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Abstract

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INVESTIGATION OF THE BASICITY OF CERTAIN HETEROPOLY COMPOUNDS BY INFRARED SPECTROSCOPY

In work (^{1}), in studying a series of heteropoly compounds (HPC) by the NMR method, it was shown that phosphotungstic acid (PTA) and silicotungstic acid (STA) contain a group of protons in amounts of 3 and 4 H^+, respectively, which determine the basicity of these acids. The interproton distance was calculated ($ $3 Å), and it was found that each proton is bound to a water molecule by a hydrogen bond, forming an oxonium-like grouping.

The presence of the H_3O^+ ion in heteropoly acids (HPA) was also noted by a number of other authors (^{2}, ^{3}). Spectroscopic studies of the vibrational spectra of complexes with hydrogen bonds showed that, upon formation of an H bridge, a strong change occurs in the parameters of the spectral band characteristic of the given OH group.

According to the coordination theory of Miolati—Rosenheim, the molecules of PTA and STA contain, respectively, 7 and 8 acid-forming protons. On this basis, trisubstituted salts of PTA and tetrasubstituted salts of STA should contain another 4 unsubstituted protons, which are present either in the form of hydroxyls or form the H_3O^+ ion with water molecules.

Taking into account the possibility of detecting the oxonium ion from the position of its band in the IR spectrum, in order to test the high-basicity theory of the structure of HPC and the data obtained by NMR, we studied the following compounds by IR spectroscopy: $H_3PW_{12}O_{40} \cdot 4H_2O$; $Na_2HPW_{12}O_{40} \cdot 4H_2O$; $BaHPW_{12}O_{40} \cdot 4H_2O$; $H_4SiW_{12}O_{40} \cdot 3H_2O$; $Na_3PW_{12}O_{40} \cdot 4H_2O$; $Ba_{1\ 5}PW_{12}O_{40} \cdot 5H_2O$; $Ba_2SiW_{12}O_{40} \cdot 4H_2O$.

The methods of synthesis and analysis of the first four preparations are given in (^{1}). Trisubstituted sodium phosphotungstate was synthesized by the interaction of sodium dihydrogen phosphate and sodium tungstate in a nitric acid medium (^{4}). For the analysis, Kermann' s method (^{5}) was used. The Na_2O content was determined in the filtrate after precipitation of the heteropolyanion by the uranyl acetate and sulfate methods. Trisubstituted barium phosphotungstate was obtained according to work (^{6}). The salt was analyzed by the quinoline method (^{5}); BaO was determined as the sulfate. Tetrasubstituted barium silicotungstate was synthesized by adding the calculated amount of $Ba(OH)_2$ to a hot solution of STA. The analysis was carried out by hydrochlorination of the heteropolyanion, previously precipitated with oxyquinoline and calcined at 700°. BaO was determined separately in the filtrate after precipitation of the heteropolyanion in the form of $BaSO_4$; WO_3 was found by difference. The results of the analyses, recalculated to the anhydrous composition, are given in Table 1.

The spectra of the HPC were studied in the regions 1750–1410 and 3700–2800 cm^{-1} on an IKS-14 instrument. The accuracy of frequency determination was 3–5 cm^{-1}. The bands of the H_3O^+ ion are of low intensity; therefore, for their correct interpretation, careful preparation of HPC samples in different matrices was carried out: suspensions in petroleum jelly oil and pressing into pellets with KBr. However, a drawback of these methods is the possibility

Table 1

Compound		WO_3	P_2O_5	Na_2O	BaO	SiO_2	H_2O	Formula
Trisubstituted sodium phosphotungstate	Found	94,87	2,46	3,22			11,51	$2{,}99Na_2O \cdot P_2O_5 \cdot 23{,}65WO_3 \cdot 42H_2O$
Trisubstituted sodium phosphotungstate	Calculated	94,44	2,41	3,15				$3Na_2O \cdot P_2O_5 \cdot 24WO_3 \cdot 42H_2O$
Trisubstituted barium phosphotungstate	Found	90,23	2,28		7,45		5,21	$3{,}001BaO \cdot P_2O_5 \cdot 23{,}97WO_3 \cdot 18{,}8H_2O$
Trisubstituted barium phosphotungstate	Calculated	90,35	2,29		7,46			$3BaO \cdot P_2O_5 \cdot 24WO_3 \cdot 18{,}8H_2O$
Tetrasubstituted barium silicotungstate	Found	88,45			9,64	1,95	11,56	$1{,}94BaO \cdot SiO_2 \cdot 11{,}98WO_3 \cdot 22{,}7H_2O$

