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A spectroscopic investigation of 12-tungstophosphoric acid alkali salts*

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In this paper the latest results of our continuing investigation of heteropoly acids and their salts are reported. Specially attention was paid to the influence of cations on the dynamic equilibrium of protonic species, as well as on the structure of the host lattice itself, *i.e.*, the Keggin anions. The investigations were done by IR and Raman spectroscopy within the range of 1200–40 cm^{-1}.

Keywords: IR spectra, Raman spectra, 12-tungstophosphoric acid, alkali salts of 12-tungstophosphoric acid, Keggin anion.

INTRODUCTION

Although heteropoly compounds (HPC) have been the subject of detailed investigation for more than 30 years, there are still many obscurities in their structure and characteristics. Especially the HPC of the Keggin structure has drawn special attention, because of the property of superionic protonic conductivity at room temperature ($\sigma = (100–1)\times10^{-3}$ S/cm).[1,2] Besides the host lattice made of Keggin anions, these compounds are characterized by the presence of a great number of water molecules. This causes the existence of a great number of protonic species[3,4] that are in permanent dynamic equilibrium, which explains their high protonic conductivity.[5,6] On the other hand, the great number of water moleculs in the structure also cause a dependence of their stability on external conditions, such as temperature and relative humidity of the surrounding. In this way, there are changes in the protonic properties, which aggruates their application as solid electrolytes in fuel cells H_2/O_2, *etc.* A moderate increase of the WPA stability, without a big reduction of the conductivity values, was noticed after the substitution of a certain number of protons, *i.e.*, oxonium H_3O^+ ions, with alkaline and earth alkaline cations.

* Dedicated to Professor Slobodan Ribnikar on the occasion of his 70th birthday

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Almost all the properties of these compounds are influenced by the nature of the cation. The nature and the strength of the hydrogen bonds between the entities as charge carriers are especially affected by the nature of the cation (ionic size, polarizability, solvatation number, *etc.*).

This paper reports the results of the influence of the nature of the cation on the host lattice of alkali WPA salts, a studied by IR and Raman spectroscopy.

EXPERIMENTAL

The examined alkali WPA salts were synthesized according to a previously reported procedure.[7]

The IR spectra of the samples, as KBr pellets and Nujol mulls, were recorded at room temperature with a Perkin Elmer 983G spectrophotometer. A variable temperature cell, model VLT-2, RIIC, London, was used for recording spectra at different temperatures. The spectra at high temperatures were recorded *in situ*, with a recording step of 10 °C.

The Raman spectra of the polycrystalline samples, sealed in glass tubes, were recorded on a Dilor RII instrument, using the 457.94 nm excitation line from a Spectra Physics laser, with a constant power of 3 mW.

RESULTS AND DISCUSSION

The observed effects of the influence of the cation on the characteristics of the investigated salts have been classified as the influence of big-strong and small-weak cations.[7,8] Thus, all the WPA salts are divided into two groups: the group of the small-weak cations (Li^+, Na^+, Mg^{2+}, Ca^{2+}) and the group of the big-strong cations (K^+, Rb^+, Cs^+, Sr^{2+}, Ba^{2+}). The WPA salts of the first group are transparent cubic crystals, slightly soluble in water, which crystallize with a large number of water molecules. During the process of calcination, these salts undergo two-step dehydrations. The second group of WPA salts are small, white crystals, slightly soluble in water.

The results of the IR and Raman spectroscopy will be discussed from the point of view of the nature of the cation and the influence of the protonic species on the host lattice. The IR spectra in the region of the stretching and bending vibration of water and proton entities were partialy analyzed in a previous paper.[7]

Data obtained from XRPD show that the structure of the investigated alkali salts is influenced by the degree of hydration. The salts of the group of small cations, with a large number of water molecules, have the structure of WPA-29 and the salts which belong to the group of big cations have a structure very similar to that of WPA-6.

