Aqueous Molybdovanadates at High Mo : V Ratio

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Aqueous molybdovanadates have been studied by ^{51}V NMR spectroscopy over a wide range of metal-ion concentrations and temperatures in the range pH 1.4–7, and by potentiometry at 25 °C. The structures of the anions *cis*-$[Mo_4V_2O_{19}]^{4-}$, *cis*-$[HMo_4V_2O_{19}]^{3-}$, $[Mo_5VO_{19}]^{3-}$, $[Mo_4V_5O_{27}]^{5-}$, $[HMo_4V_5O_{27}]^{4-}$ and β-$[Mo_7VO_{26}]^{5-}$ have been further confirmed or determined by parallel ^{17}O NMR studies. Some ^{95}Mo NMR data are also presented. Less conclusive evidence is also presented for the solution species α-$[HMo_6V_2O_{26}]^{5-}$, $[Mo_4VO_{17}]^{5-}$ and $[HMo_8V_2O_{32}]^{5-}$ with a planar structure, and several α-Keggin species with central vanadium atoms. There is also tentative evidence for α-$[HMo_7VO_{26}]^{4-}$, β-$[H_2Mo_6V_2O_{26}]^{4-}$ and for species of 'double-heptamolybdate' type. Most of the structures are closely related to the known isopolymolybdates or to decavanadate. The vanadium atoms usually prefer central sites and mutual proximity. Calculations on combined precise electromotive force data and quantitative ^{51}V NMR data [25 °C, 0.6 mol dm^{-3} Na(Cl) medium] using the least-squares computer program LAKE have established the formation constants. The chemical speciation is illustrated in distribution diagrams.

A recent paper described the first part of a comprehensive investigation of molybdovanadates (Mo^{VI}, V^{V}).[1] It showed that the vanadium-rich region was entirely dominated by three species, each with the decavanadate structure, but with either one or two 'capping' vanadiums replaced by Mo. In the disubstituted case $[Mo_2V_8O_{28}]^{4-}$, both *cis* and *trans* isomers were found, in similar proportions. The *cis* isomer was unexpected, for on simple electrostatic grounds one would expect the two molybdenum(VI) atoms to separate further. In the same paper we also commented that none of the crystals so far obtained from molybdovanadate solutions and analysed by X-ray crystallography corresponds to any major solution species. The crystals appear because of their insolubility rather than because of the relative stability of the solution species. Leparulo-Loftus and Pope[2] have described several features of the closely related tungstovanadate system. They have identified two sharp vanadium resonances as arising from the known anions $[W_5VO_{19}]^{3-}$ and *cis*-$[W_4V_2O_{19}]^{4-}$, together with the protonated form of the latter. They also offer evidence for *fac*-$[W_3V_3O_{19}]^{5-}$, at higher pH. These anions all have the double-octahedron, hexametalate structure[3] of $[Mo_6O_{19}]^{2-}$. In addition, the authors identify many smaller and generally narrow resonances as arising from species with a Keggin structure, built around a central VO_4 tetrahedron. These species include several isomers of $[V(W_{10}V_2O_{40})]^{5-}$ and of $[V(W_9V_3O_{40})]^{6-}$.

Maksimovskaya and Chumachenko[4] have reported a similar study of the molybdovanadate system. They give a fairly firm identification of $[MoV_9O_{28}]^{5-}$, $[Mo_5VO_{19}]^{3-}$ and $[Mo_4V_2O_{19}]^{4-}$, based on one-dimensional ^{51}V, ^{95}Mo and ^{17}O NMR spectra, although some expected resonances were not observed. They also find several other resonances to be present, for which they offer only very tentative assignments.

The present work began at Umeå as a potentiometric study in 0.6 mol dm^{-3} Na(Cl) ionic medium at 25 °C. The hydrolysis of V^{V} (ref. 5) and Mo^{VI} (ref. 6) had already been determined under the same experimental conditions. Moreover the ^{51}V NMR spectra of the vanadate system were known,[5,7] as were the ^{17}O NMR spectra of the isopolymolybdate species.[8–10]

Both the binary subsystems (H^+–$[HVO_4]^{2-}$ and H^+–$[MoO_4]^{2-}$) are complicated. Vanadium(V) and molybdenum(VI) prefer octahedral co-ordination to oxygen at pH < 7 and the octahedra are similar in size. Many ternary molybdovanadates were thus expected. Their existence was also evident from a number of X-ray structure determinations on single crystals,[11–14] found to contain discrete molybdovanadate anions. Our initial and extensive 65.8 MHz ^{51}V NMR survey of the system showed many peaks arising from molybdovanadate species. These did not correlate well with the known crystal structures. Thus high-field ^{51}V and ^{17}O NMR spectroscopy became essential. Our strategy has been first to survey the ^{51}V spectra resulting from various concentrations of Mo and V at various pH values, both at room temperature and at elevated temperature (99 °C). It proved valuable to perform both pH titrations at constant metal ion concentrations and also to vary metal ion ratios at constant pH. From this survey we made several tentative peak assignments, which were supported by two-dimensional ^{51}V–^{51}V correlation spectroscopy (COSY) correlations[1] where relevant. We were then able to select optimum conditions for observing the ^{17}O NMR spectra of more concentrated solutions. The resonances in these could often be associated with specific species by comparing related spectra. In particular, we had already identified all the resonances expected from structures of the decavanadate type, and from the known aqueous isopolymolybdates. In some cases, the latter resonances could also be directly removed from the spectra by exploiting our observation that isopolymolybdate oxygens exchange fairly rapidly with solvent water at pH < 5, whereas almost all the vanadomolybdate oxygens exchange more slowly. We have recently described[9] a selective solvent-peak inversion method whereby ^{17}O NMR spectra may be edited into separate spectra for labile and inert oxygen resonances.

Even with these various approaches there remain some ^{17}O NMR resonances which are observed by overlap, especially in the terminal Mo=O region from δ 810 to 870. Nevertheless, we are fairly confident of the identification and ^{17}O assignments of at least four dominant non-decavanadate type structures, two of which confirm the conclusions of Maksimovskaya and Chumachenko.[4] We also offer partial identification of nine other species.

As most of the structures we propose are based on close-packed oxygen lattices, we have chosen to present these as exploded layer diagrams, to clarify the ^{17}O NMR assignments.

Our identifications of species have been tested against quantitative ^{51}V NMR peak integral data and precise potentiometric data using the least-squares program LAKE,[15] which is capable of treating such combined data simultaneously. Being aware that the potentiometric data are somewhat affected by a few minor species not yet identified, we have in the calculations put considerable weight on the NMR data. In general, the NMR data have been more elucidative than electromotive force (e.m.f.) data. In some cases, however, where peak overlap is serious, the dependence of the potentiometric data upon concentration has been more conclusive than that of peak areas, in identifying new species and excluding related possibilities. The search for a conclusive speciation model has been laborious. The Mo:V ratio and the pH range were gradually expanded so as to include new species. By means of the computer program SOLGASWATER[16] we repeatedly calculated diagrams showing the distribution of vanadium-containing species as a function of pH. We then compared these with the experimental NMR data. The detailed pH dependence of the distributions of species have helped to establish the presence of some species and to rule out others. In the final calculation, representative e.m.f.–NMR data from the whole data region were treated simultaneously and the fit was satisfactory. The results are summarized in Table 1 and discussed below.

Experimental

Most of the experimental details are exactly as in our previous paper.[1]

NMR Measurements.—Solution-state NMR spectra were obtained at 105.2 (^{51}V), 54.2 (^{17}O) and 26.1 (^{95}Mo) MHz on a Bruker WH400 spectrometer and at 20 or 99 °C. Some complementary ^{51}V NMR spectra were also recorded at 131.6 MHz on a Bruker AM500 instrument at 25 °C. Magic angle spinning (MAS) ^{51}V NMR spectra were obtained at 94.7 MHz on a Bruker MSL 360 spectrometer.

In general, it proved harder to obtain accurate peak integrals than in our previous study, because of severe overlapping. However, there was less uncertainty regarding the dependence of peak areas upon pH and metal-ion concentration, so that these could readily be correlated with the independent potentiometric data. In the case of ^{17}O NMR spectra, the area of an isolated resonance could generally be measured to $\pm 20\%$, which was sufficient to count the oxygens of a given type in one species, and to distinguish different species by their intensity variations. Some uncertainties remain, however, in the crowded terminal Mo–O region from δ 810 to 870 and in the Mo–O–Mo region around δ 400, particularly when subtraction methods had to be used. The ^{51}V NMR chemical shifts, even at 99 °C, are quoted with respect to capillary $VOCl_3$ at 20 °C, ^{95}Mo shifts relative to 2 mol dm^{-3} external aqueous $[MoO_4]^{2-}$ at 20 °C and ^{17}O relative to solvent water.

Synthesis.—Yellow microcrystals were obtained by addition of tetramethylammonium ion to a pH *ca.* 3 aqueous solution, with the following component concentrations in mmol dm^{-3} prior to precipitation: Mo, 165; V, 41; Na = $N(CH_3)_4$, 317; found Mo:V (molar proportions) = 4.85:1. This ratio was also consistent with the ^{51}V NMR spectrum upon redissolution. The IR spectrum of the same phase is very similar to that of the Mo_6O_{19} double-octahedron unit.[3] Thus, the microcrystals probably contain Mo_5VO_{19} units.

The above phase was then recrystallized from water giving single crystals. The recorded IR spectrum differs slightly from that of the microcrystals. However, there are still enough similarities to point to a Mo_5VO_{19} unit. At the present stage of the X-ray analysis, the formula is $[N(CH_3)_4]_2H_xMo_{6-x}V_xO_{19}$ with x close to one.[17] As there was no sign of a monoprotonated Mo_5V species in the present combined e.m.f.–NMR study, its appearance in the solid phase was rather surprising, although not inconsistent with the behaviour of isopolyvanadate species.[7]

Electromotive Force Measurements.—Potentiometric data and the resulting equilibrium constants were obtained at 25 °C in a 0.6 mol dm^{-3} Na(Cl) medium. Stable e.m.f. values were obtained mostly within a quarter to half an hour. In some cases up to 24 h were needed. We had no problems with precipitation of molybdovanadates in our titration solutions, nor did any redox reactions occur.

Results

Fig. 1 presents the variation of ^{51}V NMR chemical shift with pH for solutions 40 mmol dm^{-3} in both V and Mo, at 99 °C. Possible ambiguities have been removed using peak intensity and two-dimensional COSY data. Very similar pH dependences are obtained at room temperature, although with generally poorer resolution and with shifts to lower frequency. For ease of comparison, we report only the room-temperature shifts in Table 1.

Fig. 2 is a similar plot at 99 °C, for the major species only, in solutions 60 mmol dm^{-3} in Mo and 10 mmol dm^{-3} in V. For clarity, resonances are omitted in this figure if they are more dominant in Fig. 1. Thus, an unedited version of the data in Fig. 2 would include 13 more resonances from *cis*- and *trans*-$[Mo_2V_8O_{28}]^{4-}$ (2,8),* $[HMo_4V_5O_{27}]^{4-}$ (4,5) and even $[MoV_9O_{28}]^{5-}$ (1,9) at relatively high pH. Typical spectra are shown in Figs. 3 and 4.

It is now easiest to discuss each species in turn.

