CHEMISTRY LETTERS, pp. 139 - 142, 1988.

Solid-State NMR of $H_3PW_{12}O_{40}\cdot nH_2O$ and $H_3PW_{12}O_{40}\cdot 6C_2H_5OH$

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High-resolution solid-state ^1H and ^{31}P NMR revealed that there were at least three different states for protons of $H_3PW_{12}O_{40}\cdot nH_2O$; (i) protons present in highly hydrated samples, (ii) protonated water which is hydrogen-bonded to terminal oxygen, $W = O \cdots H^+(H_2O)_2$ (n ≒ 6), and (iii) proton which is directly bonded to bridging oxygen, W - OH - W (n ≒ 0). When water was replaced by ethanol, a protonated ethanol species was detected by ^1H, ^{13}C, and ^{31}P NMR.

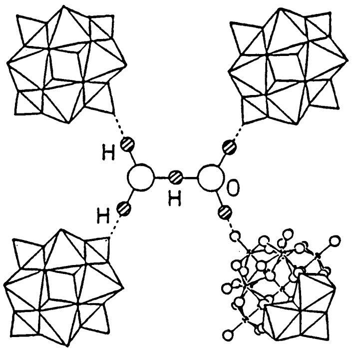
Heteropoly acids in the solid state are strong protonic solid acids.[1,2) They absorb polar molecules into the solid bulk and some catalytic reactions take place by the reactions of the absorbed molecules (reactions in "pseudo-liquid" phase). Due to this nature, high catalytic activity and unique selectivity are often observed.[3) Therefore, the elucidation of the states of protons and polyanions in that phase, as well as of their interactions with absorbed molecules, is important for the understanding of the catalysis of heteropoly compounds.

We applied high-resolution solid-state NMR (^1H and ^{31}P) to $H_3PW_{12}O_{40}$ which contained different amounts of water of crystallization. For comparison, ^1H, ^{31}P and ^{13}C NMR spectra of $H_3PW_{12}O_{40}$ which had absorbed about 6 molecules of ethanol per polyanion were also measured. To our knowledge, this is the first example, in which well-resolved ^1H NMR spectra were observed for solid $H_3PW_{12}O_{40}$, although several studies have been reported by use of wide-line NMR. The amount of water and ethanol in the samples were controlled and measured by following our previous studies.[2) $H_3PW_{12}O_{40}\cdot 17H_2O$ (sample **a**) was evacuated at room temperature to prepare $H_3PW_{12}O_{40}\cdot 6H_2O$ (sample **b**) and at 200 °C to prepare an anhydrous sample, $H_3PW_{12}O_{40}\cdot$ca.$0.5H_2O$ (sample **c**). Partial rehydration of sample **c** formed $H_3PW_{12}O_{40}\cdot$ca.$1.5H_2O$ (sample **d**). $H_3PW_{12}O_{40}\cdot$ca.$6C_2H_5OH$ was prepared by contacting sample **c** with 10 Torr (1 Torr = 133.3 Pa) of ethanol.

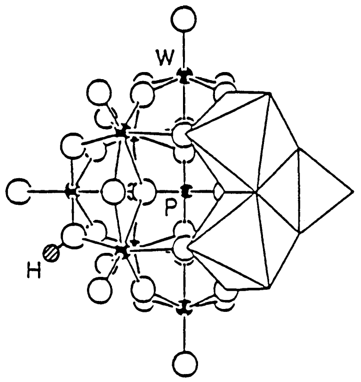
High-resolution solid-state NMR spectra were obtained with magic-angle spinning (MAS) on a Fourier transform pulsed NMR spectrometer (JEOL JNM-GX270). ^{31}P-MAS NMR spectra were obtained at 109.2 MHz with high-power proton decoupling, while ^{13}C-MAS NMR spectra were obtained at 67.8 MHz with proton decoupling. ^{1}H-MAS NMR spectra were obtained at 270 MHz with single pulses and without proton decoupling. ^{31}P chemical shifts were referenced indirectly to 15 mol dm^{-3} of H_3PO_4, and those for ^{13}C and ^{1}H to $(CH_3)_4Si$.