The Raman spectra of Na_3WPA and Cs_3WPA, as examples of salts with small and big cations, respectively, and that of WPA are shown in Fig. 1. The assignment of the characteristic band frequencies is given in Table I. The Raman spectra confirmed the difference between the two groups of alkali WPA salts in agreement with the above mentioned division. The Raman spectra of WPA salts with small cations are simillar to the spectrum of WPA. From Fig. 1 it is evident that the strongest band, characteristic for the $\nu_1(PO_4)$ vibration at about 1010 cm^{-1} appears

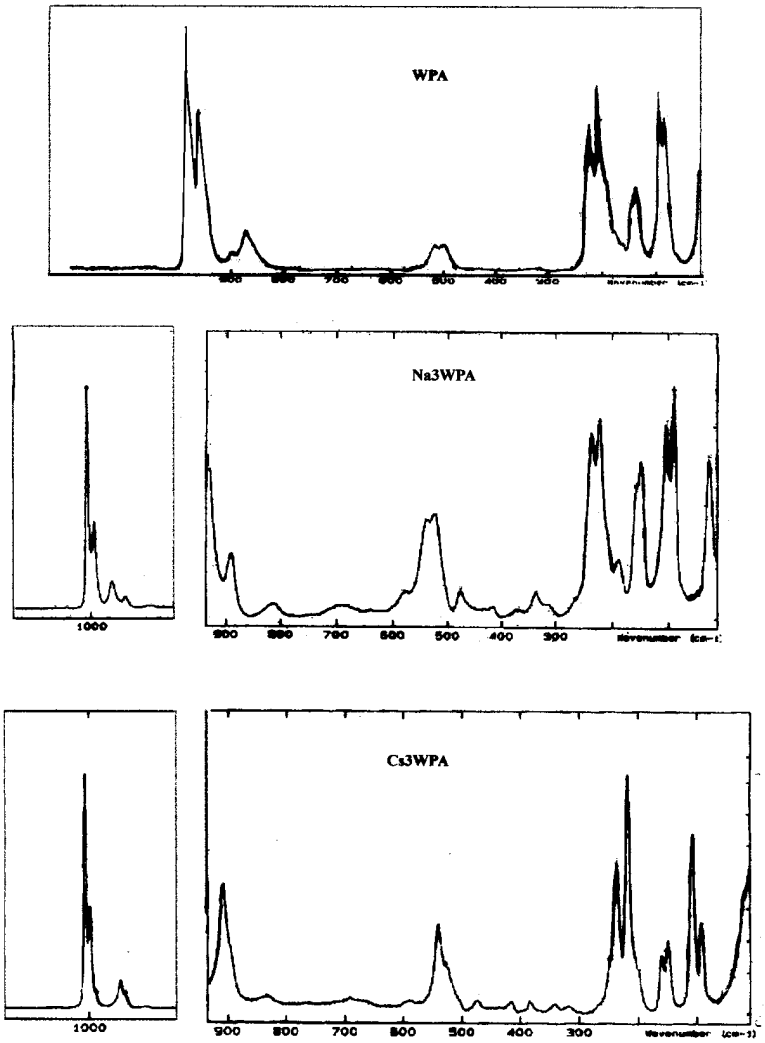

Fig. 1. Raman spectra of WPA, Na_3WPA and Cs_3WPA (region characteristic for host lattice vibrations).

as a doublet. The WPA salts of weak cations, besides this band, show another strong band at 989 cm^{-1}. For the salts of the strong cations this second band appears at 992–995 cm^{-1}. In spectra of the second group WPA salts, a band of medium intensity at 978 cm^{-1} appears, which is not registered in the Raman spectra of small cation salts. There is also a difference in the band intensities of the $\nu_2(PO_4)$ vibrations for salts with big cations and those with small cations.

The strong cations cause a dynamic dissociation of water molecules and the number of proton species (H^+, OH^- and hydrated proton entities) increase relatively to WPA and the small cation salts. These protonic species may interact with the