$[Mo_4V_2O_{19}]^{4-}$ *and* $[HMo_4V_2O_{19}]^{3-}$ (4,2).—The (4,2) species shows a single pK_a at 3.8 (297 K, see also Figs. 1 and 2). Its shift is δ −498.0, and −512.5 upon protonation. The ^{17}O NMR spectrum of unprotonated (4,2) can be reliably assigned (Fig. 5) from comparisons with known shifts, from peak areas and from broadenings due to ^{51}V couplings. From this, one can be sure that it has the same hexametalate-type double-octahedron structure as is known for (6,0).[3] One can also confirm that the vanadiums are mutually *cis*. Once again (see above) simple electrostatic considerations are insufficient to predict the correct structure. The *cis* structure was not specified by Maksimovskaya and Chumachenko,[4] but is perhaps implicit in their comparison with *cis*-$[W_4V_2O_{19}]^{4-}$.

The unprotonated (4,2) species dominates the ^{51}V NMR spectra at fairly high Mo:V ratios, unless the overall concentration is very high, or the pH below 4. This is partly because of the narrowness of its resonance. It typically accounts for 50% of the vanadium present (Mo:V 60:10 mmol dm^{-3}, pH 5–6) or 20% (40:40, pH 2–5.5). The stoichiometry of (4,2) was further verified by the experiments with crystalline α-(6,2) described below.

The protonated species is somewhat less dominant, and is partially replaced by (5,1), especially upon addition of further Mo or acid. Figs. 1 and 2 show that at 372 K the pH *vs.* shift curve is somewhat distorted, although it is normal at 293 K. We attribute this to fairly rapid chemical exchange with a small amount of α-(6,2) (see below), particularly at pH values close to 3. Diprotonation is ruled out by the potentiometric data.

The large ^{51}V NMR shift upon protonation strongly suggests that the proton attaches near to the vanadium atoms. This is supported by the ^{17}O NMR data (Fig. 5), even though the ^{17}O shifts are not easy to determine below pH 4 because of overlapping resonances and the replacement of species (4,2) by (5,1). Surprisingly, only the peak at δ 787 shifts substantially to lower frequency upon protonation. This implies that protonation takes place at the oxygen bridging the two vanadium atoms (Fig. 5) as anticipated.

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* In general, (q,r) refers to the species $[Mo_qV_rO_x]^{(2x-5r-6q)-}$, or a protonated form of the same. The fuller (p, q, r) notation is used in ambiguous cases. Here p is the number of protons required to convert q units of $[MoO_4]^{2-}$ and r units of $[HVO_4]^{2-}$ to the named compound.

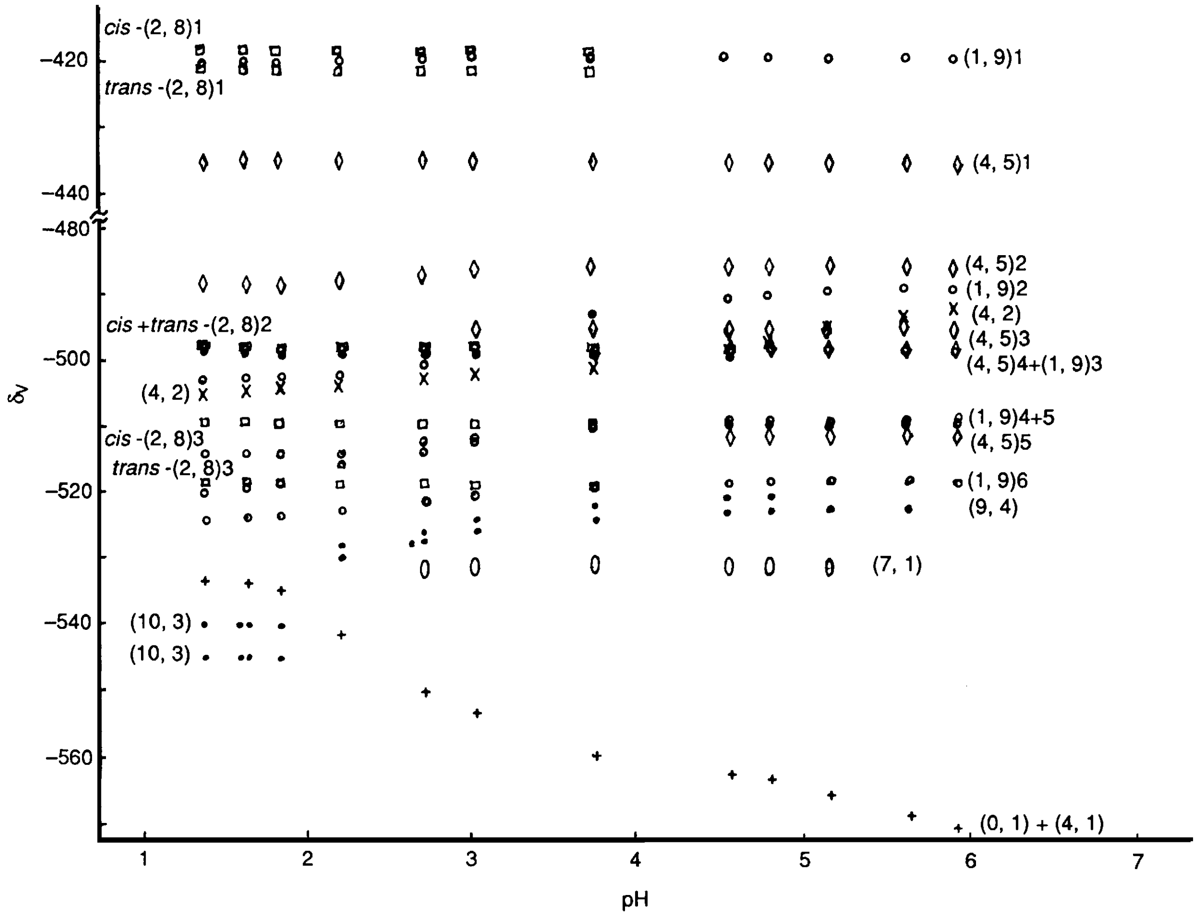


Fig. 1 pH Dependence of the ^{51}V NMR chemical shift of all but the most minor resonances detected in solutions 40 mmol dm^{-3} in both V^{V} and Mo^{VI}, 372 K, 0.6 mol dm^{-3} Na(Cl) medium

The ^{95}Mo NMR spectrum at 99 °C shows only one resolved peak, at δ 124, whose position depends slightly upon pH.

[Mo$_5$VO$_{19}$]$^{3-}$ (5,1).—This ion has already been identified in acetonitrile solutions by Klemperer and Shum.[10]

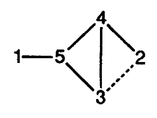
We confirm earlier observations that it gives the narrow, pH-independent resonance at $\delta_V = -506.4$. The peak area closely fits the potentiometric data at all pH values. The resonance reaches its maximum between pH 1.5 and 4.0, and its narrowness must arise from the near-zero field gradient at V, which arises because this atom is confined to an internal diagonal of the double-octahedron structure. Our detailed ^{17}O NMR data (Fig. 5) together with the peak areas (not shown) confirm this structure in every detail; the comparison with species (4,2) in the same figure and non-aqueous (6,0)[3] (δ_O = 927, 559, −32) is striking, although the shifts do differ by up to 20 ppm from those in acetonitrile.[10]

The ^{95}Mo NMR spectrum shows only one resolved peak, at δ 128. We have no clear evidence for the existence of *fac*-[Mo$_3$V$_3$O$_{19}$]$^{5-}$ at any pH value, in contrast to the tungsten analogue.[2]

The tetramethylammonium salt of species (5,1) was also prepared, as described in the Experimental section. Its solid-state ^{51}V MAS NMR spectrum was obtained at 4.5 and 10.5 kHz spinning rates, and shows a rather sharp main peak at δ −497, consistent with a very low electric field gradient at V. The sidebands reveal a moderate shift anisotropy, and may be analysed approximately to give $\delta_\perp = -580$ and $\delta_\parallel = -330$.

[Mo$_4$V$_5$O$_{27}$]$^{5-}$ *and* [HMo$_4$V$_5$O$_{27}$]$^{4-}$ (4,5).—In our previous paper we noted that the decavanadate framework can support two, but not three substitutions of Mo for V, at least in respect of aqueous species. One would therefore anticipate that the next species to become important as the proportion of Mo is increased should have a different structure. This expectation is only partially fulfilled. The next set of peaks to emerge is labelled in Fig. 1 as (4,5)1–5, in the usual order of decreasing frequency, and it is immediately obvious that their pattern of shifts resembles that of the (1,9) and (2,8) peaks, with one resonance lying to markedly higher frequency. For the same reason, it is also evident that the ^{51}V NMR resonances of this species suffer from severe overlaps with other, often stronger peaks. However, a careful study of integrals, particularly in solutions with comparable and fairly high concentrations of V and Mo, proves beyond doubt that this species yields five vanadium resonances of equal area.

One might have supposed, both on electrostatic grounds, and by analogy with the known[11,12] solid-state species [Mo$_8$V$_5$O$_{40}$]$^{7-}$ and [Mo$_4$V$_8$O$_{36}$]$^{8-}$, that the vanadium octahedra would have been separated by molybdenum octahedra. However, this is not the case. All the vanadiums show couplings to other vanadiums in COSY spectra at 99 °C. The correlations derived from several spectra at different concentrations and pH values are shown in Scheme 1 where the numbers refer to the peak labels, and the dashed line indicates uncertainty. Some of these correlations are shown in Fig. 6. One would expect them to arise[1] from edge sharing of VO$_6$



Scheme 1

octahedra, although a broader resonance such as 1 may well fail to reveal all its neighbours in such an experiment. In general, a correlation is also more likely to appear if the V–O–V link does not involve long bonds. A favourable case is that of a two-coordinate oxygen.

The data described so far suggest that the VO_6 octahedra are relatively clustered, in a manner comparable with *e.g.* species (1,9). However, as the new species is stable in the same pH range as (1,9) but with higher molybdenum(VI) content, it is likely to have less metal atoms than (1,9) in order to increase its negative charge. Some partially counterbalancing loss of O is also likely.

