Study of Heteropolyanions by Solid-state Nuclear Magnetic Resonance Spectroscopy

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Solid-state ^{31}P and ^{29}Si n.m.r. spectroscopy has been used to characterise a number of heteropolyanion salts. A significantly larger chemical shift anisotropy was seen for the phosphorus in the dimeric P : Mo = 2 : 18 Dawson structure than for the P : Mo = 1 : 12 Keggin unit. Two inequivalent phosphorus sites are seen for the 2 : 18 anion. Solution and solid-state chemical shifts agree very well allowing the identification of various degrees of tungsten substitution in the compound of nominal composition $Cs_3[PMo_{11}WO_{40}]$. Structures having the composition 1 : 11 ($[SiW_{11}O_{39}]^{8-}$) show an observable difference in the solid-state isotropic chemical shift from 1 : 12 species thus allowing the detection of the first stages of decomposition of the Keggin unit.

A variety of heteropolyanions, particularly the salts of molybdophosphoric acid $H_3[PMo_{12}O_{40}]$, are active catalysts for a wide range of heterogeneous selective oxidation reactions, for example the oxidation of methacrolein to methacrylic acid.[1] Two factors which affect the activity and selectivity are the acidity and redox characteristics of the heteropolyanions [2] as is demonstrated by the behaviour of the tungsten- or vanadium-substituted molybdophosphates, $[PMo_{12-n}Y_nO_{40}]^{3-}$ (Y = W or V, n = 1, 2, 3 . . .), and the mixed hydrogen salts, K_xH_{3-x}-$[PMo_{12}O_{40}]$ (x = 1 or 2). Thus increasing tungsten substitution leads progressively to a less efficient catalyst [3] while vanadium substitution leads initially, for n = 0.5, to a more efficient catalyst [4] and then to a less efficient one.[1] Similarly for the mixed hydrogen salts the best catalyst corresponds to an intermediate composition, around x = 2.7. A cautionary note however is that, in general, synthetic routes to substituted heteropolyanions do not lead to unique species. In addition previous studies have shown that the method of catalyst preparation and pretreatment can significantly alter the activity and selectivity for a given heteropolyanion.[5]

In view of the dependence of the catalytic behaviour on the precise nature of the heteropolyanion a full characterisation of the catalyst material is necessary. However, it is apparent from an examination of *X*-ray powder diffraction patterns and i.r. spectra that these are, in general, not sufficiently sensitive to show either the presence of mixed heteropolyanions or structural changes which occur as a consequence of, for example, calcination. On the other hand in solution the ^{31}P n.m.r. chemical shift of phosphorus in the Keggin unit,[6] $[PM_{12}O_{40}]^{3-}$, can differentiate between the parent heteropolyanions and their substituted derivatives,[7,8] similarly for the ^{29}Si chemical shift in silicon based heteropolyanions. As a consequence the solution ^{31}P and ^{29}Si n.m.r. spectra are useful for elucidating the nature of the anion in a reaction mixture. We have therefore examined the use of solid-state n.m.r. to characterise solid heteropolyanions.

Experimental

The heteropolyanions were prepared using standard procedures outlined below. Salts of 12-molybdophosphoric acid ($H_3[PMo_{12}O_{40}]$) were prepared [9] by dissolving $H_3[PMo_{12}O_{40}]\cdot nH_2O$ (BDH, 'AnalaR') in water and adding the required quantities of the appropriate counter ion in solution. In the preparation of the salts it is important to determine the number of molecules of water of hydration, n, and this was achieved by carrying out thermogravimetric analysis on a small sample of the 12-molybdophosphoric acid beforehand. To prepare the Na and K salts the carbonate was used, for the NH_4 salt the chloride, and for the Cs salt the nitrate. The Cs salt of 12-tungstophosphoric acid was prepared in a similar manner starting from $H_3[PW_{12}O_{40}]\cdot nH_2O$ (BDH, 'AnalaR'). In order to prepare $Cs_3[PMo_{11}WO_{40}]$ 12-molybdophosphoric acid and 12-tungstophosphoric acid were mixed to produce a solution of composition $PMo_{11}W$ which was then boiled for 3 h to give, after precipitation using $CsNO_3$, the solid of nominal composition $Cs_3[PMo_{11}WO_{40}]$. The $[P_2Mo_{18}O_{62}]^{6-}$ anion was prepared using the sodium molybdate method [10] with ether extraction of the anion prior to forming the NH_4 salt. 12-Tungstosilicic acid was used as supplied (Hopkin and Williams). $K_8[SiW_{11}O_{39}]\cdot nH_2O$ and $[NH_2Me_2]_8[P_2Zn(OH_2)W_{17}O_{61}]\cdot nH_2O$ were kind gifts of Dr. T. J. R. Weakley (Dundee). Powder *X*-ray diffraction patterns and i.r. spectra were obtained for all samples to verify the presence of the heteropolyanion.