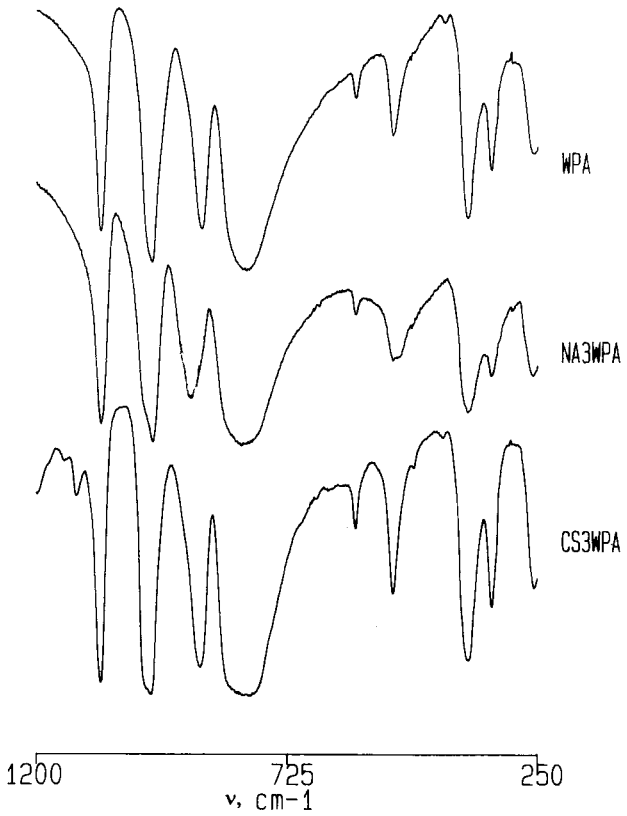

Fig. 2. IR spectra of WPA, Na_3WPA and Cs_3WPA at room temperature (KBr technique).

terminal oxygen atoms in the Keggin anions and cause a change of the distances between the oxygen atom in WO_6 octahedra and the PO_4 tetrahedra. This is reflected on the bands at about 1000 and 530 cm^{-1}, corresponding to the ν_1 and $\nu_2(PO_4)$ vibrations, which is also a doublet. The components of this band in the Raman spectra of small cations salts (at 536 and 518 cm^{-1}) are of approximately the same intensities. In the case of the big cation salts, the components have different intensities; the band at 540 cm^{-1} is more intense that that at 520 cm^{-1}, which appears as a shoulder. The frequency of the band at about 540 cm^{-1} increases with increasing cation radius. In the Raman spectra of the investigated compounds other doublet bands are also noticed; for group of small cations these are at 235–220, 157–148 and 103–89 cm^{-1}, and for the big cations at 238–218, 159–148 and 107–89 cm^{-1}.

The IR spectra, at room temperature, of WPA, Na_3WPA and Cs_3WPA, in the region below 1200 cm^{-1}, with the bands characteristic for the host lattice-Keggin anions, are shown in Fig. 2. The assignment of the bands is given in Table I. From Figs. 1 and 2 it may be noticed that the most intensive bands in the IR spectra are

very weak in the Raman spectra. From Fig. 2 and Table I it is evident that the $\nu_1(PO_4)$ band (983 cm^{-1}) is split. As the spiting could be caused by the presence of different proton entities and/or different cations, it was of interest to investigate in more detail

TABLE I. Characteristic frequencies (cm^{-1}) of the host lattice for WPA alkali salts

Li_3WPA Raman	Li_3WPA IR	Na_3WPA Raman	Na_3WPA IR	K_3WPA Raman	K_3WPA IR	Cs_3WPA Raman	Cs_3WPA IR	Assignement
	1079 vs		1078 s		1079 s		1078 s	$\nu_3(PO_4)$
1010 vs		1010.9 vs		1009.8 vs		1010.1 vs		$\nu_1(PO_4)$
988.7 s	994 sh	988.7 s	999 sh	992.1 s		995.5 s	994 sh	ν(W=O)
	982 vs		979 vs	978 m	982	978.6 m	984 s	
934 m		932 m	919 m					ν(O-W-O)
908 s			906 sh	907 s		907 m		
892.4 m	892 m	891.4 m			894	892.3 w	890 m	$\nu_2(WO_6)$
814.1 w		812.3 w	814 w	836.1 vw	813 w	831.5 vw		
	797 s						799 b s	
580.6 w	595 vw	578 w	597 vw	597.7 vw	596 vw	589.6 vw	595 w	$\nu_4(PO_4)$
536.8 m		537.6 m		542.1 s		540.3 s		$\nu_2(PO_4)$
518.8 m	524 w	524.1 m	510 w	518.7 w	526 w	525 w	523 w	
477.2 w	484 sh	477.2 w		471.7 w		474.4 w	482 sh	
	428 vw			445.2 w	428 vw		429 vw	
417.2 vw		416.3 vw		413.6 w		415.4 w		
373.4 w	378 m	367.9 vw	384 m	387.1 w	384 s	382.5 w	381 s	ν(W-PO_4)
336.3 vw	336 w	335.5 vw		340.7 w	340 m	339.9 w	337 m	ν(W-PO_4)
311.5 vw		313.5 w		315.1 w		317 w		
		267.4 sh		263.4 w			256 vw	δ(O-W-O)
				240.3 s		247.8 sh		
233.9 s		236 vs				235.8 vs		
218.1 vs		222.1 vs		219 vs		217.5 vs		ν(W-O-W)
				205 sh				R'(PO_4)
197.7 sh		188.6 m				198.6 sh		lattice modes
156.7 sh		157.8 sh		159.4 m		159.5 m		
146.4 s		149.4 vs		148.1 m		148.2		
103.2 s		103.4 vs		106.9 vs		107 vs		
88.2 s		89.3 vs		88.1 m		91 s		
49.5 w								
26.8 vs		26.1 vs						