Potentiometric measurements were attempted at this stage, together with estimates of abundance from the isolated (4,5)1

Table 1 (*a*) Major species in the H^+–$[MoO_4]^{2-}$–$[HVO_4]^{2-}$ system

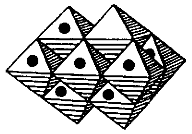
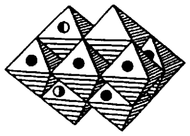
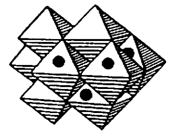
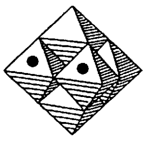
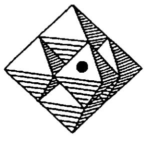
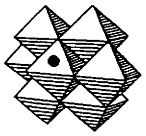
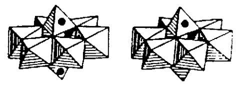
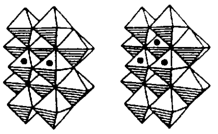
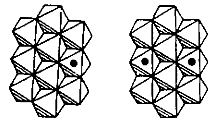
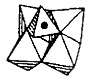
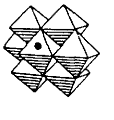
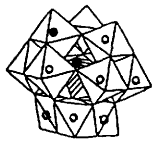
Group labels and symbols in diagrams	(*p*,*q*,*r*) Notation	log $\beta_{p,q,r}$	pK_a	δ_V	Formula	Found or proposed structure[a]
q	(15,1,9)	134.56(10)		Ref. 1	$[MoV_9O_{28}]^{5-}$	
○	(16,1,9)	137.33(16)	2.77		$[HMoV_9O_{28}]^{4-}$	
r □	(16,2,8)	133.0(2)		Ref. 1	$[Mo_2V_8O_{28}]^{4-}$	
k	(13,4,5)	105.22(4)		V^{1}[b] −440.0 V^{2} −491.6 V^{3} −501.6 V^{4} −504.4 V^{5} −518.6	$[Mo_4V_5O_{27}]^{5-}$	
◇	(14,4,5)	107.58(16)	2.36	[c]	$[HMo_4V_5O_{27}]^{4-}$	
e	(8,4,2)	60.37(5)		−498.0	$[Mo_4V_2O_{19}]^{4-}$	
×	(9,4,2)	64.11(6)	3.74	−512.5	$[HMo_4V_2O_{19}]^{3-}$	
f	(9,5,1)	59.14(5)		−506.4	$[Mo_5VO_{19}]^{3-}$	
●	(15,9,1)[d]	95.0(2)		−504.7	Not known	
g 0	(11,7,1)	74.63(5)		−537.2	β-$[Mo_7VO_{26}]^{5-}$	
(*b*) Minor species						
h	(11,6,2)	79.3(1)		−500.2	α-$[HMo_6V_2O_{26}]^{5-}$	
	(12,7,1)	76.9(2)		−502.6	α-$[HMo_7VO_{26}]^{4-}$	
i	(19,10,2)	122.1(2)		−526	$[HMo_{10}V_2O_{38}]^{5-}$	
	(17,9,3)	122.1(2)		−516	$[Mo_9V_3O_{38}]^{7-}$	
◇	(18,9,3)	125.3(2)	3.2	−525.8(2) −522.6(1)	$[HMo_9V_3O_{38}]^{6-}$	

Table 1 (*continued*)

Group labels and symbols in diagrams	(*p*,*q*,*r*) Notation	log $\beta_{p,q,r}$	pK_a	δ_V	Formula	Found or proposed structure[a]
j, (8,2)-P ○	(16,9,1) (15,8,2)	97.7(2) 101.3(2)		−515 −519	$[HMo_9VO_{32}]^{4-}$ $[HMo_8V_2O_{32}]^{5-}$	
t ◑	(5,4,1)	36.6(1)		−567[e]	$[Mo_4VO_{17}]^{5-}$	
	β-(12,6,2)	81.8(2)		−539.3	β-$[H_2Mo_6V_2O_{26}]^{4-}$	
s	21,10,3	137.0(2)		−505 −525 −547.8 −548.0	$[V(Mo_{10}V_2O_{40})]^{5-}$	
	18,10,2	119.5(2)		−511.7	Not known	Not known

[a] ●, Vanadium sites; ○, alternative vanadium sites. [b] As in Fig. 8. [c] Reliable shifts not available for species (14,4,5). [d] Minor species, evaluated together with (9,5,1). [e] Together with $[H_2VO_4]^-$.

peak. The fit to a (4,5) species, *i.e.* $[Mo_4V_5O_{27}]^{5-}$, was twice as good as that to the nearest other possibility, (5,5). The same calculation showed (8,10) to be impossible. This means that the anion can have no symmetry, and is indeed chiral.

It also proved possible to obtain ^{95}Mo NMR spectra of the species, although the resonances are broad, overlapping and complicated by the presence of molybdate at *ca.* δ 0. A spectrum is shown in Fig. 7. It is consistent with the presence of four inequivalent Mo atoms. Using all the above data, we propose the structure shown layer by layer in Fig. 8. This structure is a chimaera; at one end it is that of (1,9)[1] and at the other that of (7,0)[9] or β-(8,0).[8] To confirm the structure, we identified as many oxygen resonances of (4,5) as possible, by eliminating other known or disproportionate resonances from ^{17}O NMR spectra such as the one shown in Fig. 4. We then compared these with shifts calculated from those of known structures such as the above (1,9) and (8,0) species, and the (7,1) species described below. The comparisons are presented in Fig. 8, together with details of the other shifts. They are very satisfactory.

It is apparent from Fig. 1 that species (4,5) protonates once, with p$K_a \approx 2.5$, and this is closely confirmed by the potentiometric data. Unfortunately the protonated form is less stable, and only occurs in a pH region where precipitation occurs during prolonged heating. It has therefore proved impossible to trace its resonances reliably, even with two-dimensional NMR spectroscopy. Fig. 1 shows that peak 2 moves further than peak 1 upon protonation, as is also observed for the decavanadate or (1,9) peaks of similar shift. However, its protonation shift is small compared with any of the (1,9) resonances other than (1,9)3. Further study of many spectra probably shows that none of the ^{51}V NMR resonances of species (4,5) is particularly sensitive to pH, for otherwise they would move to less crowded regions of the spectrum. It is therefore likely that the protonation of (4,5) occurs at a site nearer to Mo than to V.

β-$[Mo_7VO_{26}]^{5-}$ (7,1).—It proved possible to identify one further new species in some detail. It gave a fairly broad ^{51}V NMR resonance whose shift of δ −537.2 was independent of pH over its entire stability range (pH *ca.* 2–6). The relative area of this resonance was maximal at very high Mo:V ratios, which suggested that the species might have an isopolymolybdate structure with minimal substitution of V for Mo. This hypothesis was supported by its concentration dependence, for this ruled out any highly polymerized species.

Because the species was dominant under appropriate conditions, it was possible to obtain fairly complete ^{17}O NMR data for it, except in the very crowded region δ 820–860. The ^{17}O shifts are provisionally assigned in Fig. 9, together with the known shifts of the aqueous β-(8,0) isopolymolybdate.[8] They correspond very closely, when one allows for the known consequences of substituting V for Mo. Furthermore, it is entirely consistent that the most favourable pH for the new species is *ca.* 4.2, whereas that for β-(8,0), with one less negative charge, is *ca.* 2.5.[6] We conclude that the new species is β-(7,1), with the structure as shown (*via* successive layers) in Fig. 9. The potentiometric data rigorously confirm this composition.

β- *and* α-$[Mo_6V_2O_{26}]^{6-}$ (6,2).—As both β-(8,0), and β-(7,1) and α-(6,2) (see below), are present in solution in significant proportions under appropriate conditions of pH and concentration, it might have seemed reasonable to expect species β-(6,2) to be present also, at the higher pH values. Indeed, crystals of β-(6,2) have been obtained from such solutions, and their structure confirmed by X-ray crystallography.[13] However,

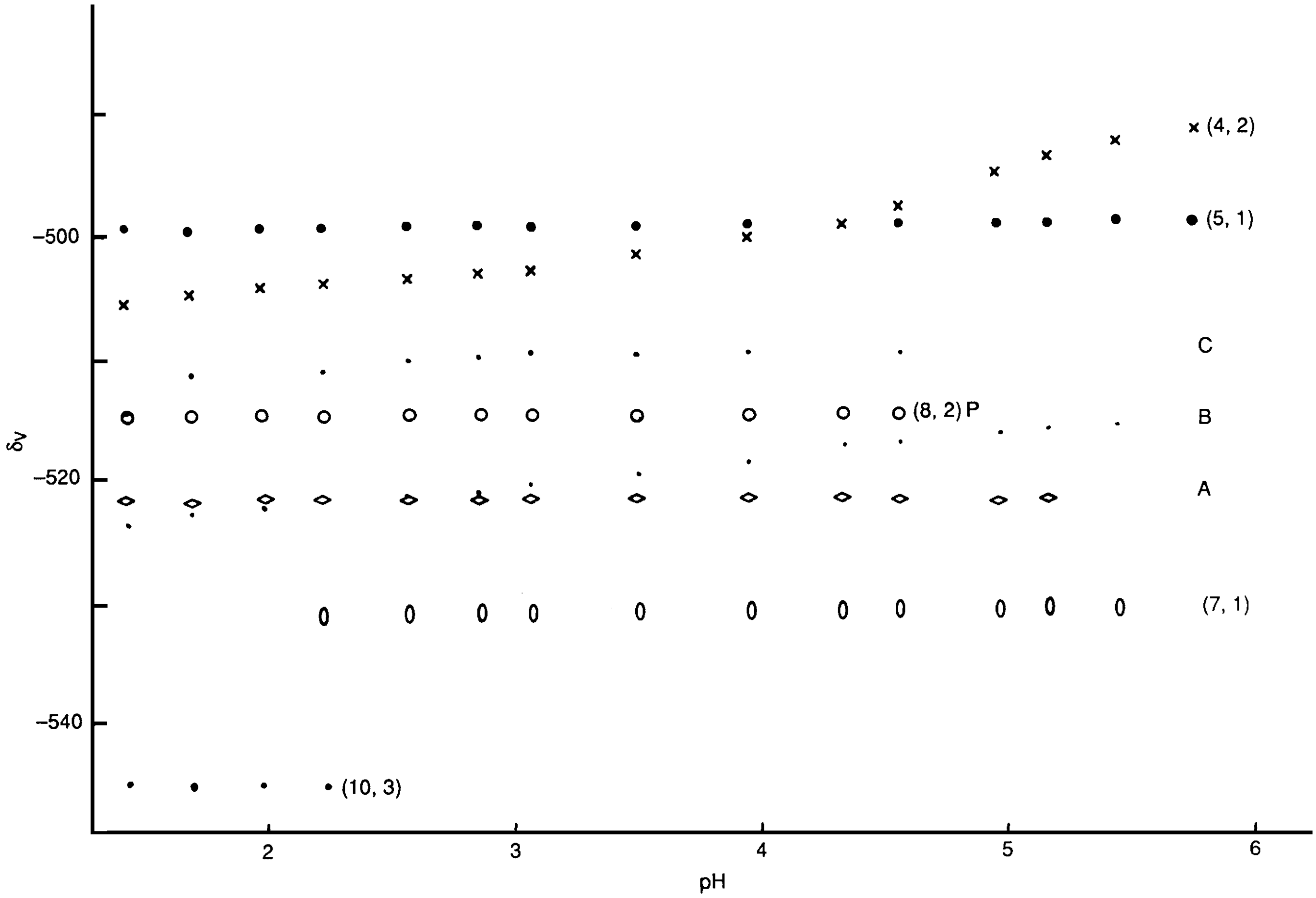


Fig. 2 pH Dependence of the ^{51}V NMR chemical shift of the major resonances detected in a solution 60 mmol dm^{-3} in Mo^{VI} and 10 mmol dm^{-3} in V^{V}, 372 K, 0.6 mol dm^{-3} Na(Cl) medium

when authentic crystals of β-(6,2) were added to water, adjusted to various pH values, they were essentially insoluble, although they did eventually dissolve after decomposition to known solution species. This insolubility ruled out any easy identification of β-(6,2), even though its original preparation shows that it must be present in solution, at least at low concentration. One might anticipate a chemical shift close to that of β-(7,1), and also the possibility of protonation. In fact, a fairly weak resonance (*ca.* 1% of total V) is resolvable, just to low frequency of that of β-(7,1), at pH values where the latter is not too dominant, and at Mo:V ratios *ca.* 3–6:1. In the pH range 1.7–3.0 it appears at δ −539.3, and in the range 4.5–5.8 at δ −540.9, and slightly broader. Our calculated distribution of species (see below) shows that the former pH range is precisely the optimum for the appearance of doubly protonated β-(12,6,2), and the latter for singly protonated β-(11,6,2) [compare the distribution of the α-(11,6,2) species]. However, because of the obscuring β-(7,1) peak, it has not been possible to link the resonances at δ −540.9 and −539.3 unambiguously. If our interpretation here is correct, then the protonation is expected to occur away from the central vanadium sites.