Compound	WO_3	P_2O_5	Na_2O	BaO	SiO_2	H_2O	Formula
Tetrasubstituted barium silicotungstate Calculated	88,36			9,73	1,91		$2BaO \cdot SiO_2 \cdot 12WO_3 \cdot 22{,}7H_2O$

chemical interaction, anionic and cationic exchange between the matrix and the substance, especially if the latter contains a considerable amount of moisture, in particular in the study of crystalline hydrates and hygroscopic substances. To eliminate the indicated shortcomings in the study of HPC, fluoroplastic-4 powder was used as the matrix material. The authors are not aware of any reports in the literature concerning the use of fluoroplastic-4 for this purpose.

The substance under investigation was ground in an agate mortar to a fine powder and then intensively mixed with fluoroplastic-4 by means of a stainless-steel "propeller" stirrer with a mechanical drive for 20–25 min. The mixture was pressed in air under a pressure of 3 t/cm^2 for 5–10 min. To compensate the IR absorption bands of the matrix, under analogous conditions a pellet of pure fluoroplastic-4 was prepared. However, in the range 1110–1340 cm^{-1}, where the intense absorption bands of the stretching vibrations of C–F lie, complete compensation cannot be achieved.

By this method the authors obtained IR spectra of a number of inorganic salts and, for comparison, present IR spectra of the same salts studied in detail by ordinary methods (Fig. 1). The advantage of this method is the high inertness of fluoroplastic-4, which excludes any possibility of chemical interaction between the matrix and the substance. Study of the spectra in different matrices showed their complete identity.

It is known that the frequencies of the OH group increase in the region of δ-vibrations and, conversely, decrease in the region of ν-vibrations if at least one of the hydrogen atoms participates in the formation of a hydrogen bond. Therefore the bands at 1690 and 1150 cm^{-1} in the deformation-vibration region and at 3250 and 2900 cm^{-1} in the stretching-vibration region in the spectra of HPA and their disubstituted salts testify to the presence of the oxonium ion.

The spectra of the disubstituted sodium and barium salts of PTA were compared with the spectra of trisubstituted salts of PTA and tetrasubstituted barium silicotungstate (Fig. 2). In the spectra of the latter, only the bands at 3600, 3460, and 1620 cm^{-1}, present in all HPC and assigned to the stretching and deformation vibrations of water molecules, were found. The absence in the spectra of 3-substituted salts in the case of PTA and 4-substituted salts in the case of STA of any bands corresponding to the oxonium ion or to water molecules perturbed by a strong hydrogen bond indicates that these salts are neutral and,

Fig. 1. 1, 2, 3, 4—the spectra of $Na_2WO_4 \cdot 2H_2O$; $K_2Cr_2O_7$; $KMnO_4$; KJO_4, respectively, recorded in a matrix of fluoroplast-4 powder; 5, 6, 7, 8—the spectra of the same compounds recorded in Vaseline oil.

Figure 1: Fig. 1. 1, 2, 3, 4—the spectra of $Na_2WO_4 \cdot 2H_2O$; $K_2Cr_2O_7$; $KMnO_4$; KJO_4, respectively, recorded in a matrix of fluoroplast-4 powder; 5, 6, 7, 8—the spectra of the same compounds recorded in Vaseline oil.

Fig. 2. IR absorption spectra: I—$Na_2HPW_{12}O_{40} \cdot 4H_2O$; II—$Na_3PW_{12}O_{40} \cdot 4H_2O$; III—$BaHPW_{12}O_{40} \cdot 4H_2O$; IV—$Ba_{1.5}PW_{12}O_{40} \cdot 5H_2O$; V—$Ba_2SiW_{12}O_{40} \cdot 4H_2O$.