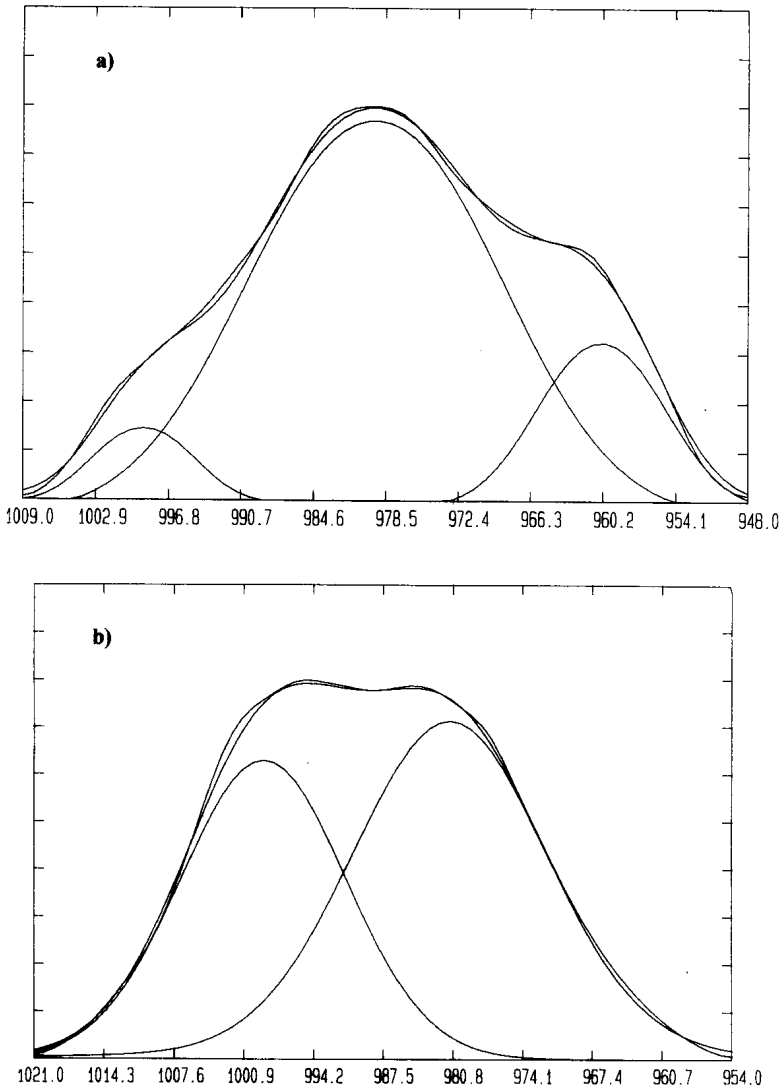

Fig. 3. Deconvolution of Na_3WPA a) and Cs_3WPA b) IR spectra (region characteristic for the $\nu_1(PO_4)$ vibration).

the influence of the cation. Hence, this band was deconvoluted, Fig. 3. From Fig. 3 it is obvious that deconvolution of this band for the small cation salts gives three bands: at 999, 979 and 960 for Na_3WPA, as in the case of WPA, and only two bands: at 999 and 979 cm^{-1}, for the group of big cations. The difference in the intensities of the common bands in these two group of sailts is also very prononced, Fig. 3.