The corresponding experiments with the authenticated species α-(6,2)[14] had a different outcome. These crystals were moderately soluble, so that a ^{51}V NMR spectrum could be obtained within 1 min, at room temperature, and a ^{17}O NMR spectrum within 3 min, using slightly enriched water. Although the process of dissolution led to substantial decomposition,[4] notably to (4,2), a reasonably narrow peak at δ_V −500.2 (pH *ca.* 4) was found which decreased within a few minutes towards a long-term value of less than half its original relative height (Fig. 10). We identify this resonance as that of the tetrahedrally co-ordinated vanadium atom *in* α-(6,2). The pH range suggests that this species is probably protonated in aqueous solution, and calculations on combined e.m.f. and NMR data strongly support this contention.

The resonance narrows relative to other resonances on cooling, which supports the existence of the exchange process discussed below. Its vanadium chemical shift at 270 K is plotted against a limited pH range in Fig. 11, along with that of (4,2), (5,1) and two other more minor species to be discussed below, which are not too seriously obscured by the larger resonances at this temperature.

As mentioned above, the resonance of species α-(6,2) is not detectable at 99 °C. Instead, one observes a deviation of the (4,2) resonance from the usual titration sigmoid. It must follow that α-(6,2) and (4,2) are in relatively rapid chemical exchange at this temperature.

The ^{51}V NMR data show that the equilibrium concentration of α-(6,2) is typically 10% of that of (4,2). Its ^{17}O NMR resonances should therefore be difficult to detect, although one might hope to find at least the 12 equivalent Mo–O oxygens. When the ^{17}O NMR spectrum was obtained rapidly, as described above at pH *ca.* 4.5, the dominant resonances were indeed those of (4,2), together with the stoichiometrically anticipated contribution from $[MoO_4]^{2-}$. This observation confirms the identification of species (4,2). However, some minor resonances were also detectable, despite substantial noise. The strongest of these, at δ_O 1005, changed with time in the same way as the ^{51}V resonance at δ −500.2. We therefore assign it to the terminal Mo–O oxygens of α-(6,2). This oxygen shift is about 150 ppm higher than these of the terminal Mo–O resonances for most of the other species studied. This may be related to the fact that the molybdenum units in α-(6,2) essentially form a ring of six MoO$_4$ tetrahedra, with only very long additional bonds (2.34 Å) to the two VO$_4$ tetrahedra above and below the Mo$_6$ ring.[14] An oxygen shift of 1000 ppm would not be unreasonable for an MoO$_4$ unit with tetrahedral Mo. The other anticipated oxygen resonances for α-(6,2) have

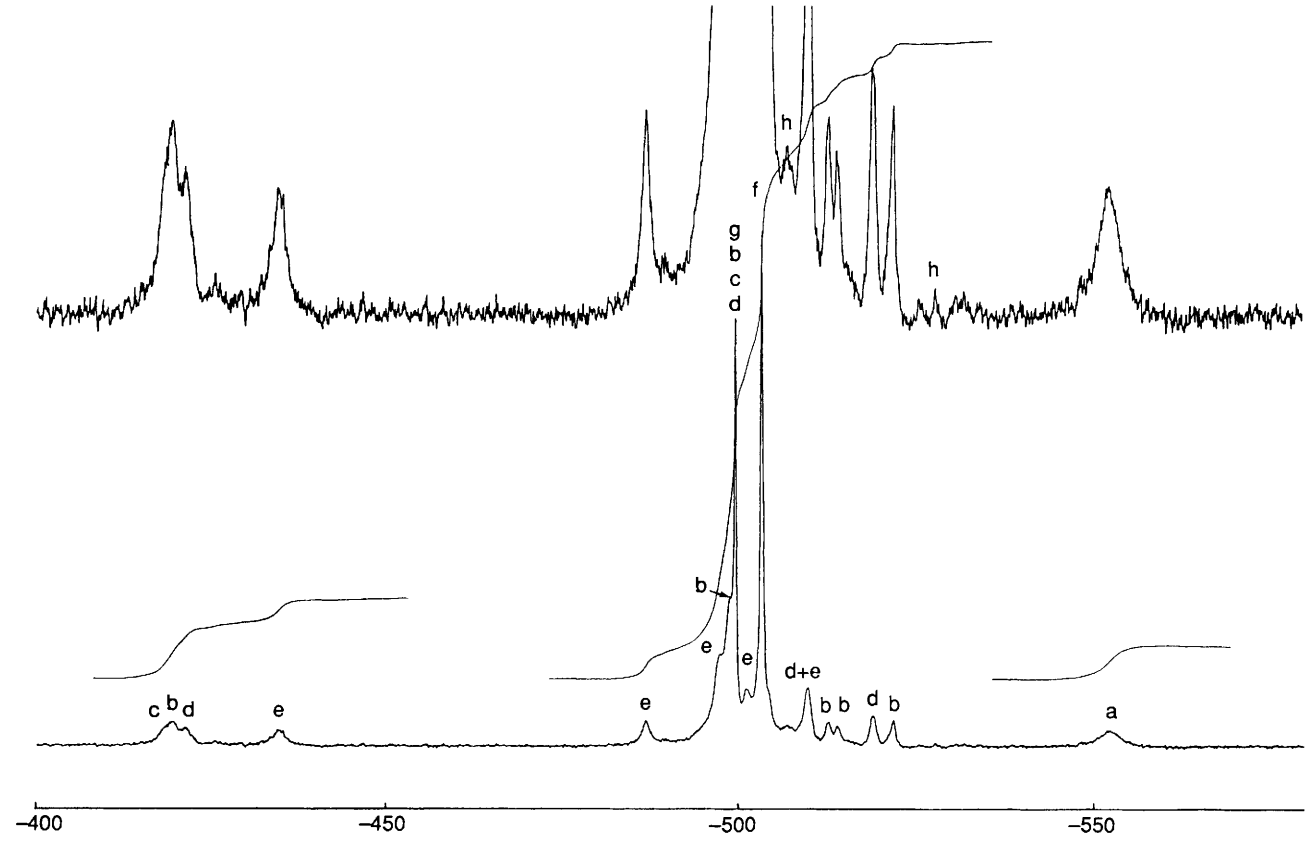


Fig. 3 Typical ^{51}V NMR spectrum plus × 8 vertical expansion: 15.1 mmol dm^{-3} Mo, 10.0 mmol dm^{-3} V, 372 K, room temperature pH 2.95. Species: a, (0,1) + (4,1); b, (1,9); c, *cis*-(2,8); d, *trans*-(2,8); e, (4,5); f, *cis*-(4,2); g, (5,1); h, probable (9,4) Keggin species

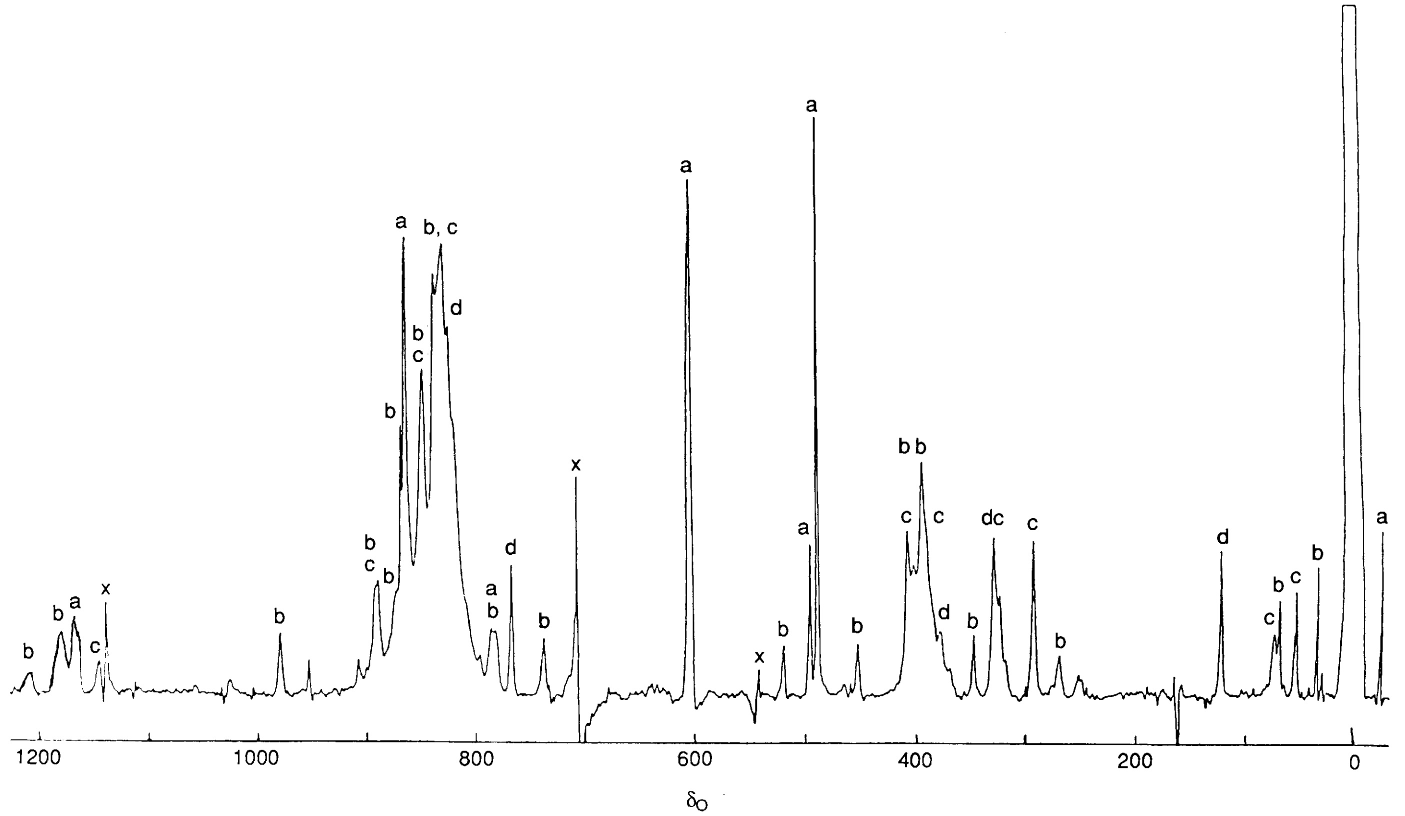


Fig. 4 Typical ^{17}O NMR spectrum, 294 K, pH 4.8, obtained after full equilibration of a saturated solution of species α-(6,2) in water enriched to 5 atom % in ^{17}O. Species: a, *cis*-(2,4); b, (4,5); c, (1,7); d, (0,7); x, known spectrometer artefact