N.m.r. spectra were acquired on JEOL FX-200 and Bruker CXP-200 spectrometers operating at 80.9 MHz for ^{31}P and 39.73 MHz for ^{29}Si. Magic angle sample spinning was carried out using Delrin rotors at 4 kHz. All spectra were acquired with high-power proton decoupling. Typically 100 transients were collected, with a recycle time of 10 s for the ^{31}P spectra and of at least 60 s for ^{29}Si spectra owing to their longer T_1. Chemical shifts were measured with respect to an external reference of 85% H_3PO_4 for ^{31}P and are reported taking upfield as positive. ^{29}Si Chemical shifts are given with respect to the secondary standard Q_8M_8,† taking the downfield resonance as +11.5 p.p.m. with upfield as negative.

Results and Discussion

The magic angle sample spinning (m.a.s.s.) spectrum of $[NH_4]_3$-$[PMo_{12}O_{40}]$ consists of a single resonance with an isotropic chemical shift, σ_{iso}, of 4.45 p.p.m. with a linewidth of 40 Hz. A non-spinning spectrum of the same salt shows a single resonance with a Gaussian lineshape and a linewidth of only 410 Hz. In order to interpret the observed linewidth it is necessary to consider the broadening arising from the dipolar couplings ^{31}P–^{31}P, ^{95,97}Mo, and ^{14,15}N. From the crystal structure of $K_3[PMo_{12}O_{40}]$ [11] we can obtain accurate internuclear distances to calculate the second moment, M_2, and by assuming a Gaussian lineshape to calculate the linewidth.[12] We can accurately

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† Q_8M_8 is a cubic siloxane; Q = quaternary unit, M = end unit. See R. K. Harris and B. E. Mann, 'NMR and the Periodic Table,' Academic Press, London, 1978, p. 324.

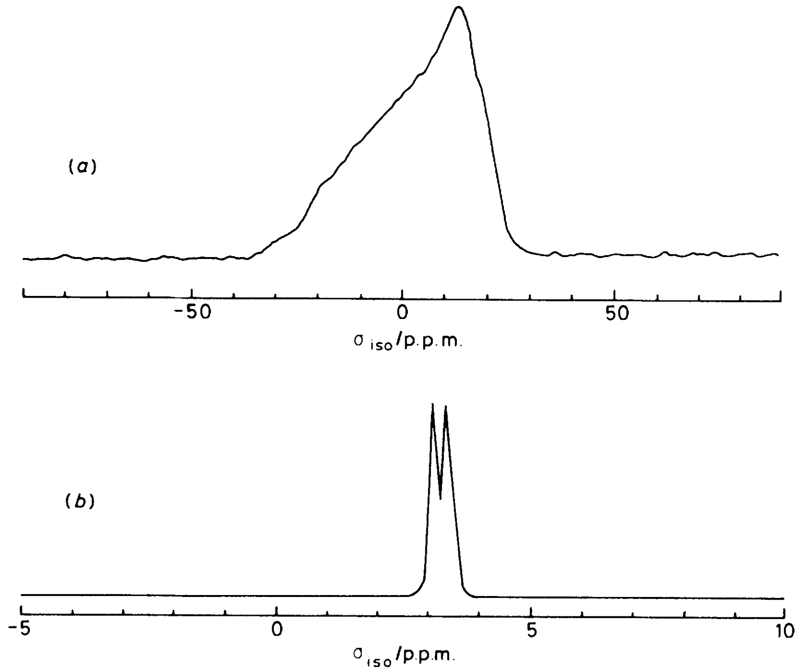

Figure 1. Solid-state ^{31}P n.m.r. spectra of $[NH_4]_6[P_2Mo_{18}O_{62}]$; (*a*) static and (*b*) m.a.s.s. at *ca.* 4 kHz

Table 1. Chemical shift tensor components (p.p.m.) of $[P_2Mo_{18}O_{62}]^{6-}$ and $[P_2Zn(OH_2)W_{17}O_{61}]^{8-}$

Unit	Atom	$\sigma_{\parallel}$	$\sigma_{\perp}$	$\Delta\sigma$ *	σ_{iso}
P_2Mo_{18}	P^1	−33	22	−55	3.4
P_2Mo_{18}	P^2	−22	16	−38	3.05
$P_2W_{17}Zn$	P(Zn)			−33	8.4
$P_2W_{17}Zn$	P(W)			−54	13.9

* $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$.

calculate the ^{31}P–^{31}P interaction over the entire lattice since the phosphorus atoms form a simple cubic lattice. The other dipolar interactions were found by summing over contributions from the anion and its next nearest neighbours. By far the largest dipolar interaction is ^{31}P–$^{95,97}Mo$ which accounts for *ca.* 97% of the dipolar linewidth of 230 Hz.

