To obtain stable structures with 1.5 mol H_2O in the case of phosphorus-containing heteropoly compounds and with 2 mol H_2O in the case of

silicon-containing heteropoly compounds, calculated per one atom of the complex-forming element, the highly hydrated acids and salts were dehydrated at 320–340° for 6–8 h. The amount of residual water was monitored by analysis.

The preparations obtained had the following composition:
$P_2O_5 \cdot 24MoO_3 \cdot 3H_2O$;
$P_2O_5 \cdot 24WO_3 \cdot 3.1H_2O$;
$SiO_2 \cdot 12WO_3 \cdot 2.1H_2O$;
$2Na_2O \cdot P_2O_5 \cdot 24WO_3 \cdot H_2O$;
$2BaO \cdot P_2O_5 \cdot 24WO_3 \cdot H_2O$.

The derivatives of the hydrogen absorption lines were recorded on an NMR spectrometer whose characteristics were given earlier ([7]). The recording regime was as follows: radio-frequency voltage on the working circuit, 0.01 V; modulation amplitude of the constant field, 0.07 G; modulation frequency, 81 Hz; scanning rate, 1 G/min, with a time constant of the synchronous detector of 0.5 s. Samples weighing 1 g were studied in powder form. To eliminate the influence of molecular motion on the line shape, all experiments were carried out at 80°K. Recording of spectra over the interval of magnetic-field variation $H_0 \pm 15$ G (H_0 being the resonance value of the field) confirmed the absence of hydrogen in the dehydrated samples in the form of water molecules. All spectra are represented by narrow lines in the region $H_0 \pm 2$ G (Fig. 1). Table 2 gives the average values from five measurements of the widths of the absorption lines between the points of maximum slope and of the second moments, calculated from the experimental derivatives.

According to Van Vleck ([8]), the expression for the second moment of a rigid lattice of a polycrystalline sample containing several kinds of magnetic nuclei has the form:

$$\overline{\Delta H^2} = {}^6/_5 I(I+1)g^2\mu_0^2 \frac{1}{N}\sum_{j>k} r_{jk}^{-6} + {}^4/_{15}\mu_0^2 \frac{1}{N}\sum_{j,f} I_f(I_f+1)g_f^2 r_{jf}^{-6},$$

where I is the spin quantum number of the resonating nucleus; μ_0 is the nuclear magneton; $g\mu_0 I$ is the nuclear magnetic moment; N is the number of magnetic moments, per

Table 2

Results of NMR measurements

No.	Substance	Line width δH (G)	Second moment ΔH^2 (G^2)	Smallest distance between protons $r_{\mathrm{H-H}}$ (Å)	Ratio of absorption-line areas
1	$H_4SiW_{12}O_{40}$	0.81	0.38	3.76	1

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No.	Substance	Line width δH (G)	Second moment ΔH^2 (G^2)	Smallest distance between protons r_{H-H} (Å)	Ratio of absorption-line areas
2	$H_3PW_{12}O_{40}$	0.69	0.17	4.02	0.73
3	$H_3PMo_{12}O_{40}$	0.68	0.31	3.63	0.64
4	$Na_2HPW_{12}O_{40}$	0.38	0.12	3.80	0.21
5	$BaHPW_{12}O_{40}$	0.50	0.10	3.91	0.20

over which the summation is taken; r_{jk} is the length of the vector joining nuclei j and k. The index f refers to magnetic nuclei of another kind.

The main contribution to the value of the second moment is made by the spins whose resonance is recorded. In our case, the contribution from nonresonating nuclei (P, Si, Na, Ba) will probably be appreciable, especially in the case of the disubstituted Na and Ba salts of phosphotungstic acid, since the distances between protons of neighboring anions may prove to be greater than the distance from a proton to the substituent nucleus. Nevertheless, without as yet making any assumptions about the possible arrangement of hydrogen ions in the unit cell, one can estimate the smallest shortest distance between protons by using only the first part of the second-moment equation. The corresponding values of r_{H-H} are given in Table 2. It may be concluded that the structures of the heteropoly acids investigated and of their salts that contain no water of crystallization represent a special case of a system of isolated protons. In this case the character of the absorption lines gives no basis for assuming any nonequivalence in the mutual arrangement of the protons. We note that for ordinary crystalline hydrates, according to data in [9], the second moment from OH groups at 90°K is ~ 3 G^2, which corresponds to interproton distances $2.2 \leq r_{H-H} \leq 2.7$ Å.

At small amplitude of the high-frequency field, the area of the absorption signal is practically independent of the relaxation conditions of the spins under investigation and is proportional to their number per unit volume of the sample. By graphically integrating the experimental derivatives and comparing the areas of the absorption lines, one can estimate the relative number of hydrogen ions per heteropolyanion, i.e., its basicity. Table 2 gives the ratios, calculated per mole, of the areas of the absorption lines of STA, PMA, and the salts of PTA to the area of the absorption line of silicotungstic acid, taken as unity. The ratios obtained indicate the low basicity of the heteropoly acids investigated—three hydrogen ions per anion for STA and PMA and four in TPA. Consequently, in this case the Miolati–Rosenheim hypothesis, which assumes heptabasicity of STA and PMA and octabasicity of TPA, is not confirmed.

Thus, investigation by the NMR method of heteropoly acids and their salts that are devoid of water of crystallization shows that the so-called "constitutional water" consists of isolated hydrogen ions with a minimum distance $r_{H-H} > 3$

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Å. The number of hydrogen ions per complex-forming agent corresponds to the tribasicity of PMA and STA and to the tetrabasicity of TPA.

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