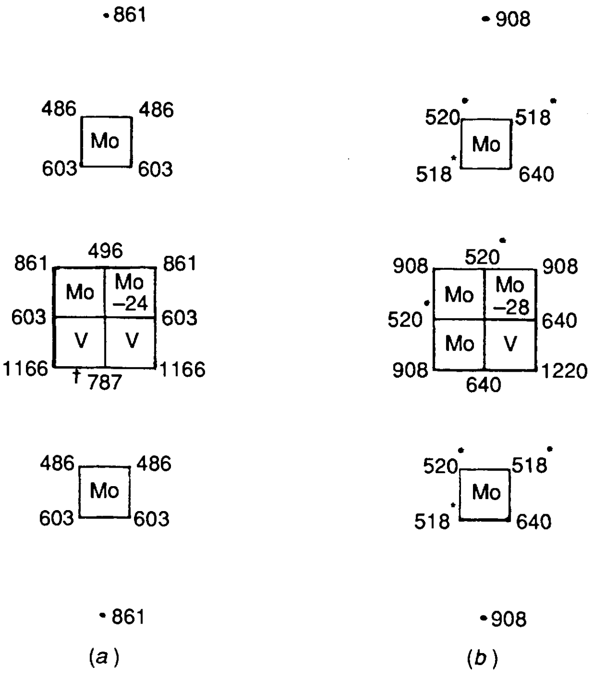


Fig. 5 Species *cis*-(4,2) (*a*) and (5,1) (*b*): structures by successive layers and ^{17}O NMR shifts at 293 K assigned as in the text. * Assignment interchangeable; † peak shifts upon protonation

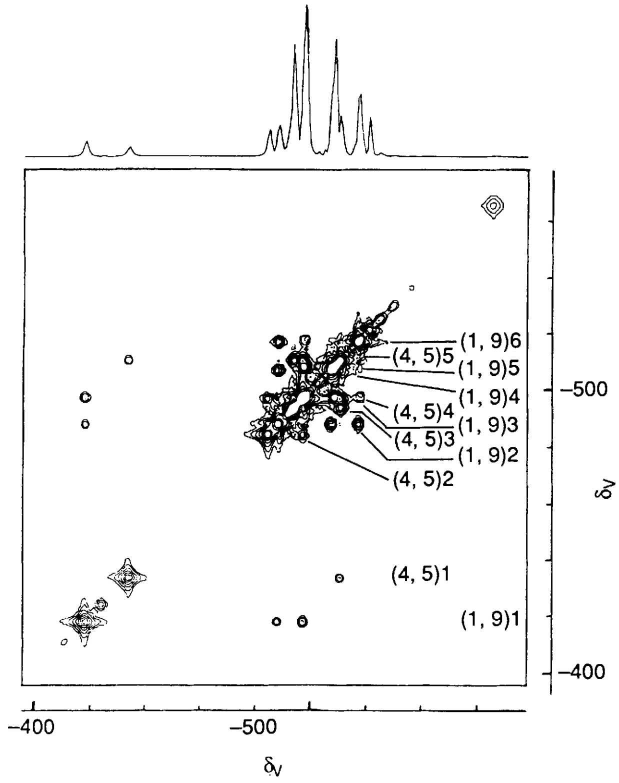


Fig. 6 ^{51}V–^{51}V COSY spectrum, 372 K, 500 mmol dm^{-3} V plus 214 mmol dm^{-3} Mo, room temperature pH 3.2

not been reliably identified. Not only are there less oxygens contributing to each resonance, but also one would expect at least those from the oxygens attached to vanadium to be broader.

The ^{51}V NMR resonance assigned to species α-(6,2) indeed reaches a maximum relative intensity consistent with Mo:V = 3:1. However, it regains some intensity at very high Mo:V ratios, and could therefore also include a contribution from α-(7,1). This species would be expected to have an almost identical ^{51}V shift, and its existence would complete the known sequences (6,2), (7,1) and (8,0) for both α and β structures.[3,13,14,18] The calculations on combined e.m.f.–NMR data support this interpretation. Without doubt an additional high-ratio species is needed to explain the shift of the α-(6,2) peak at low pH. The two species (12,7,1) and (11,6,2) explained the data fairly well. If α-(11,7,1) and α-(12,6,2) species were also to exist they would have to be present only in very low concentrations.

A solid-state MAS NMR spectrum of species α-(6,2) has also been obtained. It shows a relatively sharp single resonance at δ −480, with small sidebands only, as expected for tetrahedrally co-ordinated vanadium in an axially symmetric environment.

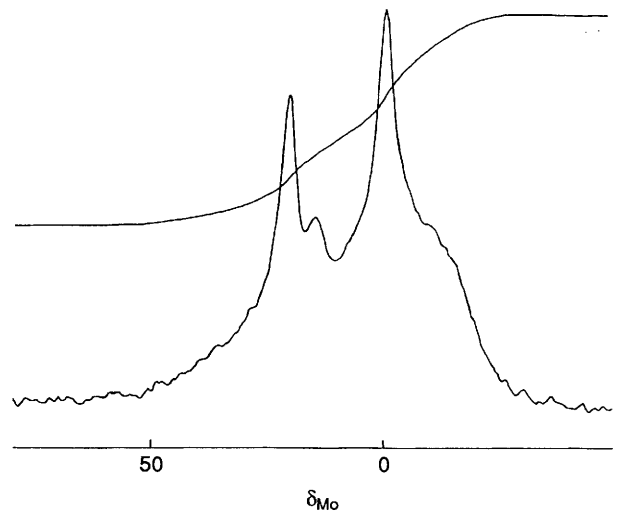


Fig. 7 Molybdenum-95 NMR spectrum, low δ region, 372 K, pH (293 K) = 5.25, 250 mmol dm^{-3} in V and Mo. Peaks arise mainly from species (4,5), (1,0) and (7,0)

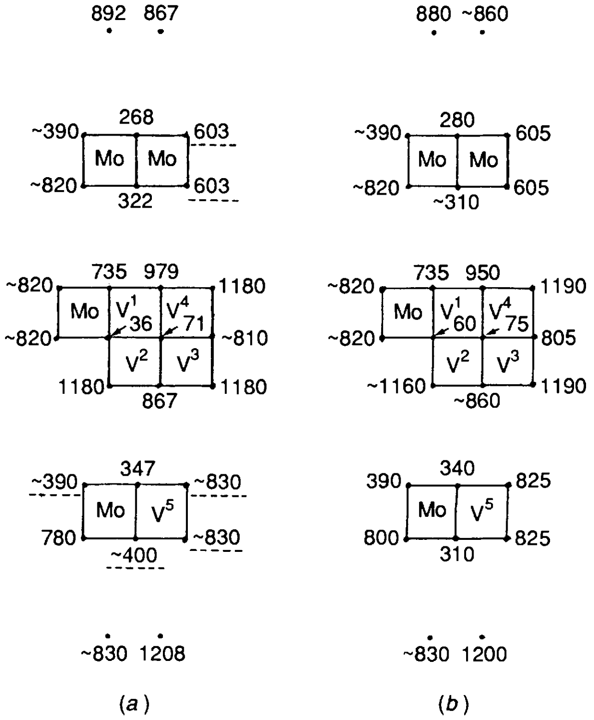


Fig. 8 Successive layer diagram structures of species (4,5) with ^{17}O NMR shifts at 293 K assigned as in the text: (*a*) experimental data; (*b*) shifts predicted by analogy with related species. Dotted underlining indicates an unresolved peak in a crowded spectral region with adequate total intensity

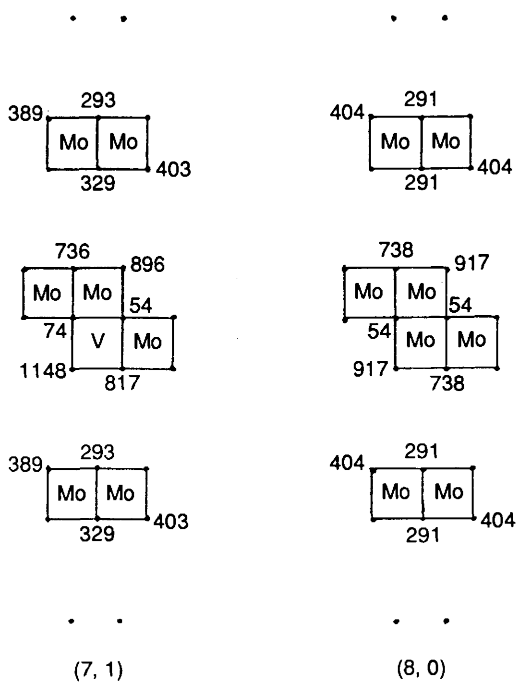


Fig. 9 Layer structure and ^{17}O NMR shifts at 293 K for species β-(7,1) compared with published[9] shifts for the isostructural β-(8,0) anion. Unmarked terminal oxygens all have resonances lying in a crowded region between δ 820 and 860

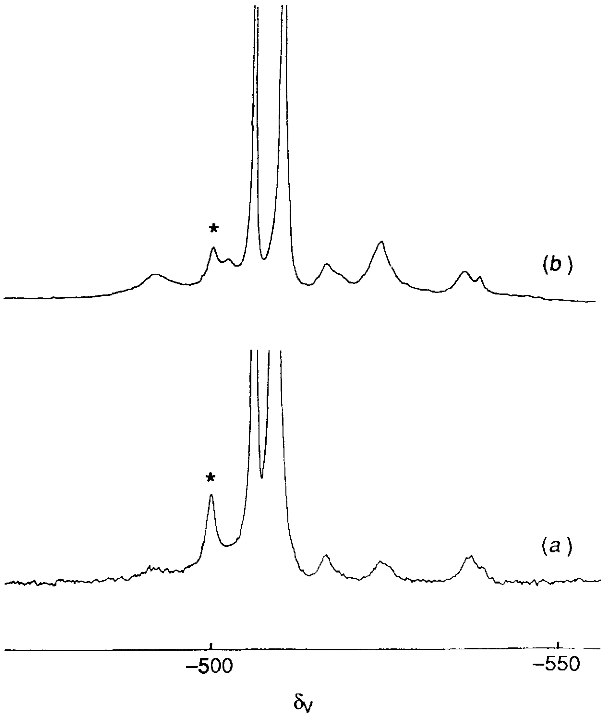


Fig. 10 Vanadium-51 NMR spectra at 293 K of (*a*) a solution obtained within 1 min of the partial dissolution of crystals of species α-(6,2) at pH ≈ 3.0 [* indicates proposed α-(6,2) resonance] and (*b*) as (*a*) but equilibrated at approximately the same pH

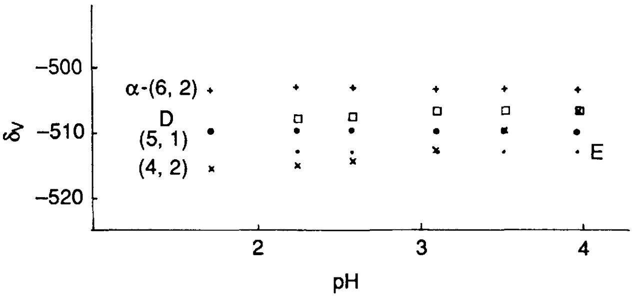


Fig. 11 Vanadium-51 NMR chemical shifts of selected narrow-line species over a limited range of pH, 60 mmol dm^{-3} Mo, 10 mmol dm^{-3} V, 270 K

Keggin Structures.—As mentioned earlier, Leparulo-Loftus and Pope[2] have identified the ^{51}V NMR resonances of many isomers of $[V(W_{10}V_2O_{40})]^{5-}$ and $[V(W_9V_3O_{40})]^{6-}$. These formulae are written to indicate that the central, tetrahedrally co-ordinated atom in the α-Keggin structure is vanadium. Its resonances, which are generally narrower than the others, fall in the range δ −550 to −560, with those for the $V(W_9V_3)$ complexes towards the higher δ values. The positions of the other vanadium resonances depend on neighbours. In general, 'isolated' VO_6 octahedra resonate between δ −520 and −535, whereas VO_6 octahedra sharing an edge with another VO_6 unit resonate between δ −500 and −510. Clusters of three VO_6 octahedra with a common vertex yield even higher shifts, *e.g.* δ −480.