Clearly the chemical shift anisotropy (c.s.a.) is small, of the order of 4 p.p.m., reflecting the high symmetry of the phosphorus nucleus within the Keggin unit. An alternative explanation for the relatively narrow line in the static spectrum, namely the presence of motion causing a reorientation of the Keggin unit, is unlikely in view of the large quadrupole/chemical shift anisotropy present in the powder pattern of ^{51}V in the anion $[PMo_{11}VO_{40}]^{4-}$.

In marked contrast to $[NH_4]_3[PMo_{12}O_{40}]$ the ^{31}P n.m.r. powder pattern of $[NH_4]_6[P_2Mo_{18}O_{62}]$ has a significant c.s.a., see Figure 1(*a*); furthermore the m.a.s.s. spectrum, shown in Figure 1(*b*) has two distinct resonances. This is consistent with both the α and β forms for the $[P_2Mo_{18}O_{62}]^{6-}$ anion. In the case of the α form, which has D_3 symmetry, the two resonances would correspond to the two molecules in the unit cell [13] while for the β form, by analogy with β-$[P_2W_{18}O_{62}]^{6-}$,[7,14] the lower symmetry C_3 makes the two phosphorus atoms within the anion inequivalent. Although the isotropic chemical shifts of the two phosphorus resonances are quite similar, σ_{iso} = 3.05 and 3.4 p.p.m., a fairly large difference appears in the c.s.a. Approximate values for the chemical shift tensor components are shown in Table 1. It is quite common to observe similar isotropic chemical shifts but widely different tensor components in phosphate groups, and although the sensitivity of the phosphate chemical shift tensor components to the local environment in the heteropolyanion is clear a complete understanding of the structural influences on these components is not. A clear example of this is the $[P_2Zn(OH_2)W_{17}O_{61}]^{8-}$ anion where substitution of a tungsten by zinc in one half-unit causes a downfield shift of 5.5 p.p.m. in this unit leaving the other unit largely unaffected and yet the unsubstituted PW_9 unit has the larger c.s.a. Consequently it is not yet possible to analyse the different c.s.a. in structural terms.

Table 2.

	σ_{iso}/p.p.m.	−δ/p.p.m.
$Na_3[PMo_{12}O_{40}]$	4.0	
$K_3[PMo_{12}O_{40}]$	4.35	3.9
$Cs_3[PMo_{12}O_{40}]$	4.50	
$[NH_4]_3[PMo_{12}O_{40}]$	4.45	
$K_4[PMo_{11}VO_{40}]$	4.2	4.05
$Cs_3[PW_{12}O_{40}]$	15.0	14.9
$[NH_4]_6[P_2Mo_{18}O_{62}]$	3.05	3.4
$H_4[SiW_{12}O_{40}]\cdot 26H_2O$	−85.0	−84.7
$[NH_2Me_2]_8[P_2Zn(OH_2)W_{17}O_{61}]\cdot nH_2O$	8.4 13.9	8.6 13.8

The isotropic chemical shifts for a variety of different heteropolyanion compounds are shown in Table 2. A comparison of σ_{iso} for a series of counter ions $M_3[PMo_{12}O_{40}]$ (M = Na, K, or Cs) indicates a small increase along the series. Although a correlation exists between σ_{iso} and the electronegativity of the counter ion, σ_{iso} should not be seen to reflect the ionic character of the lattice. This is because calculations of the c.s.a. in the phosphate group [15] and the experimental solid-state pH dependence of adenosine monophosphate [16] both indicate that the variations in σ_{iso} cannot be solely attributed to the diamagnetic term in the chemical shift tensor. In spite of small variations in the isotropic chemical shift with the counter ion