The above mentioned results show that the nature of the cation influences the number and quantity of proton species, as well the host lattice and because of this it has to have an influence on the conductivity of the salt too. The conductivity values

for some hydrates of WPA and its alkali salts are given in Table II. The higher hydrates of WPA have high conductivity caused by the large number of protonic species, as charge carriers, and the well developed network of hydrogen bonds, which enables fast proton transport. The salts with big cations also have very high conductivities because of influence of these ions on the dynamic dissociation of water molecules, resulting in an increased number of protons and oxonium ions. From the obtained results and the results published in a previous paper,[7] it is evident that the influence of the nature of the cation (ionc size, polarization, hydration number *etc.*) is more pronounced in the H_2O–H_2O than in the H_2O–H_3O^+ interaction. With increasing ionic radius, the strength of the hydrogen bond also increases, which may be followed by the R_{O-O} distances and by the shift of the band characteristic for this interaction. The $\Delta\nu$ value of about 40 cm^{-1} and the decrease in the R_{O-O} distance from 0.282 to 0.271 nm follow the order from Li^+ to Rb^+. The changes of the R_{O-O} distances for the H_2O–H_3O^+ hydrogen bonds are smaller and decrease from 0.269 to 0.266 nm in the same order.

TABLE II: Conductivity values of WPA and its alkali salts

Compound	conductivity (S/cm)
$H_3PW_{12}O_{40}\cdot 29H_2O$	8×10^{-2}
$H_3PW_{12}O_{40}\cdot 14H_2O$	3.3×10^{-4}
$Li_3PW_{12}O_{40}\cdot 27H_2O$	1.25×10^{-2}
$Na_2HPW_{12}O_{40}\cdot 15H_2O$	1.7×10^{-4}
$Na_3PW_{12}O_{40}\cdot 16H_2O$	6.6×10^{-5}
$K_3PW_{12}O_{40}\cdot 10H_2O$	1.7×10^{-2}
$Rb_3PW_{12}O_{40}\cdot 6H_2O$	1.7×10^{-2}
$Cs_3PW_{12}O_{40}\cdot 8H_2O$	2.5×10^{-2}

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И З В О Д

СПЕКТРАЛНО ИСПИТИВАЊЕ СОЛИ АЛКАЛНИХ ЕЛЕМЕНАТА 12-ВОЛФРАМФОСФОРНЕ КИСЕЛИНЕ

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У овом раду саопштени су последњи резултати наших систематских испитивања хетерополикиселина и њихових соли. Посебна пажња посвећена је утицају катјона на динамичку равнотежу протонских врста, као и на структуру кристалне решетке, односно

Кегинових анјона. Испитивања су вршена методама инфрацрвене и раманске спектроскопије у области 1200–40 cm^{-1}. Добијени резултати су важни за објашњење механизма проводљивости, као и за решавање проблема практичне примене ових једињења као чврстих електролита.

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REFERENCES

1. O. Nakamura, T. Kodama J. Ogino, Y. Miyake, *Chem. Lett.* (1979) 17
2. O. Nakamura, I. Ogino, T. Kodoma, *Solid State Ionics* **3/4** (1981) 347
3. U. Mioč, Ph. Colomban, A. Novak, *J. Mol. Struct.* **218** (1990) 123
4. U. Mioč, M. Davidović, N. Tjapkin, Ph. Colomban, A. Novak, *Solid State Ionics* **46** (1991) 103
5. R. C. T. Slade, H. A. Pressman, E. Skou, *Solid State Ionics* **38** (1990) 207
6. R. C. T. Slade, I. M. Thomson, R. C. Ward, C. Poinsignon, *J. Chem. Soc., Chem. Commun.* (1987) 726
7. U. B. Mioč, M. Davidović, B. R. Stanisavljev, M. R. Todorović, Z. P. Nedić, S. Uskoković, *J. Serb. Chem. Soc.* **61** (1996) 759
8. E. A. Uksche, L. S. Leonova, A. I. Korosteleva, *Solid State Ionics* **36** (1989) 219.