These Keggin species dominate the tungstovanadate spectra, once the solutions have slowly reached equilibrium. In contrast, our spectra show that they can only be minor components of the corresponding molybdovanadate solution. However, these do show a number of small resonances other than those described so far, whose relative areas, linewidths and dependence upon pH and concentration is consistent with similar formulae and structures, *i.e.* $[V(Mo_{10}V_2O_{40})]^{5-}$ and $[V(Mo_9V_3O_{40})]^{6-}$. Evidently they are somewhat less stable than the corresponding tungstovanadate Keggin species in comparison with structures based exclusively on edge-shared octahedra. The structure of a related singly reduced heteropoly blue, $K_6[V(Mo_{10}V_2O_{40})]\cdot 13H_2O$, has been reported by Björnberg.[19]

The position of some of these resonances are shown in Figs. 1 and 2. Their total area never exceeds 3% of the ^{51}V NMR spectrum. Other similar resonances are undoubtedly present, under other larger peaks. In general, the central vanadium resonance appears at somewhat higher shift than for the corresponding tungstovanadate. Thus at lower pH, where $[V(Mo_{10}V_2O_{40})]^{5-}$ should be favoured, two small and rather sharp resonances appear in constant ratio at δ −547.8 and −548.0 (Fig. 12). (At higher temperatures one of these in particular shifts to higher frequency.) It is unlikely that resonances as sharp as this could arise from octahedral V. At higher pH values other sharp, pH-dependent, resonances appear around δ_V −525. Further similarly weak but broader resonances are detectable under some conditions around δ_V −505, and one appears as high as δ −425.5. This latter resonance may perhaps arise from a species with different structure. All the other resonances, however, correspond acceptably with the tungstovanadate Keggin-structure shifts, once one bears in mind that the vanadiums in molybdovanadates generally resonate to high frequency of the corresponding tungstovanadates (*cf.* aqueous $[Mo_5VO_{19}]^{3-}$, δ_V −506.4; $[W_5VO_{19}]^{3-}$, δ_V −522.9).[2] Of course, it remains possible that some of them nevertheless arise from other species, as yet unidentified.

More Condensed Species.—The resonances thus far assigned explain essentially all the data at Mo : V < 1 : 1, and much of that at higher ratios. Two other vanadium resonances are sufficiently prominent to permit ^{17}O NMR spectra to be obtained, even though these have not been as reliably assigned. They both dominate the spectra only at the highest concentrations achievable, and therefore must arise from species of relatively high molecular mass.

The first resonance, δ_V −519.0 at room temperature, is one of those which dominates at lower pH values, and is also maximal at Mo : V ≈ 4 : 1. It forms relatively slowly, taking 24 h at room temperature to reach full height. Its dependence on concentration and pH fit well with a formula [HMo$_8$V$_2$O$_{32}$]$^{5-}$. Because it can be made fully dominant at very high concentration, one can obtain its ^{17}O NMR spectrum, having physically removed the resonances of the more labile isopolymolybdates by selective saturation of the water resonance,[9] and mentally removed known (5,1) resonances (Fig. 13). Surprisingly few peaks remain, indicating high symmetry for the species. A planar structure (Fig. 14) fits the ^{17}O NMR data acceptably. The detailed assignment of the terminal Mo–O resonance group (δ 800–870) and of the bridging oxygens is only tentative here, and reliant on the assumption that the broader resonances experience coupling to V. The proposed structure is a relatively novel one in the polymetalate area, although the Mo$_4$ units relate to the [Mo$_4$O$_{10}$(OCH$_3$)$_6$]$^{2-}$ anion reported

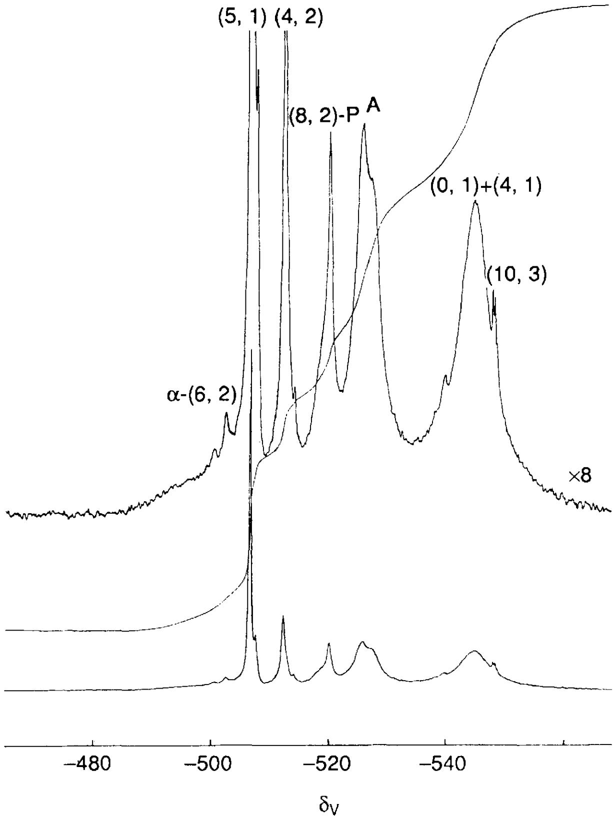


Fig. 12 Partial ^{51}V NMR spectrum plus × 8 vertical expansion, 294 K, pH 1.70, 60 mmol dm^{-3} Mo plus 10 mmol dm^{-3} V, showing narrow peaks at δ −548 attributed to the central V atom in species (10,3) with a α-Keggin structure

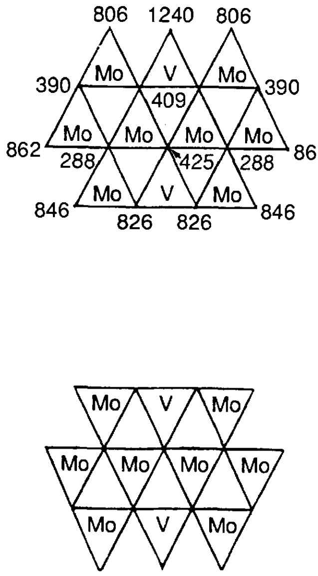


Fig. 14 Proposed layer structure and experimental ^{17}O NMR shifts at 323 K of species (8,2)-P. The precise assignments of the terminal oxygens (δ 806–862) and of the bridging oxygens (δ 288–409) are not known

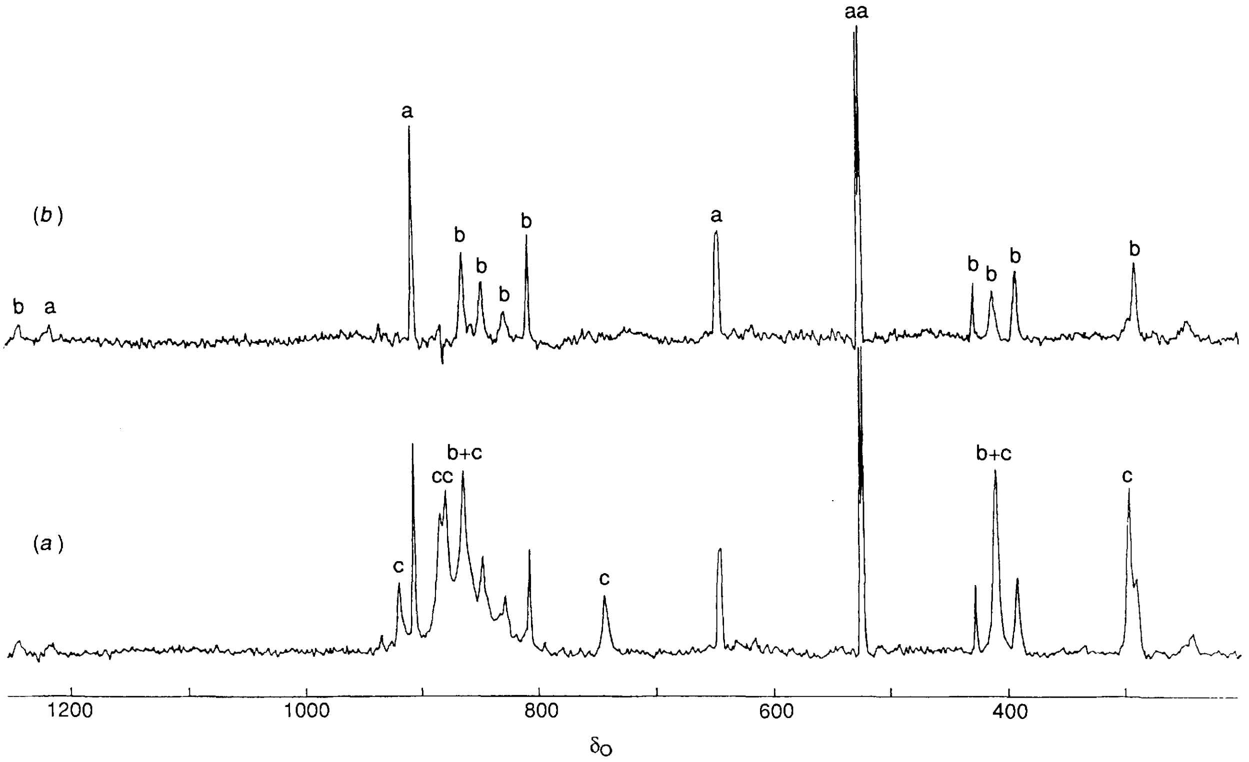


Fig. 13 Partial ^{17}O NMR spectra at 323 K, *ca.* 1 mol dm^{-3} Mo plus 100 mmol dm^{-3} V, pH 2.2: (*a*) normal spectrum; (*b*) solvent-labile oxygens subtracted as described in the text. Species: a, (5,1); b, proposed (8,2)-P resonances; c, (8,0)