Figure 2: Fig. 2. IR absorption spectra: I—$Na_2HPW_{12}O_{40} \cdot 4H_2O$; II—$Na_3PW_{12}O_{40} \cdot 4H_2O$; III—$BaHPW_{12}O_{40} \cdot 4H_2O$; IV—$Ba_{1.5}PW_{12}O_{40} \cdot 5H_2O$; V—$Ba_2SiW_{12}O_{40} \cdot 4H_2O$.

consequently, once again proves the untenability of the concept of high basicity of the HPC investigated.

The bands with frequencies of 1150, 1690, 2900, and 3250 cm^{-1} in HPA (Fig. 3) and their acid salts show that, probably, water molecules first are arranged at the more active centers, which are the salt-forming protons, with formation of the oxonium ion, and then are grouped near coordinatively unsaturated oxygen atoms located at the unshared vertices of WO$_6$ octahedra, bearing excess-negative charge and therefore capable of forming a proton-acceptor bond.

Fig. 1. *1, 2, 3, 4*—the spectra of $Na_2WO_4 \cdot 2H_2O$; $K_2Cr_2O_7$; $KMnO_4$; KJO_4, respectively, recorded in a matrix of fluoroplast-4 powder; *5, 6, 7, 8*—the spectra of the same compounds recorded in Vaseline oil.

Fig. 2. IR absorption spectra:
I—$Na_2HPW_{12}O_{40} \cdot 4H_2O$; *II*—$Na_3PW_{12}O_{40} \cdot 4H_2O$; *III*—$BaHPW_{12}O_{40} \cdot 4H_2O$; *IV*—$Ba_{1.5}PW_{12}O_{40} \cdot 5H_2O$; *V*—$Ba_2SiW_{12}O_{40} \cdot 4H_2O$.

Fig. 3. IR absorption spectra: *I*—$H_3PW_{12}O_{40} \cdot 4H_2O$; *II*—$H_4SiW_{12}O_{40} \cdot 3H_2O$.

It is interesting to note the broadening of the band in the region of deformation vibrations for HPAs in comparison with their salts. This can probably be explained by the increased migration of protons in HPAs, as well as by a different set of distances between water molecules. Apparently, in acid salts the protons are more rigidly bound to the lattice owing to the additional influence of the cation.

Fig. 3. IR absorption spectra: I—$H_3PW_{12}O_{40} \cdot 4H_2O$; II—$H_4SiW_{12}O_{40} \cdot 3H_2O$.

Figure 3: Fig. 3. IR absorption spectra: I—$H_3PW_{12}O_{40} \cdot 4H_2O$; II—$H_4SiW_{12}O_{40} \cdot 3H_2O$.

Thus, the application of the IR spectroscopy method to the study of the basicity of certain HPAs made it possible to establish that 3-substituted sodium and barium phosphotungstates and 4-substituted barium silicotungstate are medium salts and, consequently, confirms the results obtained by the NMR method concerning the 3-basicity of PWA and the 4-basicity of SWA.

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REFERENCES

1. Vikt. I. Spitsyn, V. F. Chuvaev, S. A. Bakhchisaraitseva, DAN, 160, No. 3 (1965).
2. N. B. Mikheev, Vikt. I. Spitsyn, ZhKh, 3, 2320 (1958).
3. T. V. Yukhnevich, ZhKh, 6, 231 (1961).
4. Vikt. I. Spitsyn, N. B. Mikheev, ZhKh, 2, 11 (1957).
5. F. Kehrmann, R. Mellet, Helv. chim. acta, 6, 656 (1923); Zs. anorg. Chem., 4, 142 (1893).
6. E. A. Nikitina, N. E. Kulakova, ZhKh, 4, 564 (1959).
7. F. A. Miller, C. H. Wilkins, Anal. Chem., 24, 1253 (1952).

Note: Figure translations are in progress. See original paper for figures.