Figure 1 shows the ^{1}H and ^{31}P NMR spectra of $H_3PW_{12}O_{40}\cdot nH_2O$. ^{31}P lines were all sharp, and the chemical shifts were -15.1 ppm for highly hydrated sample (**a**), -15.6 ppm for hexahydrated sample (**b**) and -11.1 ppm for anhydrous one (**c**). Rehydrated sample (**d**) exhibited two major peaks at -11.1 and -15.6 ppm, indicating coexistence of **b** and **c**. The ^{13}P chemical shifts for **a** and **c** are in general agreement with those reported previously.$^{4)}$ The sharp ^{1}H NMR line for **a** indicates that the protons are in a uniform state and highly mobile, as is expected from the pseudo-liquid behavior of this compound. When the water content decreased, the lines became much broader and weaker, probably owing to lower mobility of protons. The ^{1}H spectra, **b**, **c**, and **d**, shown in Fig. 1 are those after the subtraction of background signal, which originated from the sample holder and had a comparable intensity (in these spectra, the most intense peaks are drawn with an equal height. Actually, the peak height of ^{1}H was **a** ≫ **b** > **c**, **d**.). A chemical shift similar to **a** was found for **b** at 7.3 – 7.5 ppm. The shifts for **c** and **d** were about 9.2 ppm, but these values are less reliable because of the low signal to noise ratio, and peaks at 0.9 and 6.4 ppm might be ghost peaks due to the subtraction of the background.

Close correspondence may be noted between the ^{1}H and ^{31}P spectra in Fig. 1; hydrous samples showed a ^{31}P peak at -15.1 – -15.6 ppm and a ^{1}H peak at 7.3 – 7.5 ppm (**a**, **b**), and for anhydrous ones ^{31}P peak was at -11.1 ppm and a broad and weak ^{1}H peak at 9.2 ppm (**c**). It is known that $H_3PW_{12}O_{40}\cdot 6H_2O$ is relatively stable,$^{3)}$ and has a structure, in which protonated water molecules, $H(H_2O)_2^{+}$, connected heteropoly anions by hydrogen-bonding at terminal oxygens (see **A**).$^{5)}$ Hence, the NMR spectrum, **b**, may be assigned to this structure. As the water molecules are removed from this structure, protons which were left would directly attach to the oxygen atoms of the polyanions; the site of bonding may be a more basic bridging oxygen. The structure like **B** may be assigned to **c**.



A



B

Stronger bonding of a proton to the polyanion in **B** explains the broader ^{1}H peak (lower mobility) and low-field shift of ^{31}P peak (lower electron density). Since it has previously been shown that the powder X-ray diffraction pattern little changed by the dehydration of $H_3PW_{12}O_{40}\cdot 6H_2O$,[6)] the secondary structure of **c** may be similar to that of **A**.

The highly hydrated sample (**a**) showed a chemical shift of ^{31}P slightly different from **b** (-15.1 vs. -15.6 ppm), and a much narrower and stronger ^{1}H signal. These differences between **a** and **b** were reproducible. Probably, they