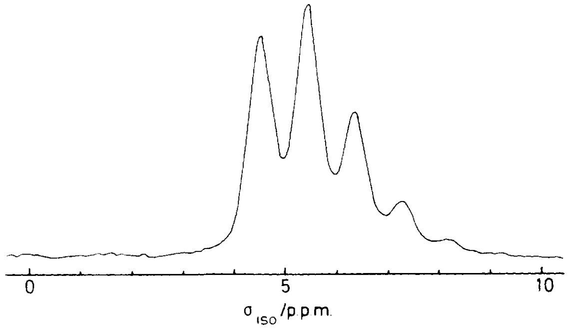

Figure 2. ^{31}P M.a.s.s. spectrum (4 kHz) of $Cs_3[PMo_{11}WO_{40}]$

the principal factor which determines the chemical shift is the nature of the heteropolyanion, this is apparent from the values of σ_{iso} for the various heteropolyanions shown in Table 2. Moreover, solution and solid-state chemical shifts agree quite well. An important consequence of this agreement is that solid-state n.m.r. can be used to characterise heteropolyanion materials, providing that the chemical shift ranges do not significantly overlap. For example the m.a.s.s. spectrum of a compound of stoicheiometry $Cs_3[PMo_{11}WO_{40}]$, Figure 2, shows five resonances that correlate well with the spectrum observed from the solution reaction mixture. Since it is known that synthetic routes to tungsten- and vanadium-substituted molybdophosphates can lead to mixtures containing a variety of species with differing degrees of substitution we can identify the multiple resonances as corresponding to $Cs_3[PMo_{12-x}W_xO_{40}]$ (x = 0—4). Table 3 shows a comparison between the solution and solid chemical shift data, reinforcing the close similarity between the solution and solid mixtures. We can draw two conclusions from these data: first, the solid-state ^{31}P n.m.r. spectra have sufficient resolution and correspondence to solution n.m.r. data to enable us to identify different heteropolyanions and, secondly, in this case the precipitate $Cs_3[PMo_{11}WO_{40}]$ has a composition which is very similar to that of the mother-liquor from which it was precipitated. This is of particular interest since correlations based on tungsten or vanadium substitution have generally assumed the compounds to be pure and now this can be verified using solid-state n.m.r.

An important aspect of the solution chemistry of the heteropolyanions is their degradation to less polymerised species such as $[PMo_{11}O_{39}]^{7-}$ at higher pH. Since the preparation of the salts *via* the carbonate involves an increase in pH we might expect such species to be present as impurities. It would therefore be useful to know the chemical shifts expected for the ^{31}P or ^{29}Si nuclei in degraded Keggin units. We have found it difficult to prepare pure $[PMo_{11}O_{39}]^{7-}$ salts; however, in the case of tungstosilicic acid the $[SiW_{11}O_{39}]^{8-}$ anion can be isolated. Thus in $K_8[SiW_{11}O_{39}]\cdot nH_2O$ the ^{29}Si chemical shift is -83.9 p.p.m., a small downfield shift from $[SiW_{12}O_{40}]^{4-}$ but still easily resolvable because of the narrow lines observed for these anions. We can therefore be confident that the $H_4[SiW_{12}O_{40}]$ sample used was pure and free from degradation products. Evidence for the presence of $[PMo_{11}O_{39}]^{7-}$ is not so clear-cut. In solution under conditions when $[PMo_{11}O_{39}]^{7-}$ is expected an additional resonance to that of pure $[PMo_{12}O_{40}]^{3-}$ is seen at δ -1.5 p.p.m. This resonance is also observed in the ^{31}P spectrum of $Na_3[PMo_{12}O_{40}]$ which suggests that this sample contains the $[PMo_{11}O_{39}]^{7-}$ species as an impurity. No evidence was found from the *X*-ray powder diffraction pattern for a sodium phosphate phase which is another possibility for this resonance. Despite some uncertainty concerning the assignment of the resonance at δ -1.5 p.p.m. the solid-state ^{31}P n.m.r. spectrum of the sodium salt clearly shows that decomposition of the Keggin unit has occurred.

Table 3. Chemical shifts for $Cs_3[PMo_{12-x}W_xO_{40}]$ (x = 0—4)

	PMo_{12}	$PMo_{11}W$	$PMo_{10}W_2$	PMo_9W_3	PMo_8W_4
Solid [a]	4.5	5.45	6.4	7.3	8.21
Solution [b]	3.9	4.9	5.8, 6.0	6.9, 7.1	8.0

[a] σ_{iso} in p.p.m. [b] $-\delta$ in p.p.m.

Conclusions

The ^{31}P and ^{29}Si m.a.s.s. spectra of the heteropolyanions shown above demonstrate the value of this technique in characterising heteropolyanion materials. A close correspondence was found between the solution chemical shifts and the solid-state isotropic chemical shifts. Only a small chemical shift anisotropy was found for the anions based on the $[PM_{12}O_{40}]^{3-}$ structure, reflecting the high symmetry of the central phosphorus atom. A larger anisotropy was found for the dimeric $[P_2Mo_{18}O_{62}]^{6-}$, although an understanding of the anisotropy in structural terms is unclear. Further studies on the different types of heteropolyanion are in progress in order to clarify this relationship.

Of particular interest was the ability to identify various degrees of tungsten substitution in the material of stoicheiometry $Cs_3[PMo_{11}WO_{40}]$. This will be useful for studying practical catalyst formulations.

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