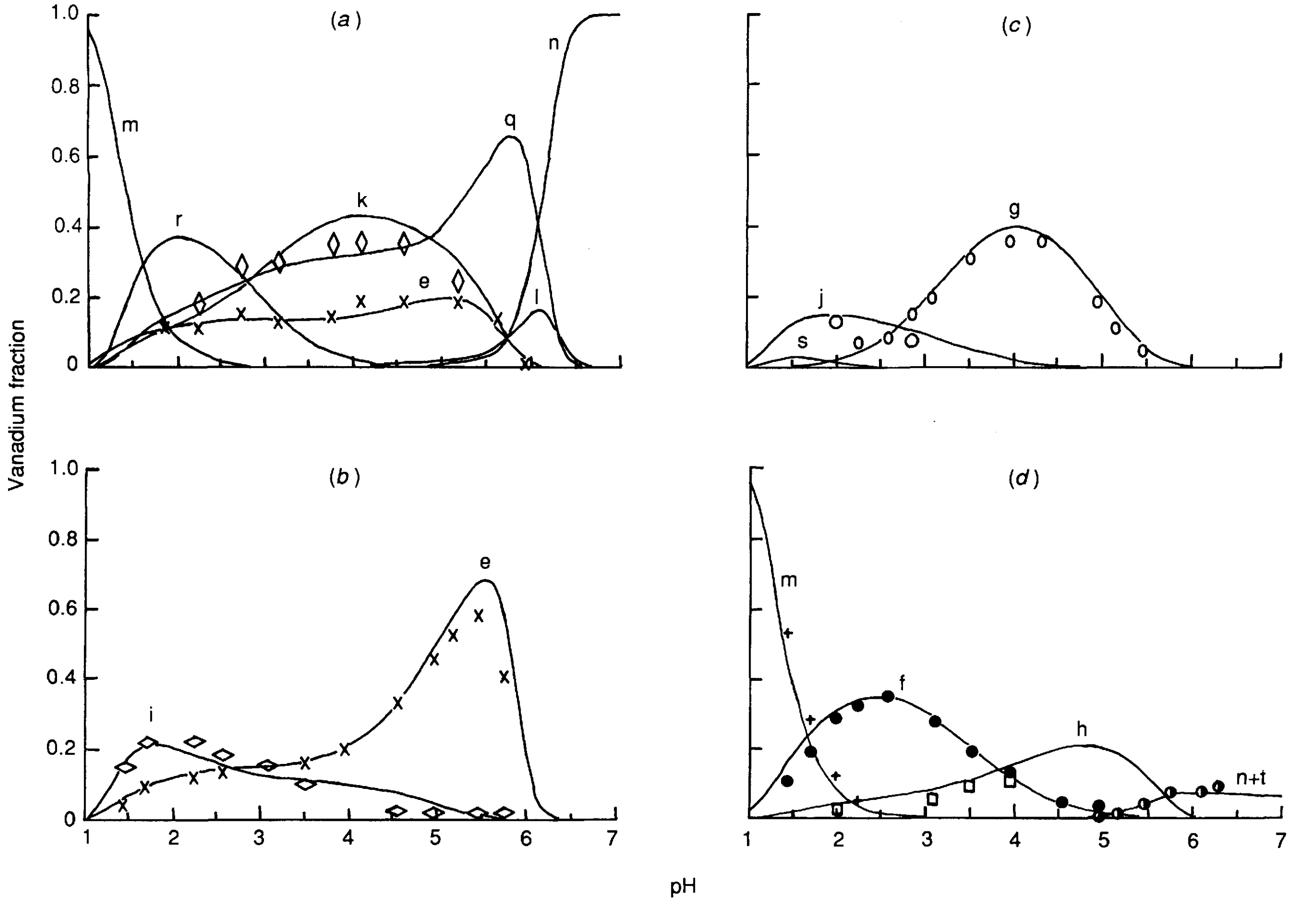


Fig. 15 Concentrations of selected species, measured as the fraction of vanadium present in each, *versus* pH. Solid lines are calculated as described in the text. Symbols are as in Table 1 and Figs. 1 and 2. They show experimental ^{51}V NMR integral data. Proposed structures are shown in Table 1. (*a*) [Mo] = [V] = 40 mmol dm^{-3}. ◇, (13,4,5) +(14,4,5), k; ×, (8,4,2) + (9,4,2), e; q, (15,1,9) + (16,1,9); r, (16,2,8); l, (10,0); *m*, $[VO_2]^+$; *n*, (1,0,1). (*b*) [Mo] = 60, [V] = 10 mmol dm^{-3}. ◇, (19,10,2) + (17,9,3) +(18,9,3), i; ×, (8,4,2) + (9,4,2), e. (*c*) [Mo] = 60, [V] = 10 mmol dm^{-3}. ○, (15,8,2) + (16,9,1), j; 0, (11,7,1), g; s, (21,10,3) (Keggin). (*d*) [Mo] = 60, [V] = 10 mmol dm^{-3}. +, $[VO_2]^+$, m; ●, (9,5,1) + (15,9,1), f; ◑, (5,4,1), t + (1,0,1), n; □, (11,6,2) + (12,7,1), h

by Ma *et al.*[20] We refer to it below and in Fig. 2 as (8,2)-P to indicate its planarity.

The second resonance is more correctly described as a group of resonances, labelled A, B and B′ in Fig. 2, and dominated at high concentration and pH 2–3 by a peak with δ_V −525 at room temperature. The area of this group fits closely with the calculated distribution (see below) for the sum of the three species $[Mo_9V_3O_{38}]^{7-}$ [(9,3)], $[HMo_9V_3O_{38}]^{6-}$ [H(9,3)] and $[HMo_{10}V_2O_{38}]^{5-}$ [H(10,2)]. The ^{51}V NMR spectrum in this region is complex, implying the presence of several species, but it simplifies in the range pH 4.3–5.0 to show two medium-width resonances at δ_V −525.8 and −522.6, in the area ratio 2:1. We propose that these arise from the two distinct vanadium types in species (9,3), whose structure has already been determined[21] to be of 'double-heptamolybdate' type.

The ^{17}O NMR spectra of a relatively concentrated solution with an Mo:V molar ratio of 3:1, at pH *ca.* 4, are too complex for full analysis. However, two similar groups, of three peaks each, are observed for these solutions in regions removed from those usually found with isopolymolybdates, under conditions where the ^{51}V resonance in the δ −525 region is relatively dominant. The first group is at δ_O = 1094, 1072 and 545, with the approximate area ratio 1:2:2. The second group is at δ 1011, 998 and 582, with the same area ratio. All these peaks show evidence from their shapes of couplings to ^{51}V, which is not surprising in view of their unusual shifts. Either group is consistent with the species (9,3), for the resonances could arise from the V–O–V (bridging), VO (terminal) and the V–O–Mo (bridging) oxygens on the two equivalent vanadiums. The presence of two groups of course shows that another rather similar species must also be present. The other, severely overlapped, new oxygen resonances occur mainly in the regions associated with Mo–O (terminal) and Mo–O–Mo (bridging) oxygens, and are thus not inconsistent with the above partial assignment.

The composite resonance B in Fig. 2 has a strong component at low pH (B′) which disappears by pH 4.7, leaving only the more minor B component. The dependence of B′ upon concentration is consistent with a species (10,2) as mentioned above. Its structure is not known, but may be related to the double-hepta (9,3) species.

Further Minor Species.—The above discussion covers most of the ^{51}V NMR resonances detectable at 99 °C and above pH 2, other than for species (0,1) (see below), a broad resonance at δ −495, representing typically 5% of the spectrum area, peaks C (Fig. 2) and D (Fig. 11). Peak C is narrow and constitutes *ca.* 1% of the vanadium present at room temperature. It is maximal at Mo:V ≈ 4:1, but is not resolved over a sufficient pH range to allow a precise correlation with any calculated distribution. One possible formulation could be $[H_4Mo_4VO_{18}]^{3-}$, with a structure derived from (5,1) by removal of the Mo *trans* to V, along with its associated terminal oxygen, followed by protonation at the four previously bridging oxygens. Such a species would also relate structurally to the different species (4,1) described below.

Peak D represents up to 5% of the V present at 270 K and at very high Mo:V ratios. This implies a species such as a (9,1). Its shift at room temperature is δ −504.7, and its structure is unknown. A smaller peak, E, has a similar dependence on Mo:V but insufficient data exist for a structural proposal.

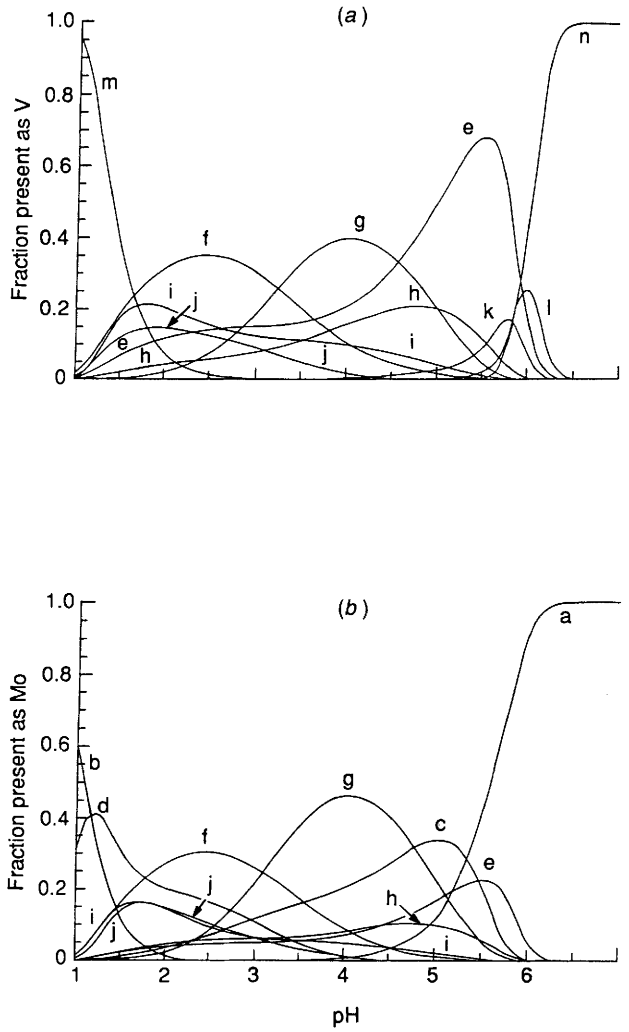


Fig. 16 Overall calculated distribution diagrams, with [Mo] = 60, [V] = 10 mmol dm^{-3}, (*a*) as fraction of V present and (*b*) as fraction of Mo present. Not all minor or previously described species are shown, for clarity. Species: a, (0,1,0) + (1,1,0) + (2,1,0); b, (5,2,0); c, (8,7,0) + (9,7,0) + (10,7,0); d, (12,8,0) + (13,8,0) + (15,8,0); e, (8,4,2) + (9,4,2); f, (9,5,1) + (15,9,1); g, (11,7,1); h, (11,6,2) + (12,7,1); i, (19,10,2) + (17,9,3) + (18,9,3); j, (15,8,2) + (16,9,1); k, (13,4,5) + (14,4,5); l, (14 to 17,0,10); m, (3,0,1); n, (*n*,0,*n*) where *n* = 1, 2, 4 or 5

Labile Species.—It is generally found that although the isopolymolybdates show considerable lability, the molybdovanadates are inert on the NMR time-scale. However, a minor labile species would be hard to detect by NMR spectroscopy. We propose one such species, in order to explain not only discrepancies in the potentiometric data at pH 4.9–6.3 (a relatively uncrowded region), but also our observation that the resonance from monomeric vanadate $[H_2VO_4]^-$ in the relevant pH range shifts to higher frequency and increases substantially in both width (up to × 2.2) and relative area (at least five times that expected). These observations are particularly evident at high temperature, when they are made in comparison with molybdenum-free solutions. The perturbations are largest at Mo:V ≈ 4:1, and the best fit to the potentiometric data is obtained with a species (5,4,1). If proton-free, this composition corresponds to the formula $[Mo_4VO_{17}]^{5-}$. The direction and magnitude of the shift perturbations also fit this formulation precisely if the shift is δ −566.7 for the labile species. The value of this shift probably indicates tetrahedrally co-ordinated vanadium. A possible structure might be that known for $[(CH_3)_2AsMo_4O_{15}H]^{2-}$,[18] deprotonated and with a VO_2^+ unit replacing a $(CH_3)_2As^{3+}$ unit. The structure is shown in Table 1. Another might involve the $[HMo_5O_{17}]^{3-}$ structure reported by Zubieta and co-workers,[22] with one replacement of a tetrahedral Mo by V.