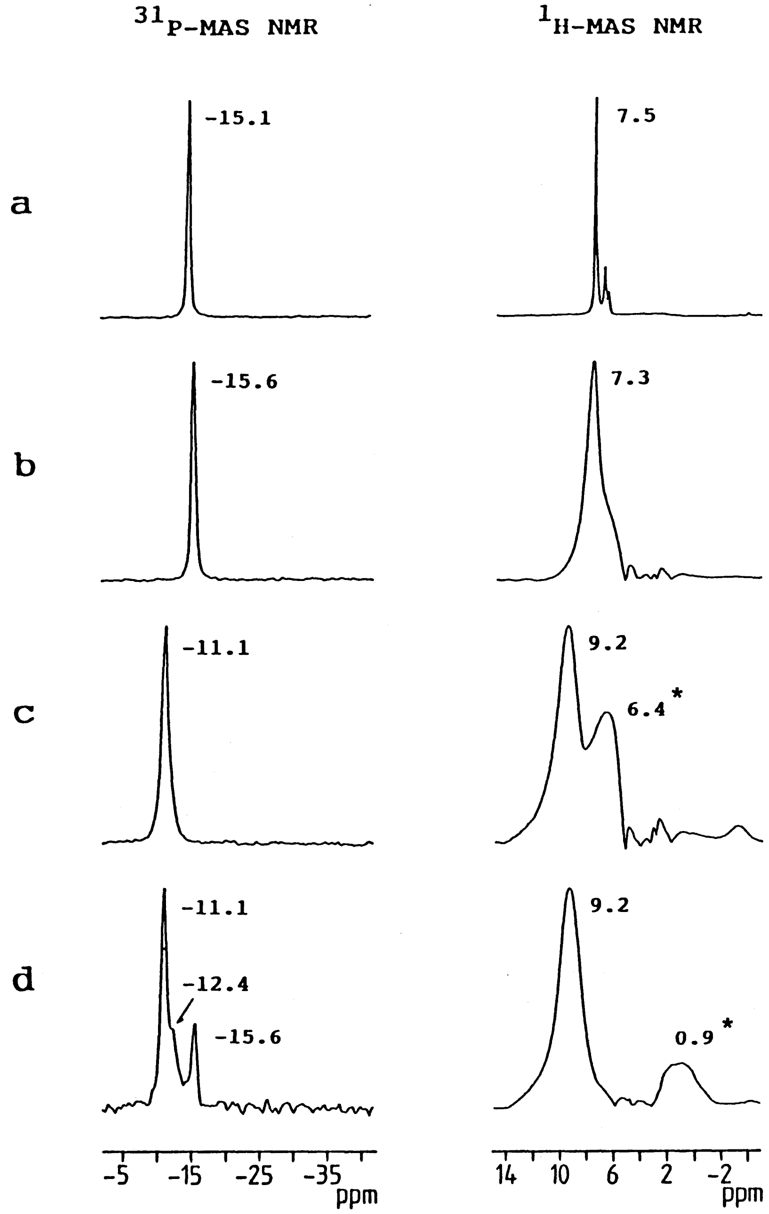


Fig. 1. ^{31}P and ^{1}H MAS NMR spectra of $H_3PW_{12}O_{40}\cdot nH_2O$, (**a**) n=17, (**b**) n=6, (**c**) n≑0.5, (**d**) n≑1.5. Chemical shifts with reference to H_3PO_4 and TMS.
* Ghost peaks(?). See text.

reflect the number of water or protonated water molecules interacting with the polyanion. The highly hydrated structure of **a** may be much less rigid and protons are more mobile, so that the narrower lines are understandable. Small ^1H peaks present near the main peak for **a** are probably due to portions of the sample containing different amounts of water. A shoulder peak at -12.4 ppm in the ^{31}P spectrum of **d** indicates the presence of another type of proton, although the structure is not known at present.

Figure 2 shows ^{31}P, ^{13}C, and ^1H NMR of $H_3PW_{12}O_{40}\cdot 6C_2H_5OH$. The ^1H peaks at 9.4, 4.1,and 1.5 ppm which are assignable to OH, CH_2, and CH_3, respectively, are in agreement with those reported for protonated ethanol in superacid.[7)] The relative intensity (OH : CH_2 : CH_3 = 1.45 : 1.8 : 3.0) indicates that this species is a dimer, $(C_2H_5OH)_2H^+$. The ^{31}P shift was close to that for the hexahydrate. The XRD patterns were also similar for the two samples.

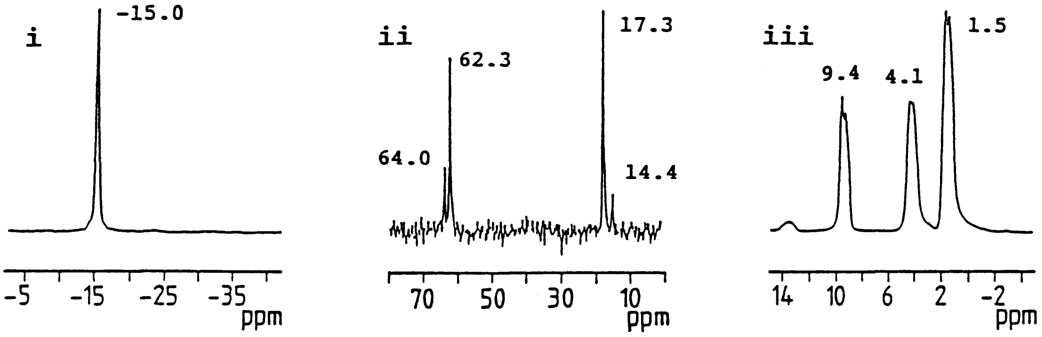


Fig. 2. (i)^{31}P, (ii)^{13}C, (iii)^1H MAS NMR spectra of $H_3PW_{12}O_{40}\cdot nC_2H_5OH(n=6)$.

Although further studies are necessary to establish the assignments, the above observation not only demonstrates that high-resolution solid-state NMR is useful for the study of heteropoly compounds, but also indicates that heteropoly compounds are good cluster models for the study of the catalysis of mixed oxides.

References

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(Received October 27, 1987)