Chemical Speciation: Distribution of Complexes.—The speciation at Mo:V < 0.25:1 was reported in the foregoing paper.[1] At these low Mo:V ratios the predominant monovanadate species present are monosubstituted (MoV_9) and disubstituted (Mo_2V_8) decavanadate species. At higher Mo:V ratios the system becomes far more complex. Many species coexist, and the adjustment of formation constants to obtain an optimal fit to the combined e.m.f. and NMR data was therefore very laborious. The highly acid region at pH < 2 proved impossible to model until we became aware that a cationic isopolymolybdate species must be present, in addition to previously known isopolymolybdate anions. A satisfactory fit was obtained upon including the species (5,2,0) with log β = 19.25 ± 0.15.

In order to establish a reliable model of the speciation, it is essential to use as wide a region of data as possible. In the final calculation the ranges 0.5 < Mo:V < 12:1 and 1.4 < pH < 7 were covered, by both e.m.f. and NMR data. Representative data, namely 583 e.m.f. titration points and 41 NMR integrals, were selected in order to avoid regions of peak overlap, and so as not to make the calculations too time-consuming. The final results are summarized in Table 1, together with those from the foregoing study.[1]

In a complicated system like this, it is necessary to construct distribution diagrams in order to see which species are significant under given conditions of pH and concentration. Moreover, such diagrams can and should be used to reveal how well the calculated equilibrium model fits the experimental peak integral data. Therefore we show in Figs. 15 and 16(*a*) the fractional concentrations of the molybdovanadate species which contribute to each reasonably well defined NMR peak. The calculated fractions are expressed as vanadium content, and are hence directly compared with the ^{51}V NMR peak integrals in Fig. 15, which is divided into four sections for clarity. In some cases these integrals correspond to a single species, and in others to mixtures of species. The fits are very satisfactory in terms of general shape, but the calculated lines sometimes overshoot the NMR data points because some minor species of the same or similar formula contributes to the e.m.f. measurement but not to the specified NMR peak. Although the metavanadate species $[H_2VO_4]^-$, $[H_2V_2O_7]^{2-}$, $[V_4O_{12}]^{4-}$ and $[V_5O_{15}]^{5-}$ in fact have separate resonances at room temperature, only their sum is shown, for simplicity.

The Mo:V ratio varies from 1:9 to 9:1 and, not surprisingly, the speciation depends strongly upon this ratio. A comparison of Fig. 15(*a*) (Mo:V = 1:1 with 16(*a*) (Mo:V = 6:1) illustrates this, by showing that the high-ratio species (7,1) predominates at pH ≈ 4 and Mo:V = 6:1 but is negligible when Mo:V = 1:1 at the same pH. The opposite is true for the low-ratio species (1,9), (2,8) and (4,5).

Because the above figures only include species that contain V, we also show Fig. 16(*b*), which refers to the same solutions as in Fig. 16(*a*) but expresses the species, now including the isopolymolybdates, in terms of their net contribution to the overall molybdenum concentration of 60 mmol dm^{-3}. One notes that, for example, the two (4,2) species account for *ca.* 70% of total V but only *ca.* 20% of total Mo at the same pH. Another interesting observation at the ratio Mo:V = 6:1 is that although all the vanadium is bound as molybdovanadate species in the range pH 2.5–5.5, nevertheless considerable Mo is not thus bound, so that 20–50% of Mo is present as isopolymolybdates. A similar absence of isopolyvanadates also pertains at much lower Mo:V ratios in this pH range.[1] Clearly vanadates can accommodate Mo better than molybdates can accommodate V.

Fig. 17 shows the data of Fig. 16(*a*) together with full data for all the other species included in the calculation. Each line

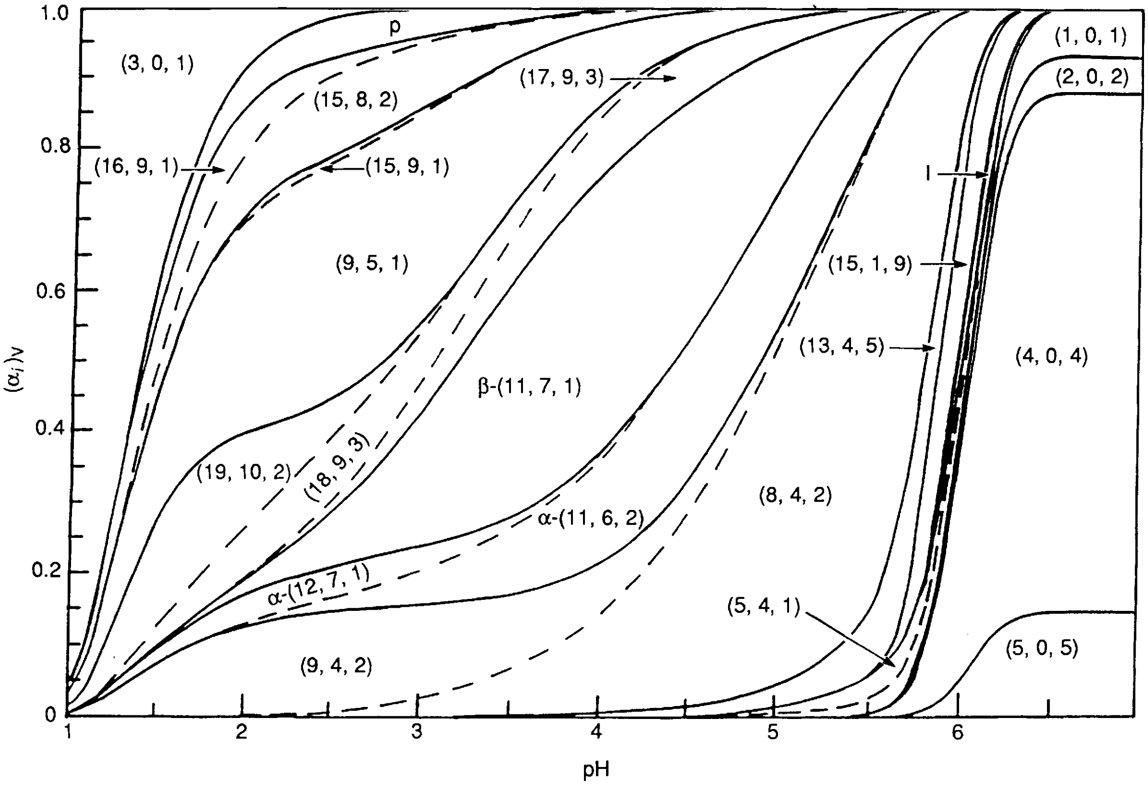


Fig. 17 Plot of $(\alpha_i)_V$, the calculated cumulative contribution to the total vanadium content (10 mmol dm^{-3}), due to the addition of successive species *i*, *versus* pH. [Mo] = 60 mmol dm^{-3}, 293 K. Each species is represented by an area, and its fraction (expressed as V) at a given pH is the vertical height of its area at that pH. Species: l; (14 or 15,0,10), p; β-(12,6,2) + (18,10,2) + (21,10,3). Dashed lines separate species whose NMR integrals were only evaluated together

represents the cumulative fractional contribution $(\alpha_i)_V$ of species *i*, as specified in the area below, to the total vanadium content. This format avoids any crossing of lines. For clarity, the area p is that of the combined areas of the broad resonances of three species whose shifts are listed at the end of Table 1. The structures of the first two are discussed above, as they are known independently. That of the species (18,10,2) is as yet unknown, but this formulation is necessary for an acceptable fit. The combined resonance is very broad. At least 98% of the vanadium is accounted for in Fig. 17.

Conclusion

Because our measurements include all species present in aqueous solution, they allow an overview of the relative thermodynamic stability of many competing structures. The aqueous ionic medium demands a molybdovanadate anion charge between 3− and 7−, depending on pH and ionic strength, and this is what we observe. The known aqueous isopolyanions which represent the two extremes of Mo:V ratio also exist with those ranges of charge. The decavanadate structure is stable with charges of 6− to 3− depending on protonation. The heptamolybdate structure can support a 6− or 5− charge,[8] and also 4− and perhaps 3− in concentrated ionic media.[18] The β-octamolybdate is found as 4− only.[8] The hexametalate structure of $[Mo_6O_{19}]^{2-}$ is only known in non-aqueous solution,[3] because of its low charge, but would also be anticipated in aqueous solution if its charge were raised by substitution of V^V for Mo^{VI}.

Perhaps the most surprising feature of the present results is that these four structures also dominate aqueous molybdovanadate chemistry. We have already shown [1] that the V-rich molybdovanadate range belongs almost exclusively to the decavanadate structure, with up to two substitutions of Mo for V. Here we have also shown that the Mo-rich range belongs largely to known isopolymolybdate structures, with their charges raised by substitution of up to two V atoms for Mo. Even the unusual asymmetric $[Mo_4V_5O_{27}]^{5-}$ structure at Mo:V ≈ 1:1 is a hybrid of the above, and in fact the only exceptions are our tentative proposals for two distinct (4,1) species, and a major but slowly forming (8,2)-P planar structure.

The species (8,2)-P is also the only exception to the observation that if two or more VO_6 octahedra are present they prefer to share an edge. Evidently the steric requirements normally outweigh electrostatic considerations. Charge, however, probably explains the general preference of V for central rather than peripheral sites in the polyanions. One source of instability of an isopolyanion is the relative concentration of positive charge at its centre. This can be mitigated by substitution of V for Mo in this region. Conversely, unlike Mo, V is unlikely to be found with two or more terminal oxygens in the larger aqueous anions.

The ^{51}V NMR chemical shifts cover only a modest range. Those for octahedrally co-ordinated V with no terminal O lie only between δ −420 and −440; with one terminal O they lie between δ −490 and −540. They have the usual dependence upon pH,[1] and are consistent with those observed by Leparulo-Loftus and Pope[2] for tungstovanadates with Keggin structure. They also in general support these authors contention that vanadiums sharing an octahedral edge experience an increase in δ_V, if this is not offset by the normal decrease of δ_V upon protonation.

The few ^{95}Mo NMR shifts measured so far cover a rather larger range, as might be expected for a second-row transition metal, and their qualitative association with structure is similar to that for ^{51}V. The ^{17}O NMR shifts are also closely consistent with known principles.[23,24]

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